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General, Physical, and Inorganic Chemistry.

Problem of fine structure. L. JANICKI and E. LAU (Z. Physik, 1925, **35**, 1—6).—New measurements of $\Delta\nu$ in the Balmer lines have been made on the Lummer–Gehrcke photographic plates previously obtained by Gehrcke and Lau. The distance apart of the blackening maxima is $\Delta\lambda = 0{\cdot}132$ Å. and therefore $\Delta\nu$ for $H_\alpha = 0{\cdot}307$. This is in agreement with Sommerfeld's original selection rule (cf. Birge, A., 1921, ii, 666), based on measurements on the helium spark line 4686, but not with the theory of Rubinowicz, Bohr, and Kramer, which involves the conception of an electric field. The values of $\Delta\nu$ for H_β and for H_γ found were 0·305 and 0·315, respectively. These are lower than those found by earlier investigators. All experimental values in these two cases are lower than the theoretical. M. S. BURR.

Excitation of the spectra of nitrogen by electron impacts. O. S. DUFFENDACK and D. C. DUNCAN (Physical Rev., 1924, [ii], **23**, 295).—On excitation of the spectra of nitrogen in low-voltage arcs in a mixture of nitrogen and mercury vapour below the ionising potential and in nitrogen alone above that potential, also in a three-electrode tube at low pressures, the first and second positive bands appeared below the ionising potential and are assigned to the neutral molecule. Two new low-potential groups were found in the ultra-violet. The negative bands are emitted by the ionised molecule, and are physically related to a new group in the ultra-violet. The line spectrum appears at about 70 volts in ordinary arcs, or at 30 volts in intense arcs.

A. A. ELDRIDGE.

New members in the series spectrum of trebly ionised silicon. R. A. SAWYER and R. F. PATON (Physical Rev., 1924, [ii], **23**, 108).—The close relationship between the series spectrum of trebly ionised silicon (Fowler, A., 1923, ii, 447) and that of doubly ionised aluminium (Paschen, A., 1923, ii, 672) is pointed out. Lines in the vacuum spark spectrum of silicon have been examined for the presence of series members. A. A. ELDRIDGE.

Structure of the spectra of elements of the iron series. M. A. CATALÁN (Anal. Fis. Quím., 1925, **23**, 395—408).—Considering the arc and spark spectra of the elements 19 (potassium) to 28 (nickel), it appears that the spectra of the first five elements resemble those of the second five elements. The azimuthal quantum numbers of the fundamental levels are the same for corresponding elements. The multiplicity of the term of greatest stability increases to a maximum for "24 (manganese)." Some correlations are found between the resonance lines and the multiplicity of their terms. Certain regularities are also found for the "raies ultimes" for these elements. The experimental rule that the "raies ultimes" are always found in multiplets of the type $k \rightarrow k+1$ is explained. Both in arc and spark spectra terms are regular when multiplicity is increasing, inverted when multiplicity is decreasing, whilst both regular and inverted terms occur at the maxima and minima.

G. W. ROBINSON.

Under-water spark spectrum of a number of elements. (MISS) M. C. W. BUFFAM and H. J. C. IRETON (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 113—118).—The under-water spark spectra of gold, silver, copper, cobalt, nickel, antimony, and bismuth have been investigated. The wave-lengths observed as showing inversion are tabulated. J. S. CARTER.

Line and band absorption of copper and its fine-structure lines. H. STÜCKLEN (Z. Physik, 1925, **34**, 562—585).—The source of the spectra was the oscillatory discharge between copper electrodes under water. In addition to a spectrum resembling that of the alkalis, there is one the ground lines of which form a multiple-system—probably quadruplets. This indicates that in the case of copper, not only the 4_1 electron, but also a 3_3 electron functions as a valency electron. Satellites accompany many lines and are attributed to unstable copper molecules. An absorption band at 2240·69 Å. was resolved into its branches, and from the calculated moment of inertia it is probably due to a copper hydride.

E. B. LUDLAM.

Spectrum of rubidium at low voltages. F. H. NEWMAN (Phil. Mag., 1925, [vi], **50**, 1276—1282; cf. A., 1925, ii, 1014).—Rubidium vapour has been subjected to bombardment by electrons of known energy, and the corresponding emission spectra have been photographed. The method was the same as that previously used in experiments with sodium and potassium vapour. With increasing electron energy, the spectral lines of rubidium are excited in the order corresponding with the displacement of the valency electron to, and its return from, the various outer non-radiating orbits. At 1·7 volts (calc. 1·58 volts), the first doublet of the principal series appeared. When the electron energy reaches the ionisation potential, 4·2 volts (calc. 4·16 volts), the complete arc spectrum is emitted. A. B. MANNING.

Structure of the mercury green line 5460·74 Å. and of the Balmer lines of hydrogen. J. C. MCLENNAN and H. J. C. IRETON (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 77—86).—The mercury line 5460·74 Å. has been resolved into 12 components by means of a 45-plate echelon. When crossed with a smaller echelon, it was shown that two components had overlapped, the number of components being in reality 13. An attempt has been made to obtain a photographic record of the third member of the predicted fine structure of the Balmer lines. Examination of the H_α and H_β lines revealed no indication of this third member. If it exists, its intensity is many times less than that predicted. J. S. CARTER.

Analysis of the spectra of thallium by electrodeless discharge. W. C. MCQUARRIE (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 57—62).—About 140 lines in the region 3700—6500 Å. are tabulated and classified as arc lines, and the three successive groups of spark lines in order of their difficulty of excitation—which, it is probable, correspond with the spectra of singly, doubly, and trebly ionised atoms, although it is possible they include lines of higher order. It is suggested that the line 5488·79 Å., measured by Paschen (A., 1910, ii, 1014) in the arc, might be a spark line superimposed on the arc line.

J. S. CARTER.

Coloured photographs of line spectra. C. SCHAEFER and C. BORMUTH (Physikal. Z., 1925, **26**, 697—698).—The spectra of neon, helium, and hydrogen can be successfully photographed on "Agfa" colour plates by suitable adjustment of the time of exposure of the different regions of the spectra. This is done by introducing screens of black paper in front of the plate in the spectrograph. In photographing the mercury spectrum, however, the yellow line (579 $\mu\mu$) is always shown as green, although the sodium D-line (589 $\mu\mu$) is correctly rendered. The red granules of the colour plate transmit the latter but not the former, and the green granules transmit only the yellow mercury line. A. B. MANNING.

Theory of broadening of spectral lines. L. MENSING (Z. Physik, 1925, **34**, 611—621).—The mutual effect of the same kind of atoms in the same quantum state is greater than that produced by unlike atoms. The broadening of spectral lines in consequence of the Stark effect due to the electric field of neighbouring molecules must be greater for the same gas than for the same pressure of a foreign gas. If this is so, the effect should be observable in the case of absorption in the principal series of the alkali metals. E. B. LUDLAM.

Theory of the continuous spectrum. R. D. KLEEMAN (Physical Rev., 1924, [ii], **23**, 295).—A theory of the continuous spectrum is based on the facts that the mass of an atom is located mainly at its nucleus, and that its electrical moment $M=10^{-19}N^{2/3}$, where N is the atomic number. A. A. ELDRIDGE.

Soft X-rays from certain metals. C. T. CHU (J. Franklin Inst., 1925, **200**, 615—627).—Soft X-rays from nickel, iron, and copper have been examined by bombarding a target of the metal under investigation with electrons from a hot filament in as high a vacuum as possible, and studying the photo-electric emission from a second electrode exposed to the resulting radiation from the target. The curves obtained by plotting the photo-electric current against the accelerating potential between filament and target, which was never more than 120 volts, display breaks at voltages 52, 68, and 80 for iron, 49, 75, and 98 for nickel, and 30, 49, 62, 79, and 90 for copper. These values are not in very close agreement with those obtained by other investigators, but there is no agreement among the latter. Various possible interpretations of the results are discussed, and it is suggested that they are to some extent consistent with what might be expected from the position and order of the elements in the periodic table. Experiments with selenium were not successful owing to its vaporisation. M. S. BURR.

Fine structure of certain X-ray absorption edges. K. CHAMBERLAIN (Physical Rev., 1925, [ii], **26**, 525—536).—K-Absorption edges for titanium, vanadium, chromium, and manganese were found at 2489·5, 2261·9, 2064·9, and 1891·4 X, respectively, and L_{III}-absorption edges for tin and antimony at 3146·9 and 2991·5 X, respectively, in good agreement with the positions of the white lines observed by Coster. Coster's lines are therefore due, in the case of compounds of higher valency, to the reduced elements. The edges observed by Lindh near 4988 X for sulphur compounds are probably due to sexavalent sulphur, owing to the oxidation of sulphides or sulphites in the X-ray beam. Evidence was obtained of the reduction of iodic acid and of potassium permanganate by exposure to X-rays; sulphurous acid also is oxidised in the absence of free oxygen. A theoretical explanation of the valency changes is advanced. A. A. ELDRIDGE.

Fine analysis of the Stark effect for H_β and He 4686 Å. J. S. FOSTER (Physical Rev., 1924, [ii], **23**, 765—766).—Many photographs taken by Lo Surdo's method show all the components observed by Stark which agree with the theory, and no others. It is suggested that the spurious components are produced by variations in the direction of the applied field. The explanation is supported by analyses of He 4922, 4472 Å. A. A. ELDRIDGE.

Quadratic Stark effect of the alkalis. W. THOMAS (Z. Physik, 1925, **34**, 586—601).—A formula is developed for the quadratic Stark effect and calculated results compared with experimental.

E. B. LUDLAM.

Dissociation of hydrogen and nitrogen by mercury atoms excited in an arc. K. T. COMPTON and O. S. DUFFENDACK (Physical Rev., 1924, [ii], **23**, 109).—In an electric arc discharge, hydrogen is apparently dissociated abnormally rapidly when excited mercury atoms are present in large concentration, the effect being ascribed to a transfer of energy on collision. Nitrogen is less affected.

A. A. ELDRIDGE.

Metastable $2p_3$ state of mercury atoms. S. LORIA (Proc. Nat. Acad. Sci., 1925, **11**, 673—679).—Mercury atoms activated by 2537 Å. remain in the $2p_2$ state for about 10^{-7} sec. In a gaseous system containing mercury, thallium, and nitrogen, the two latter in excess, collisions between activated mercury atoms and thallium atoms result in thallium activation followed by its fluorescence and a constant energy distribution between the different lines. Collisions between nitrogen atoms and activated mercury atoms may be (*a*) of the second kind (activation energy converted into kinetic energy of the colliding particles) or (*b*) of such a kind that the main part of the activation energy is retained in the $2p_3$ state of the mercury atom and the remainder is converted into kinetic energy. Such a partly activated atom should retain its energy for a definite time, depending on its environment. The intensity of the indirectly excited fluorescence spectrum of thallium is a measure of the total number of activated mercury atoms. It is shown theoretically that an estimate of the order of magnitude of the duration of the $2p_3$ state may be obtained from a comparison of the blackening of the photographic plate by a given thallium fluorescence line excited first with and afterwards without the presence of nitrogen in the sealed tube. Photographs by the author have been measured by a registering microphotometer. The duration of the $2p_3$ state would be infinite in a vacuum, and actually varies with the gaseous pressures and temperatures. The calculated order of magnitude, 10^{-4} sec., agrees with Webb's values.

R. A. MORTON.

Normal cathode fall in krypton and xenon. A. GÜNTHER-SCHULZE (Z. Physik, 1925, **34**, 549—552).—The normal cathode fall of potential is taken as the lowest voltage obtained as the distance between the anode and cathode is reduced. With an iron cathode, the values are 215 and 306 volts for krypton and xenon, respectively. Krypton gives with an aluminium cathode 188 volts and with a platinum cathode 237 volts. The heavier gas is more difficult to ionise.

E. B. LUDLAM.

Photo-electric valve coated with potassium. V. M. ALBERS (Physical Rev., 1925, [ii], **26**, 671—677).—A further investigation of Tykocinski-Tykociner and Kunz's observation (A., 1924, ii, 586) of the amplification on exposure to light of the electron current passing through a valve bearing a transparent film of potassium on the walls.

A. A. ELDRIDGE.

Photo-electric threshold for mercury. C. B. KAZDA (Physical Rev., 1925, [ii], **26**, 643—654).—Using carefully purified mercury flowing in a vacuum, the intrinsic photo-electric threshold for mercury was observed to be 2735 Å., corresponding with a photo-electric work function of 4·52 volts.

A. A. ELDRIDGE.

Variation in the photo-electric emission from platinum. A. E. WOODRUFF (Physical Rev., 1925, [ii], **26**, 655—670).—Clean platinum was insensitive to mercury arc radiation, but became sensitive when heated electrically at about 250°, although not at higher temperatures obtained by means of an electric oven. Insensitivity can be induced by prolonged heating at a high temperature and low pressure, owing to a shift of the threshold to short wave-lengths. The results may be accounted for by the assumption of an initial adsorbed layer of gas on the surface, retarding the escape of the photo-electrons, but the layer formed when the whole apparatus is heated at a high temperature is probably not identical with that originally present.

A. A. ELDRIDGE.

Chemical statics of electronic phenomena. L. ROLLA and G. PICCARDI (Atti R. Accad. Lincei, 1925, [vi], **2**, 334—336; cf. A., 1925, ii, 1018).—It follows, from the application of the mass action law to the phenomenon of atomic ionisation, that in a mixture of two types of atoms the degree of ionisation of each type is proportional to its ionisation constant. This relationship is confirmed by an examination of data for the ionisations in systems containing the following pairs of atoms: barium–strontium, lithium–sodium, sodium–molybdenum, thallium–molybdenum, and sodium–potassium.

F. G. TRYHORN.

Scattering of electrons in ionised gases. I. LANGMUIR (Physical Rev., 1925, [ii], **26**, 585—613).—Experiments with hot cathodes indicate the presence of three groups of electrons: primary, secondary, and ultimate; in the uniform positive column of arcs, only ultimate electrons are present. The velocity distribution of the electrons is examined, and a theory of the mechanism of electron scattering is advanced.

A. A. ELDRIDGE.

Motion of electrons in gases. J. S. TOWNSEND (J. Franklin Inst., 1925, **200**, 563—590).—The motion of electrons through a gas has been investigated by determining experimentally the velocity of agitation U and also the velocity W in the direction of an applied electric field. The method employed for measuring U consists in determining the divergence of a stream of electrons moving in a uniform field. If three electrodes in one plane receive the electrons, the ratio R of the amount of charge received by the central electrode to the total charge on all three decreases as the divergence increases, and is a function of U. R tends to diminish as the gas pressure is reduced, indicating an increase in U. R may be plotted as a function of Z/k, where Z is the electric field and k is the ratio of the energy of agitation of a charged particle in the gas to the energy of agitation of a molecule of the gas, and is a function of Z/p, p being the pressure of the gas. In moist gases, where the charged particles are mainly ions, k is approxim-

ately 1, and, for a given electric field, the same value of R is obtained for different gases over a large range of pressure; this indicates that there are no free electrons. In dry gases, the values of R are much smaller than in moist, for certain ranges of electric force and pressure. Also, in dry gases the divergence obtained with a given electric force increases as the pressure is reduced. Thus the value of k is large and increases as p is reduced. It can hence be shown that the mass of the charged particles must be small compared with that of a molecule, that is, electrons move freely in the gas. From a comparison of the divergences of streams of electrons in different gases at 20 mm. pressure, it has been shown that, with the same field and pressure, the energy of agitation of electrons is greater in helium than in nitrogen, and greater in nitrogen than in hydrogen. U is found to be $(1{\cdot}15\times10^4\times\sqrt{k})$ cm./sec. The velocity W in the direction of the field has been determined experimentally in the same apparatus by superposing on the electric field a magnetic field at right angles, and measuring the deviation thus produced in the electron current. W is not proportional to Z, but is a function of the ratio Z/p. Agreement between the values of U and W for a given value of Z/p for a large pressure range indicated the absence of ions in nitrogen, carbon dioxide, carbon monoxide, argon, neon, and helium. Ions were detected in oxygen, nitrous oxide, and nitric oxide. The mean free path of the electrons in different gases for several values of Z/p has been deduced, and also the proportion λ of the energy of an electron lost by collision with a molecule. M. S. Burr.

Evaporation of electrons. W. Schottky (Z. Physik, 1925, **34**, 645—675).—It is not the specific heat of the electrons in a metal but the change in the specific heat by loss of electrons which determines the variation with temperature of the thermodynamic potential of the electrons in the metal. This change of specific heat is related to the Thomson effect and the thermo-electric force between the same metal hot and cold; the latter can exist only when the effect of heat is to produce in the metal an internal state differing from the normal state.

E. B. Ludlam.

Electron paths. A. Günther-Schulze (Z. Physik, 1925, **34**, 639—644).—A method is given for calculating the path of an electron emitted from a hot filament in a homogeneous field and in a simple case for a field which is not homogeneous.

E. B. Ludlam.

Absorption coefficient for slow electrons in mercury vapour. R. B. Brode (Proc. Physical Soc., 1925, **38**, 77—79).—See A., 1925, ii, 1020.

Collisions of the second kind. H. D. Smyth (Proc. Nat. Acad. Sci., 1925, **11**, 679—682).—The electron affinity of iodine has been employed in an attempt at the direct verification of the existence of collisions of the second kind. If an electron comes within the field of a neutral iodine atom, and before the electron affinity of 3·5 volts is fully satisfied, *i.e.*, before the process of binding the electron is completed, a second electron "collides" with the new system, the second electron may gain kinetic energy by a collision of the second kind. Experiments have been carried out which, although not conclusive, support the idea. Preliminary work on the decomposition of ozone affords promising but not yet definitive results. R. A. Morton.

Relative production of negative and positive ions by electron collisions. F. L. Mohler (Physical Rev., 1925, [ii], **26**, 614—624).—In an investigation of the ionisation produced by electron collision, current–voltage curves were obtained for mercuric chloride and hydrogen chloride which were similar to those for mercury and iodine, respectively, the negative ion current being small compared with the positive for electron currents of the order of 10^{-6} amp., and pressures of about 0·001 mm. The results do not support the theory that electron collisions dissociate polar molecules into positive and negative ions, but indicate that the primary effect is the production of a positive molecular ion.

A. A. Eldridge.

Free path of slow protons in helium. A. J. Dempster (Nature, 1925, **116**, 900—901).—Positively charged hydrogen atoms with velocities acquired by falling through 300—900 volts possess an unexpected range in helium and other gases, and they remain charged throughout the entire path. Apparently no free electrons are produced by protons of the velocity used; the result is anticipated in the case of helium from energy considerations. Singly-charged helium atoms disappear when the pressure is increased to 0·027 mm. of mercury; charged hydrogen molecules, which disappear at 0·07 mm., are probably dissociated on collision without alteration of velocity or direction.

A. A. Eldridge.

Ions from hot platinum. H. A. Erikson (Physical Rev., 1925, [ii], **26**, 625—628).—Measurements of mobility and of current–voltage relations indicate that the single negative ion and the final positive ion from platinum are air ions; the initial positive ion may also be an air ion (cf. *ibid.*, 1923, **21**, 720; A., 1925, ii, 6). A. A. Eldridge.

Mobility of the ions of the active deposits of thorium and radium. H. A. Erikson (Physical Rev., 1925, [ii], **26**, 629—632).—In each case, as with actinium, two positive, active substances differing in mobility were found; probably one is singly, and the other doubly charged (cf. A., 1925, ii, 79).

A. A. Eldridge.

Chemical action of gaseous ions produced by α-particles. VI. Reactions of oxides of carbon. S. C. Lind and D. C. Bardwell (J. Amer. Chem. Soc., 1925, **47**, 2675—2697; cf. A., 1919, ii, 210; 1924, ii, 11, 12, 840).—In many reactions produced by α-particles from radon, the ratio $-M/N$ of molecules decomposed to α-particles is a few units greater than unity. This is ascribed to the formation of clusters of a primary ion and one or more neutral molecules. When a gas like oxygen is present, which has a great affinity for free electrons, these are trapped to form O_2^-, which can then react and may also form clusters with neutral molecules, thus further

increasing the ratio $-M/N$. When this occurs, oxidation replaces all reactions that would take place in its absence, and it is assumed that final chemical action does not result until electrical neutralisation is brought about by recombination of the positive and negative ions or clusters. The chemical reactions taking place in a number of gases mixed with radon have been followed by the pressure changes and by chemical analysis of the final gaseous products; in some cases, pressure measurements have also been made at sufficiently low temperatures to freeze out one or more components. In the decomposition of carbon monoxide, the ratio $-M/N$ is about 2, but falls as the reaction progresses. The products are carbon dioxide, carbon, and a substance which is deposited on the wall of the vessel and is probably a suboxide of carbon; the ratio of carbon monoxide lost to carbon dioxide formed is 3 : 1. In the presence of radon, carbon monoxide is oxidised by oxygen and the ratio $-M/N$ is 6; it is concluded that clusters $CO{\cdot}O_2{\cdot}CO$ with single positive or negative charges are formed from CO^+, O_2^+, or O_2^-, but not from CO^-, and that the final reaction is $(CO{\cdot}O_2{\cdot}CO)^+ + (CO{\cdot}O_2{\cdot}CO)^- = 4CO_2$. The rate is practically unaffected by the carbon dioxide formed. At the temperature of liquid air, the velocity was half that at 25°, proving that moisture is unnecessary for the ionic reaction. Under α-radiation, carbon monoxide and hydrogen combine to form a white solid, which may be a polymeride of formaldehyde, and the ratio $-M/N$ is 3. Carbon dioxide is not decomposed, but it is probable that ionisation and complex formation take place, the complexes re-forming carbon dioxide when neutralised. Hydrogen and carbon dioxide react, forming water, a very little carbon monoxide, probably carbohydrates, but no methane; the ratio $-M/N$ is 1·7. In the various mixtures of carbon monoxide, carbon dioxide, hydrogen, and oxygen, the ions of both reactants are active.

A. GEAKE.

Ionisation in reacting gases. A. K. BREWER (Physical Rev., 1925, [ii], **26**, 633—642).—See A., 1925, ii, 919.

Revision of the atomic weight of germanium. II. Analysis of germanium tetrabromide. G. P. BAXTER and W. C. COOPER (J. Physical Chem., 1925, **29**, 1364—1378).—The material from the analysis of the tetrachloride (A., 1924, ii, 690) provided the germanium used. Germanium tetrabromide, prepared by heating the metal in a current of pure nitrogen charged with bromine, was purified by thirteen fractional distillations in a vacuum. Neglecting the first four fractionations, the most volatile and least volatile portions were then analysed separately. The tetrabromide used was free from bromine, hydrogen bromide, arsenic, and silicon tetrabromide. Thirty-two analyses, in all, gave the ratios $GeBr_4 : 4Ag$ and $GeBr_4 : 4AgBr$, from which the atomic weight of germanium is found to be 72·60 (Ag 107·880, Br 79·916), a value identical with that obtained from the analysis of the tetrachloride (*loc. cit.*). This agrees with Aston's results (Phil. Mag., 1924, [vi], **47**, 394) on the isotopes of germanium.

L. S. THEOBALD.

Energy liberated by radium. R. W. LAWSON (Nature, 1925, **116**, 897—898).—The total heat development of 1 g. of radium, free from its disintegration products, is calculated to be 23·28 or 25·47 cal. per hour, according as the number of atoms of radium disintegrating per second per 1 g. of the element is taken to be $3{\cdot}40$ or $3{\cdot}72 \times 10^{10}$, respectively. Hess' experimental value is 25·2 cal./hour, but when cognisance is taken of the amount of γ-radiation unabsorbed under the experimental conditions employed, it is computed that the corrected value cannot greatly differ from 25·5 cal./hour. Support is thus given to the essential correctness of the value $Z = 3{\cdot}72 \times 10^{10}$, in harmony with Kovarik's work. The data employed in the calculations are quoted.

A. A. ELDRIDGE.

Extraction and purification of the active deposit of long life from radium. (MLLE.) I. CURIE (J. Chim. physique, 1925, **22**, 471—487).—The method of recovery, from tubes which have contained radon, of the active deposit containing radium-*D*, radium-*E*, and polonium is described, together with their separation, and in particular the isolation of the polonium. The methods employed for measuring their activities are also described.

A. E. MITCHELL.

Theory of the range of α-particles. L. LOEB and E. CONDON (J. Franklin Inst., 1925, **200**, 595—607).—According to previous calculations of the ranges of α-particles by applying the concept of quantised energy exchanges to the classical dynamical treatment, assuming initially free electrons at rest (cf. Bates, A., 1924, ii, 813), the calculated stopping power of the inert gases for α-particles is from 0·6 to 0·8 of the observed stopping power. An error in these calculations has now been indicated, but on correcting for this the discrepancy becomes still greater. Thus the energy of the α-particle is spent in processes other than ionisation and radiation, or else the energy is spent more freely in ionisation than the theory employed permits. The error may be due to the assumption that the electron is initially at rest and responds to the α-particle as if absolutely free, whereas the velocity of the electron in its orbit is probably of the same order as that of the α-particle.

M. S. BURR.

Absorption of β-rays by matter. (MME.) J.-S. LATTÈS and G. FOURNIER (Compt. rend., 1925, **181**, 855—856).—The mass coefficient of absorption, x, of bands of secondary β-rays is given by the relation $x = a + bN$, where N is the atomic number of the absorbent, $a = 5{\cdot}73$ and $b = 0{\cdot}0547$. The ratio, a/b, is the same as for the β-rays of radium-*E*, which also obey the linear law. For an explicit emission potential, V, the relation $x = (a + bN) \cdot f(V)$ is proposed; the nature of $f(V)$ is not given.

S. K. TWEEDY.

Number of particles in the β-ray spectra of radium-*B* and radium-*C*. R. W. GURNEY (Proc. Roy. Soc., 1925, **A**, **109**, 540—561).—The origin of the "continuous" β-ray spectrum of a radioactive material is still open to discussion. It has been uncertain whether it consists of the electrons ejected from the nucleus during disintegration or whether it

is merely a secondary effect. This problem has now been attacked by measurements both of velocity-distribution in the spectrum and of the total number of particles which constitute the spectrum. The spectrum was resolved by the usual magnetic method, and the particles were focussed on a slit opening into a Faraday cylinder, by which the charge associated with any part of the spectrum could be measured. It is concluded that both radium-*B* and radium-*C* possess a genuine continuous β-ray spectrum, quite distinct from the line spectrum which is superimposed on it. The continuous spectrum contains rather more than one electron for each atom disintegrating, which is to be expected if it is formed of the electrons ejected from the nucleus. The continuous spectrum of radium-*B* rises to a maximum at 170,000 volts, and has an upper limit at 650,000 volts. The spectrum of radium-*C* rises to a maximum at about 400,000 volts, and has a definite upper limit at 3,150,000 volts. The line spectrum is attributed to the conversion of γ- into β-rays, the probability of which is about 1 in 7. The heating effect of the β-rays of radium-*B*+*C* is 5·6 cal. per hour per g. Of this, 1·3 cal. are ascribed to radium-*B*, and 4·3 cal. to radium-*C*. S. BARRATT.

β-Ray spectrum of the natural *L*-radiation from radium-*B*. D. H. BLACK (Proc. Camb. Phil. Soc., 1925, **22**, 832—833).—Fifteen lines of a comparatively low-energy β-ray spectrum with energies extending from 4290 to 12670 volts have been obtained from a source of radium-*B* in equilibrium with radium-*C*. Under the same experimental conditions, radium-*C* gives no such lines, which are therefore attributed to radium-*B*. It is suggested that the electrons are ejected by *L X*-rays, from atoms of atomic number 83, acting on the *M*, *N*, and *O* levels of the same atom. A. E. MITCHELL.

Natural *X*-ray spectrum of radium-*B*. (SIR) E. RUTHERFORD and W. A. WOOSTER (Proc. Camb. Phil. Soc., 1925, **22**, 834—837; cf. preceding abstract).—By the original method of Rutherford and Andrade (A., 1914, ii, 408, 698), with a rock salt crystal and a radon tube as source, the separation of the strongest lines α_1 and β_1 of the *L*-spectrum of radium-*B* has been measured. The results are in accord with the separation deduced with the aid of Coster's data for an element of atomic number 83. The results were confirmed by similar measurements using a calcite crystal. It is certain therefore that the earlier measurements of Rutherford and Andrade were in error and that the *L*-spectrum has its origin in an atom not of atomic number 82 but of atomic number 83, or that in this type of disintegration the emission of the γ-ray follows instead of precedes the escape of the electron. A. E. MITCHELL.

Analysis of the β-ray spectrum due to the natural *L*-radiation of radium-*B*. D. H. BLACK (Proc. Camb. Phil. Soc., 1925, **22**, 838—843; cf. preceding abstracts).—By assuming that the β-ray spectrum from radium-*B* has its origin in the action of rays corresponding with *L X*-rays, generated within the atom, on various other atomic levels, it is shown that eleven of the fifteen lines obtained correspond with an atom of number 83, whilst with an atom of number 82 it is possible to account for only six of them. The results support the hypothesis that electrons are ejected by γ-rays after the nuclear change in the atom has taken place. Similar measurements with thorium-*B* show that its β-ray spectrum is practically identical with that of its isotope radium-*B*, and it is suggested that in this case also the γ-rays are emitted subsequently to the disintegration. A. E. MITCHELL.

Atomic number of a radioactive element at the moment of emission of the γ-rays. C. D. ELLIS and W. A. WOOSTER (Proc. Camb. Phil. Soc., 1925, **22**, 844—848; cf. preceding abstracts).—The energies of the three main γ-rays from radium-*B* and the strongest of radium-*C* have been measured to 1%. The results are in agreement with those calculated when the emission follows the nuclear disintegration and confirm those of Black and of Rutherford and Wooster. A. E. MITCHELL.

β-Ray type of disintegration. C. D. ELLIS and W. A. WOOSTER (Proc. Camb. Phil. Soc., 1925, **22**, 849—860; cf. preceding abstracts).—In view of the results of Black, of Rutherford and Wooster, and of Ellis and Wooster, it is considered established that in the β-ray type of disintegration the emission of the γ-ray takes place after the ejection of the electron from the nucleus. The mechanism of γ-ray and disintegration electron emissions is discussed. The view of Meitner that the γ-rays are emitted during the reorganisation of the nucleus after the disturbance caused by the disintegration electron has been extended to the idea that the γ-rays are emitted by the electronic system of the nucleus. The similarity of electronic systems in successive nuclei of the same radioactive family is stressed. The results are interpreted in terms of level systems. Meitner's proposals for the explanation of the inhomogeneity of the velocities of disintegration electrons are discussed, and it is concluded that the electron is actually emitted from the nucleus with a varying velocity, but no explanation of this is advanced. A. E. MITCHELL.

Nuclear structure of radioactive atoms and the emission of γ-ray spectra. J. THIBAUD (Compt. rend., 1925, **181**, 857—859).—On the assumption that the nucleus of a radioactive atom consists of a condensed kernel, surrounded by positive corpuscles revolving in quantised circular orbits, it is shown that the observed γ-ray spectra may be explained by the passage of a positive corpuscle from one orbit to another of higher energy level causing the emission of one quantum of γ-radiation. In certain cases, the existence of fine structure within the nucleus must be supposed. S. K. TWEEDY.

Effect of sunlight on the radioactivity of lead and uranium. (MLLE.) S. MARACINEANU (Compt. rend., 1925, **181**, 774—776; cf. A., 1925, ii, 348).—When exposed to sunlight, ordinary inactive lead acquires radioactive properties, which may persist for some months after the insolation. The activated lead affects a photographic plate, causes scintillations on a screen of zinc sulphide, and has slight

ionising properties. After exposure to sunlight, the activity of uranium oxide shows marked variations which may amount to as much as 50% of the total activity. If the uranium oxide is exposed simultaneously to sunlight and to bombardment by the α-particles from polonium, the variations after exposure are more frequent than for sunlight alone. W. HUME-ROTHERY.

Possible significance of tetrahedra numbers in the natural system for atomic mass and atomic structure. H. STINTZING (Z. Physik, 1925, **34**, 686—697).—All the atomic masses, including isotopes, can be represented by a scheme of tetrahedra. One element passes into the next higher by the addition of two hydrogen nuclei about a new axis of symmetry. Each fourth element requires a special structure, the carbon type; each eighth element reverts to the noble gas type. When iron is reached, a type of closer packing is introduced, and in the sixth period, rare earths and platinum group, the packing is still closer. The increase in the number of isotopes with increasing atomic weight is represented by the increased possibility of adding protons centrally to the tetrahedra; more are predicted than have yet been found. E. B. LUDLAM.

Magnetism and the structure of atoms and molecules. B. CABRERA (J. Phys. Radium, 1925, [vi], **6**, 273—286; cf. A., 1925, ii, 1107).—The variation of paramagnetism with atomic number provides a means of fixing the position in the atom of the last electron acquired by the atom or cation concerned. For the iron and rare-earth groups, Stoner's scheme of atomic levels is in accord with experiment. An explanation is given of the differences in magnetic behaviour exhibited by the tervalent ions of chromium and cobalt and also of differences within the group of rare earths. The constant Δ of the Curie–Weiss equation, $\chi_m(T+\Delta)=C_m$, is still obscure from the point of view of physical significance. Its importance is, however, emphasised, and the suggestion is made that it depends on the interaction of paramagnetic atoms with neighbouring atoms. R. A. MORTON.

Physical structure of the elements. C. G. BEDREAG (Bull. Acad. Sci. Roumaine, 1925, **9**, [9—10], 8—14; cf. A., 1925, ii, 363).—The alteration in valency and in spectral multiplicity (multiplets) with atomic number is discussed. J. S. CARTER.

Nuclear numbers. D. DE BARROS (Compt. rend., 1925, **181**, 719—722).—By insertion of the nuclear numbers, A [the nearest integer to the value $\frac{1}{2}(M-N)$, where M is the atomic weight and N the atomic number], in a rearranged periodic table, in which the elements are classed in sixteen columns of five rows each, a table is obtained almost exactly the same as that found experimentally by Mayer for the arrangement of magnetised needles round a magnetic pole. For each element in any one column, the relation $M_x=2N_x-A_{x-1}$ holds, where x indicates the row in which the element occurs. Some doubtful atomic weights, and also those of undiscovered elements, are calculated by this relationship. S. K. TWEEDY.

Doublet and triplet separations in optical spectra as evidence whether orbits penetrate into the core. D. R. HARTREE (Proc. Camb. Phil. Soc., 1925, **22**, 904—918).—From an analysis of doublets and triplets in optical spectra by means of the formula of Landé (A., 1924, ii, 711), it is concluded that, except for lithium-like atoms, the p-terms of all known spectra correspond with orbits which penetrate into the core. This is not in agreement with Bohr's assignment of quantum numbers for the p-terms of the spectra of neutral atoms of the copper and zinc sub-groups. The evidence for d-terms is not so complete, but suggests that at least in Cs I and Tl I these correspond with penetrating orbits not in agreement with Bohr's quantum number assignment. When the terms belong to a Ryberg sequence the Landé formula holds approximately for separations in multiplet systems. A. E. MITCHELL.

Optical constants. I. Optical behaviour of certain atomic models. II. Lateral scattering from a gas. C. G. DARWIN (Proc. Camb. Phil. Soc., 1925, **22**, 817—823, 824—831).—Mathematical.

Structure of manganese. H. COLLINS (Chem. News, 1925, **131**, 355—358).—Speculative.

Striated discharge in hydrogen. D. A. KEYS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 143—148).—Single striations suddenly become double when the $P.D.$ applied to the tube is raised to a certain critical value, the magnitude of which depends upon the pressure of the gas. Under certain conditions in a new discharge tube, the striations may be made to revolve rapidly by the application of a magnetic field at a certain region of the discharge and in a particular direction. The spectra of the light from the negative glow and from a striation show that there are more excited atoms than molecules in the negative glow and that the reverse is true of the striations. The spectra from the two sides of a single striation are not the same nor is the distribution of intensity in the spectral lines from different parts of a single striation that of the light from the corresponding part of a double striation. J. S. CARTER.

Secondary spectrum of hydrogen. O. S. DUFFENDACK (Physical Rev., 1924, [ii], **23**, 107; cf. A., 1925, ii, 333).—With a low-voltage arc in a mixture of hydrogen and mercury vapour the Fulcher bands and other strong lines, particularly groups at 4625—4634 and 4562—4580 Å., appear at 13 volts. H_α appears at 11 volts and H_β at 12 volts. Hydrogen excited in a three-electrode tube gave a complete spectrum at 15 volts, but only faint traces of Balmer lines below 16·5 volts. Presumably they arise in the mixture by dissociation of hydrogen by impacts with excited mercury atoms. A. A. ELDRIDGE.

Characteristics and spectra of low-voltage arcs in hydrogen, nitrogen, and mixtures of hydrogen with mercury and nitrogen. C. T. KWEI (Physical Rev., 1925, [ii], **26**, 537—560).—In hydrogen, the arc broke at $16{\cdot}23\pm0{\cdot}03$ volts, in agreement with Duffendack's value for the ionisation potential of the hydrogen molecule; that of the hydrogen atom is $13{\cdot}67\pm0{\cdot}14$ volts. In nitrogen,

the arc broke at 16·18±0·05 volts, but the lowest voltage at which the arc could be maintained without oscillations is 16·90±0·07 volts, which is regarded as the ionisation potential of the nitrogen molecule. With mercury in a tube appended to the discharge tube, two arcing and two breaking potentials could be obtained, the difference between the two arcing potentials (about 10·4 volts) corresponding with the ionisation potential of mercury; under other conditions, a single breaking potential was observed. Similar results were obtained with a mixture of hydrogen and nitrogen; there appears to be a critical potential of nitrogen at 22·7 volts. In hydrogen, the Balmer lines and the secondary spectrum always appeared together, the former being more intense; in mixtures of mercury vapour and hydrogen, the mercury lines and the Balmer series lines were much enhanced relative to the secondary spectrum after passing the second arcing potential. The results indicate that between the first and second breaks hydrogen molecules were dissociated into atoms. The ultra-violet band of ammonia, associated with the 22·5 volt critical potential, was observed with mixtures of hydrogen and nitrogen in any proportion, but not with either gas alone. It is considered to be due to a molecule NH_x, where x is probably 3. The Schuster bands are ascribed to a molecule containing nitrogen, hydrogen, and oxygen, possibly NH_4OH, which is extremely unstable, and is formed only at voltages above 70, the critical voltage for active nitrogen.

A. A. ELDRIDGE.

Band spectrum of nitrogen and its theoretical interpretation. R. T. BIRGE (Physical Rev., 1924, [ii], **23**, 294—295).—It is concluded that a common final quantum state of the second and fourth band groups is also the initial state of the first group. Only one possible assignment of true vibration quantum numbers is indicated, leading to a possible explanation of various changes in physical appearance. Active nitrogen is apparently a metastable, energised, neutral N_2 molecule, chiefly with vibration quantum number 11. The quantum structure of triplet bands is established; the moment of inertia of the N_2 neutral molecule in the non-vibratory initial state of the second group is $17·2\times10^{-40}$. CN and N_2 bands are not identical.

A. A. ELDRIDGE.

Excitation potentials of the band spectrum of nitrogen. H. SPONER (Z. Physik, 1925, **34**, 622—633).—The spectrum was observed when nitrogen was excited by electron impact in a tube which was first calibrated by using a neon–helium mixture. The excitation potentials for the zero band of the positive and negative groups were measured (1st, 2nd, and 4th positive, 9·3, 13·0, and 14·8 volts, respectively; 1st negative, 19·6 volts; ionisation potential, 16·5 volts). The suggestion is made that active nitrogen consists of atoms which undergo a threefold collision with 1 mol. of nitrogen, as a result of which the two atoms can unite, and the energy of dissociation which they lose is acquired by the molecule with which they collided, and the glow is due to the radiation from this excited molecule. This gives as the energy of dissociation of the nitrogen molecule a value lying between 260,000 and 296,000 cal., *i.e.*, between 11·4 and 13·0 volts.

E. B. LUDLAM.

Absorption spectra of various elements in the ultra-violet. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 89—111).—Absorption spectra of gold, silver, copper, iron, manganese, cobalt, nickel, and chromium have been obtained with a quartz spectrograph and of gold, silver, copper, iron, antimony, bismuth, arsenic, and manganese with the fluorite spectrograph. A large number of absorbed wave-lengths are tabulated.

J. S. CARTER.

Flame spectra of carbon monoxide and water gas. II. F. R. WESTON (Proc. Roy. Soc., 1925, **A, 109**, 523—526; cf. A., 1925, ii, 928).—Previous results have been confirmed by experiments with an improved disposition of the apparatus. On the supposition that the direct burning of carbon monoxide in oxygen gives rise to the continuous and banded flame spectrum of carbon monoxide, whilst indirect burning by reactions with water molecules causes the emission of the " ·OH " bands only, it is concluded that for an equimolecular mixture of carbon monoxide and hydrogen, the combustion of the former gas is effected almost exclusively by the indirect process. The addition of this proportion of hydrogen almost eliminates the normal flame spectrum of carbon monoxide.

S. BARRATT.

One-valency-electron emitters of band spectra. R. S. MULLIKEN (Physical Rev., 1925, [ii], **26**, 561—572).—Evidence is collected showing that the molecules BeF, BO, CO^+, CN, and N_2^+, together with the molecules MgF, AlO, and SiN, are all ready emitters of band spectra, and a close similarity of these molecules is indicated. The nature of multiplicity in band spectra is discussed.

A. A. ELDRIDGE.

Ultra-violet absorption spectra of butenonitriles and butenoic acids. P. BRUYLANTS and A. CASTILLE (Bull. Soc. chim. Belg., 1925, **34**, 261—284).—The absorption spectra of the following acids and their nitriles have been studied: crotonic acid, *iso*crotonic acid, their β-chloro-derivatives, methylacrylic acid, *cyclo*propanecarboxylic acid, and β-hydroxybutyric acid. The results obtained show that the crotononitrile, b. p. 108° (Bruylants, A., 1922, i, 817, 924; 1924, i, 1053), possesses the same structure as solid crotonic acid, and that the nitrile, b. p. 121°, is identical in structure with *iso*crotonic acid. These results are in agreement with those obtained from measurements of the heat of combustion of the two isomerides. The isomerisation of vinylacetonitrile into crotononitrile (cf. Bruylants, *loc. cit.*; Auwers, A., 1923, i, 661) is incomplete in N/1000- and N/10000-sodium hydroxide; even after 15 days, the curve is not identical with that of crotononitrile in alkaline solution. In very dilute solutions of sodium hydroxide (N/1000), only a single variety of crotononitrile is produced. With more concentrated alkaline solutions (N/100- or N/20-sodium hydroxide), the change is more marked, and the spectrum is displaced towards the visible region in comparison with that of *iso*crotononitrile, b. p. 121°, in N/10-

sodium hydroxide, a result which does not appear to be due to any modification of the -CN group, nor to conversion into β-hydroxybutyronitrile. It is not possible to state whether the isomerisation of sodium vinylacetate (Bruylants, A., 1924, i, 1053) in sodium hydroxide solution results in the formation of a single variety of sodium crotonate. The spectra of *cyclo*propanecarboxylic acid and its nitrile show a much more intense absorption than is indicated by their formulæ. When the intensities of absorption are compared, vinylacetic acid occupies a position intermediate between *cyclo*propanecarboxylic acid and the crotonic acids, whilst the position of the double linkings in the various acids exercises a considerable influence on the nature of the curves.

The nitrile of *cyclo*propanecarboxylic acid (Bruylants and Stassens, A., 1923, i, 213) in hexane, water, and *N*/20-sodium hydroxide gave spectra showing a band with a strong inflexion at 2400 Å., $e=1$. The nitrile of methylacrylic acid, b. p. 91·3—91·5°/763 mm., in hexane solution showed a moderately marked inflexion at 2400, $e=2·7$. Vinylacetonitrile (A., 1922, i, 817) in hexane and in water showed an inflexion at 2350, $e=1·75$. In alkaline solution, the spectrum varies with the concentration and with the interval between preparing the solution and taking the photograph. With this interval at a minimum, the spectrum of a solution of *N*/100-nitrile in *N*/10000-sodium hydroxide is very similar to those in water and in hexane. The displacement of the spectrum and increased absorption, which reach a maximum after 15 days, using the above solution, is much more rapid in more concentrated alkaline solution, and the maximum effect is obtained after 10 days, whilst if *N*/20-sodium hydroxide is used the change is immediate. The curves obtained using varying concentrations show the isomerisation of vinylacetonitrile into crotononitrile. Crotononitrile, b. p. 108°, in the three solvents hexane, water, and *N*/20-sodium hydroxide, gives a continuous spectrum. Crotononitrile, b. p. 121°, on the other hand, gives a spectrum showing a marked incurvation in the region of high concentrations. β-Hydroxybutyronitrile, b. p. 102°/10·5 mm. (Henri, A., 1899, i, 182) in aqueous solution shows a slight inflexion at 2650, $e=0·87$. The spectra of alkaline solutions vary with the concentration, that of *N*-nitrile in *N*/20-sodium hydroxide being almost identical with that of an aqueous solution. *cyclo*Propanecarboxylic acid (Bruylants and Stassens, *loc. cit.*) in hexane solution shows an inflexion at 2500, $e=35$. Vinylacetic acid (A., 1924, i, 1053) in hexane, water, and sodium hydroxide shows weak inflexions at 2500, $e=14$ in hexane, and at 2500, $e=17·5$ in alkali. On keeping the alkaline solution, a progressive displacement to the red and an increased intensity of absorption and more marked inflexions are observed; these reach a maximum after 16 days, at 2604, $e=30$. Crotonic acid in hexane solution shows a weak inflexion at 2450, $e=175$; in aqueous and alkaline solutions, it is a little more pronounced, at 2620, $e=42$. Similarly, *iso*crotonic acid, m. p. 15·5°, shows a weak inflexion at 2450, $e=359$. The curves for β-chlorocrotonic acid, m. p. 94°, and β-chloro*iso*crotonic acid, m. p. 61°, are also given. J. S. H. Davies.

Correlation of absorption spectra with ionisation in violuric acid. R. A. Morton and A. H. Tipping (J.C.S., 1925, **127**, 2514—2517).—Aqueous solutions of violuric acid containing known amounts of alkali or acid or salt have been examined spectrographically and p_H values have been determined by means of the quinhydrone electrode. The colour band at 5380 Å. is common to the violurate ion and to the undissociated sodium salt, but not to the undissociated acid, which is therefore colourless. In the presence of varying quantities of mineral acid, the intensity of the absorption is quantitatively proportional to the violurate-ion concentration. Violuric acid in aqueous solution shows two bands in the ultra-violet, one with a maximum at 3120, $e=3000$, and the other at 2490, $e=10,300$. The former is due to the violurate ion and persists in aqueous solutions of the neutral salt, e (max.) becoming 13,300. The latter is due to the undissociated molecule, and it alone persists in alcoholic solution e (max.) becoming 13,400. The sum of the extinctions of the two bands observed in the aqueous solution of the acid is almost equal to that observed both for the undissociated acid (13,400) and for the completely dissociated salt (13,300). E. E. Walker.

Absorption spectra and lactam–lactim tautomerism. R. A. Morton and E. Rogers (J.C.S., 1925, **127**, 2698—2701).—The work of Hartley and Dobbie on the absorption spectra of isatin, carbostyril, *o*-hydroxycarbanil, and their *O*- and *N*-ethers has been repeated, giving special attention to the position of the maxima of the absorption curves. The absorption spectra of the *O*- and *N*-ethers of isatin and *o*-hydroxycarbanil resemble each other so closely that no conclusion can be drawn with regard to the constitution of the parent substance. On the other hand, Hartley and Dobbie's observations that the absorption spectrum of carbostyril is very similar to that of its *N*-ether and different from that of its *O*-ether is confirmed. The similarity between the absorption spectra of phloroglucinol and its trimethyl ether is also confirmed. The following wave-lengths of absorption band maxima in Å. are recorded: isatin: 2430, 2950, 4130; ψ-methylisatin (*N*-ether): 2465, 3000, 4195; methylisatin (*O*-ether): 2447, 2965, 4140; 5-iodoisatin (red form): 2500 and 4250; carbostyril: 2690 and 3270; *N*-methyl ether: 2705 and 3280; *O*-methyl ether: 3222 and 3085; *O*-ethyl ether: 3226 and 3085; *o*-hydroxycarbanil 2736, *N*-ether 2738, *O*-ether 2735; phloroglucinol (in alcohol) 2665, trimethyl ether 2646.

E. E. Walker.

Infra-red absorption spectrum of molten naphthalene. F. K. Bell (J. Amer. Chem. Soc., 1925, **47**, 2811—2816).—The infra-red absorption spectrum of molten naphthalene is in satisfactory agreement with that reported by Coblentz (Carnegie Inst. Publ., 1905, **35**, 127) for naphthalene in carbon tetrachloride solution, and shows marked correspondence with the infra-red absorption spectrum of benzene in the region of the shorter wave-lengths, up to 5·5 μ, beyond which the dissimilarity of the two spectra increases. A simple electrically-heated

cell is described for maintaining substances in the molten condition when their absorption spectra are being plotted. F. G. WILLSON.

Influence of p_H on the ultra-violet absorption spectra of certain cyclic compounds. W. STENSTRÖM and M. REINHARD (J. Physical Chem., 1925, **29**, 1477—1481).—The absorption bands of a mixture of certain amino-acids in water show a shift towards longer wave-lengths when the mixture is made alkaline. Other cyclic compounds have been examined for a shift in absorption bands with a change in hydrogen-ion concentration. The changes in wave-length with p_H have been followed at a selected value of the extinction coefficient of the substance concerned. Curves for phenol, resorcinol, and tyrosine in water are given. It is found that the bands in the ultra-violet, between 2200 and 3600 Å., depend on hydrogen-ion concentration for aqueous solutions of the following compounds: phenol, tyrosine, resorcinol, *p*-hydroxybenzoic acid, salicylic acid, and *p*-hydroxybenzaldehyde. No shift occurs with benzoic acid, phenylalanine, or tryptophan. The relation between p_H and structure of the band is that the latter will move towards the red end of the spectrum and increase in intensity when a certain alkalinity is reached. The presence of an hydroxyl group in the benzene ring of the compound seems essential. In the case of tyrosine, the shift is explained as a change from a curve characteristic of the molecule to one characteristic of the compound ionised at the carboxyl group. A curve showing the shift for blood-serum is also given. L. S. THEOBALD.

Line fluorescence of cadmium vapour. W. KAPUSCINSKI (Nature, 1925, **116**, 863—864).—Fluorescence was first observed at about 350°, when the pressure of the cadmium vapour was 0·2 mm.; it rapidly increases with rise of temperature, changing in colour from bluish-green (with intense emission of the arc triplet 5086·06, 4800·09, 4678·37 Å.) to blue. The lines 3261·2 and 2288·8 were observed, and the lines 2748·7 and 2573·1 Å. may also be present. The effect of using an aluminium, iron, lead, copper, or mercury spark instead of a cadmium spark as the source of light is described. A. A. ELDRIDGE.

Dissociation and fluorescence of iodine vapour. E. G. DYMOND (Z. Physik, 1925, **34**, 553—561; cf. Franck, A., 1925, ii, 1077).—The absorption bands of iodine were examined which converge at 4995 Å., thereafter extending as a continuous absorption of diminishing intensity towards the violet. When iodine vapour was excited by light of wave-length longer than 4995 Å., fluorescence was observed, but ceased suddenly at this wave-length. Hence, up to this point the iodine could radiate the energy it received; beyond it, this ceased to be possible, and it is concluded that the molecule must have dissociated into a normal atom and an excited atom. The amount of energy left in the excited atom would be represented by 1 volt; this corresponds with the calculated value 0·9 volt for the difference of the terms $2p_2$—$2p_1$. No evidence of dissociation could be observed by means of a quartz-fibre manometer. Three new series of resonance spectra are described, excited respectively by lines in the cadmium, copper, and sodium spectra. E. B. LUDLAM.

Indirectly excited fluorescence spectra. S. LORIA (Physical Rev., 1925, [ii], **26**, 573—584).—In the fluorescence spectrum of thallium excited by collision with activated mercury atoms, every line expected theoretically was identified; the life of the $2p_1$ state for thallium atoms is of the order of 10^{-6} sec. In confirmation of the results of Donat, enhancement of the lines was observed in the presence of argon or nitrogen, the effect being neutralised by a trace of oxygen. The results indicate that the metastable mercury atom may survive many collisions with normal argon or nitrogen molecules, but easily gives up its energy when colliding with normal thallium or mercury atoms, probably more easily to the former than to the latter. A. A. ELDRIDGE.

Phosphorescent flame of carbon disulphide. H. B. DIXON and W. F. HIGGINS (Mem. Manchester Phil. Soc., 1924—25, **69**, 19—23).—A mixture of air and carbon disulphide ignites when heated to 156°, and the addition of carbon disulphide to any combustible gas greatly reduces the ignition point. In general, the substitution of oxygen for air lowers the ignition temperature by about 25°. Methane containing 50% of carbon disulphide ignites rapidly in air at 195°, and in oxygen at 173°. With only 20% of disulphide, it ignites rapidly at 191° in oxygen, but not below 485° in air. Above 200°, luminescent clouds are obtained in the last mixture. This phenomenon has been investigated. The luminous cloud begins to form at about 180° and a reddish-brown deposit, carbon monosulphide, separates from it. Traces of coal-gas, or of acetylene or ethylene, destroy the luminosity and prevent the formation of the monosulphide. The luminous cloud may be obtained as a large, cool, phosphorescent flame easily passing through metallic gauzes which prevent the passage of hot flames. The "poisoning" gases must be mixed with the gases before combustion in order to produce an effect. Steam, carbon dioxide, hydrochloric acid, and carbon tetrachloride vapour act as inert gases. Sulphur dioxide, although not an active poison like ethylene, has a marked effect, as also have the vapours of ethyl alcohol and ethyl ether. The effect of the paraffins increases with the mol. wt. It is suggested that the following reaction takes place: $CS_2+O_2=CS+SO_2$. The carbon monosulphide molecules coalesce with each other and with disulphide molecules, the latter then being more readily attacked, leaving further monosulphide molecules joined to the original nuclei. Thus the latter increase in size and condensing power until the chemical action at their surface is sufficient to give luminosity. The "poisoning" gases condense preferentially on the monosulphide molecules and prevent the attachment of disulphide. The same apparatus can be used to show the analogous phosphorescent flame of ether vapour. M. S. BURR.

Mechanics of the perturbed molecule. L. MENSING (Z. Physik, 1925, **34**, 602—610).—For diatomic molecules of the type in which the electrons of one atom do not also describe an orbit round the

other, the moment of the electrons is in the direction of the line joining the nuclei; for one model in two dimensions the moment is perpendicular to this line, but for like atoms this model is unstable and for unlike atoms the stability depends on the ratio of moments of the electrons. An oblique moment is not in accord with quantum theory.

E. B. LUDLAM.

Glaser's experiments and the orientation of molecules in a magnetic field. G. BREIT (J. Washington Acad. Sci., 1925, **15**, 429—434).—Mathematical.

Molecular refractivity of some simple salts. K. F. HERZFELD and K. L. WOLF (Ann. Physik, 1925, [iv], **78**, 195—203; cf. A., 1925, ii, 1119).—Previous measurements of the optical dispersion of sodium and potassium chlorides are used as a basis for the calculation of the molecular refractivity of some simple salts, the ions of which are electronically of the type of the inert gas atoms. The calculation involves the electron numbers and the characteristic frequency of the ions. The former are taken as equal to the atomic number of the corresponding inert gas atoms. The latter are obtained from the limiting value of the continuous absorption spectrum of the ion, by adding, in the case of an anion, or subtracting, in the case of a cation, the Coulomb portion of the lattice energy to the electron affinity of an anion, or to the work of ionisation of a cation. The wave-length of the resonance line, which occurs in the second term of the molecular refractivity expression, is about 1·6 times that of the characteristic wave-length. The energy of ionisation of the ions Li^+, Rb^+, and Cs^+ is assumed to be 1·85 times the ionisation energy of the corresponding inert gas atom, the factor being obtained as the ratio of the experimental values of the ionisation energies of Na^+ and of K^+ to those of neon and argon. The same ratio is assumed to hold between the ionisation energies of the bivalent ions Mg^{++} and Ca^{++} and those of the univalent ions Na^+ and K^+. The molecular refractivities are calculated of the alkali halides, of the oxides of beryllium, magnesium, and calcium, and of the halogen acids. Where experimental values are available for comparison, the agreement is satisfactory, except for salts with large anions and small cations, for which the theoretical refractivities are too small.

F. G. TRYHORN.

Dispersion of carbon disulphide in the ultra-violet. G. BRUHAT and M. PAUTHENIER (J. Phys. Radium, 1925, [vi], **6**, 287—294).—See A., 1925, ii, 478.

Effects of chemical combination on the energy of the intra-atomic levels. R. BRUNETTI (Atti R. Acad. Lincei, 1925, [vi], **2**, 323—328).—Theoretical. A possible electronic mechanism of the formation of polar compounds is suggested with a view to account for the displacement of the high-frequency lines of an element as a result of chemical combination. The formation of a polar compound may be regarded as occurring in two stages, first, the transformation of the atoms into ions by addition or subtraction of electrons, and, secondly, the aggregation of the ions into a crystal lattice. The former stage may involve, in addition to a change in the number of electrons in the outer sheaths of the atoms, a change in the number of electrons in the internal shell, consequent on a change in volume of the interior of the atom. It is supposed that the effect of these changes will be to alter the effective atomic number of the atom. This latter will be influenced also by the complex action of attractive and repulsive forces between the ions in the lattice. Empirical terms are suggested for these effects, and expressions derived for the work of introducing an ion into a crystal lattice, and for the variation of the sheath number in the transition of an element from the free to the combined state. It is shown that the variations in the molecular sheath number will depend on the sign and magnitude of the electrostatic potentials existing at the lattice points in the crystal, and that the molecular sheath number may be calculated from a knowledge of the lattice potential. The difference in energy of intra-atomic levels as a result of these changes in the number of electrons in the various levels will result in corresponding differences between the short-wave spectra of an atom in the free and combined states, respectively.

F. G. TRYHORN.

Theoretical calculations of physical properties of certain crystals. J. E. LENNARD-JONES and P. A. TAYLOR (Proc. Roy. Soc., 1925, **A**, **109**, 476—508; cf. A., 1925, ii, 16, 91, 253).—Theoretical. Methods are given of obtaining the forces between certain neon-like and argon-like ions, and these are successfully used to account for the observed distances in certain crystals of the rock-salt type, and for the prediction of other crystal constants yet unmeasured, such as those of calcium chloride. Compressibility, elasticity, and other constants of these crystals are also calculated. The conclusion is that the repulsive force of neon-like ions in crystals is represented by an inverse 11th power law, and that for argon-like atoms by an inverse 9th power law. The latter law does not hold at large distances, when an inverse 15th power law fits the experimental results better.

S. BARRATT.

Forces between atoms and ions. J. E. LENNARD-JONES (Proc. Roy. Soc., 1925, **A**, **109**, 584—597; cf. preceding abstract).—From the interatomic distance and compressibility of crystals of rubidium bromide, and the refractivities of krypton and of the ions of bromine and rubidium, the force-field of krypton is calculated. Similarly, the force constants of the xenon group are deduced from measurements of cæsium iodide, and from the fields of krypton and xenon those of the associated ions are derived. By previous methods (*loc. cit.*), the fields between any two of a series of neon-like, argon-like, krypton-like, and xenon-like ions are then deduced. The law of force between both atoms and ions is of the form λr^{-n}, and λ and n are calculated. The results are utilised to find the interatomic distances of 32 crystals, including 16 alkali halides. In the latter case, the calculated values are found to lie, with one excep-

tion, within 1% or 2% of the observed distances. Compressibilities and crystal energies of the alkali halides are also calculated, moderate agreement being found with the observed values.

L. L. BIRCUMSHAW.

Law of force and size of diatomic molecules as determined by their band spectra. R. T. BIRGE (Nature, 1925, **116**, 783—784).—Assuming for the law of force the function $F=k_1(r-r_0)+k_2(r-r_0)^2+k_3(r-r_0)^3$ etc., where r and r_0 are the nuclear separation and equilibrium nuclear distance, respectively, and for the rotational energy of a non-vibrating molecule the usual function $Em=Bm^2+Dm^4+Fm^6$ etc., the values of k may be expressed as explicit functions of B, D, F, etc., and evaluations of k may be made with varying accuracy. The underlying theory is confirmed by measurements of the CN band at 3883 Å., whereby $k_1=16{\cdot}12\times10^5$ dyne-cm.$^{-1}$, and $k_2=-6{\cdot}18\times10^{14}$ dyne-cm.$^{-2}$, whereas from vibrational energy data $k_1=16{\cdot}00\times10^5$ and $k_2=-5{\cdot}44\times10^{14}$. Similarly, values of k_1 have been obtained for the initial and final states of the CN, CuH, N_2, and N_2^+ molecules, the discrepancy being in all cases within the limits of error. The explanation of the alternation of intensity of successive lines in band series of such molecules as N_2 and N_2^+ is discussed.

A. A. ELDRIDGE.

Determination of Avogadro's number by measurements of the birefringence of solutions of dialysed iron. L. TIERI (Atti R. Accad. Lincei, 1925, [vi], **2**, 331—334; cf. *ibid.*, 1923, [v], **32**, 155).—Measurements of the magnetic birefringence at 23°, and in a field of 4000 gauss, have been used to determine the number of particles in different strata of preparations of dialysed iron which had been allowed to remain for 90 days in order to attain statistical equilibrium. Three preparations showing positive and one showing negative birefringence were examined. Two of the former gave a distribution of particles in satisfactory accord with Laplace's law. The density of the granules was determined by means of a pyknometer and their average radius by the application of Stokes' law to measurements of their rate of fall in a long capillary tube. From these data, the values 66×10^{22} and 50×10^{22} were obtained for Avogadro's number.

F. G. TRYHORN.

Eka-cæsium and eka-iodine. F. H. LORING and J. G. F. DRUCE (Chem. News, 1925, **131**, 321).—The lines on the X-ray photograph ascribed to eka-cæsium and eka-iodine were obtained during the examination of material from pyrolusite after the bulk of the rhenium had been removed and not from the examination of crude rhenium oxide as previously reported (A., 1925, ii, 1124). The plate also showed a line at 0·693 Å., which corresponds with the $L\alpha$ line of element 93.

A. R. POWELL.

Eka-cæsium. II. F. H. LORING (Chem. News, 1925, **131**, 371; cf. A., 1925, ii, 1124, and preceding abstract).—Further X-ray evidence is given in support of the author's claim to have discovered element 87.

A. R. POWELL.

Search for element 93. II. Examination of crude dvi-manganese (rhenium). III. Foreshadowing elements 75, 85, 87, and 93. F. H. LORING and J. G. F. DRUCE (Chem. News, 1925, **131**, 337—341).—Crude rhenium chloride has been isolated from pyrolusite and from "pure" manganese salts by removing the manganese with ammonium sulphide in the presence of ammonia and ammonium chloride, evaporating the solution to dryness, removing calcium with ammonium oxalate in acetic acid solution, expelling the ammonium salts by heating, dissolving the residue in hydrochloric acid, and concentrating the solution until short, feathery crystals deposited on cooling. The chloride solution gives a white precipitate with ammonia which slowly darkens on exposure to the air. Except for the absence of a precipitate with ammonium sulphide, rhenium gives similar reactions to manganese. A further discussion of the lines observed on a film obtained by exposing the crude oxide obtained to X-rays on a copper anticathode is given. (Cf. A., 1925, ii, 1124.)

A. R. POWELL.

Examination of nickel catalysts with X-rays. G. L. CLARK, W. C. ASBURY, and R. M. WICK (J. Amer. Chem. Soc., 1925, **47**, 2661—2671).—Powder-diffraction photographs of various nickel catalysts have been taken with a new type of X-ray spectrograph. Catalysts prepared by reduction with carbon, alcohol, ethyl acetate, and hydrogen, and having widely different activities, gave identical lines for nickel, $d_{100}=3{\cdot}536$ Å.; that prepared by reduction with sodium hypophosphite in solution gave no definite lines and was apparently colloidal. The intensities of the lines, as measured by a photodensitometer, were approximately the same for the various catalysts, and agreed with the values calculated for a face-centred lattice. A rough parallelism exists between decreasing line width and increasing catalytic activity. Nickel monoxide (simple cubic) gave $d_{100}=4{\cdot}16$ Å., the dioxide and nickelo-nickelic oxide gave no lines, and the sesquioxide gave only the lines of the monoxide, showing it to be a mixture of this with the dioxide.

A. GEAKE.

Model gratings to illustrate the diffraction of X-rays by crystals. W. L. BRAGG (Mem. Manchester Phil. Soc., 1924—25, **69**, 35—38).—Gratings of varying types of complexity have been obtained with the aid of a photographic plate ruled with 400 lines to the inch. These were reproduced on a second plate by putting the two in contact and exposing to light. By then moving the original plate a fraction of the distance between the lines and exposing once more, repeating this as often as desired, gratings with 400 groups of lines to the inch, of any required complexity, could be produced. Gratings reproducing the same effects as the crystal gratings, formed by the planes of rock-salt or diamond, for example, have thus been obtained.

M. S. BURR.

X-Ray interference in mixed crystals. M. VON LAUE (Ann. Physik, 1925, [iv], **78**, 167—176).—Tammann's contention (A., 1925, ii, 20) that X-ray crystal photographs should be very sensitive to slight deviations from the "normal" distributions

of the atoms in the lattices of mixed crystals, is disproved by a mathematical investigation of the positions and intensities of the interference points resulting from a purely random distribution of two types of atom constituting a simple cubic lattice. The case is also considered in which, as a result of the conditions of preparation, an atom in a mixed crystal is surrounded by more atoms of its own kind than would correspond with a uniform distribution of the constituents of the mixture. F. G. TRYHORN.

Crystal structure of carbon dioxide. J. C. MCLENNAN and J. O. WILHELM (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 51—56).—The crystal structure of carbon dioxide solidified by liquid air has been investigated by means of an X-ray method. Carbon dioxide crystallises in a cubic system with 4 mols. in each unit cell and a lattice distance of 5·76 Å. The distance between carbon and oxygen atoms is 1·25 Å.; the moment of inertia is $8·2 \times 10^{-39}$ g. cm.^{2} J. S. CARTER.

Structure of α- and β-quartz. (SIR) W. H. BRAGG and R. E. GIBBS (Proc. Roy. Soc., 1925, **A**, **109**, 405—427).—The only elements of symmetry possessed by an ordinary (α-) trigonal crystal of quartz are a trigonal and three digonal axes. It is impossible to determine the crystal structure completely by consideration of these symmetry restrictions and of the distances and angles between the various reflecting planes in the crystal for X-rays. The problem could be solved by studying, in addition, the intensities of the X-ray reflexions, if the principles governing these intensities were sufficiently understood. Actually more indirect methods have to be applied. Chemical considerations have been employed, but with unsatisfactory results. The method here proposed utilises the fact that trigonal (α-) quartz passes into hexagonal (β-) quartz at 575°. The symmetry of the hexagonal form is much higher, and the details of its structure can be fixed with ease. There is evidence that the structure of the crystal is but slightly changed during the transformation from the α- to the β-form, and hence the structure of the β-form gives a powerful clue to the structure of the α-form. A structural model of the α-form, deduced in this manner, accounts for the piezo-electrical properties of the crystals, and for the varieties of twinning which are recorded.

The electrical conductivity of quartz is hundreds of times greater along the crystal axis than across it. This fact may be correlated with the spacings of the atoms in the crystal, as the structure suggested has more open and direct passages along than across the axis. S. BARRATT.

Crystal structure of barytes, celestine, and anglesite. R. W. JAMES and W. A. WOOD (Proc. Roy. Soc., 1925, **A**, **109**, 598—620).—Assuming the sulphate ion to be a tetrahedron of oxygen atoms surrounding a central sulphur atom, the distance S—O being 1·5 Å. (cf. Bradley, A., 1925, ii, 638), it has been found possible to assign structures to the three isomorphous crystals investigated which are practically identical, and account completely for the observed intensities of the X-ray spectra given by them. The structure is based on a simple orthorhombic lattice containing 4 mols. to the unit cell (from the specific gravity and mol. wt. of the crystal), and the space group is V_h^{16}. The parameters fixing the relative positions of the different kinds of atoms were determined by X-ray intensity measurements.

For barium sulphate, the dimensions of the unit cell are: $a=8·85$, $b=5·43$, $c=7·13$ Å. and the axial ratio is 1·6304 : 1 : 1·3136. For strontium sulphate, $a=8·36$, $b=5·36$, $c=6·84$ Å., and the axial ratio is 1·5580 : 1 : 1·2800. For lead sulphate, $a=8·45$, $b=5·38$, $c=6·93$ Å., and the axial ratio is 1·5704 : 1 : 1·2894. The structure appears to be one in which each positive metallic ion is surrounded as closely and as uniformly as possible by negative oxygen ions, perfect freedom of adjustment of the ions being hampered, because they are attached together in fours in the sulphate groups.

In calculating the structure factors, the figures for the diffracting power of ions at different angles, calculated by Hartree (A., 1925, ii, 735), were employed with slight modifications. A comparison of the absolute intensity of reflexion actually observed with that calculated on the classical theory showed that the observed intensity is always lower than, although of the same order of magnitude as, the calculated value. A possible reason for the structure which is common to a number of crystals of the type XRO_4 is discussed. Observations on potassium permanganate and potassium perchlorate confirm the view that the structures are essentially similar to those of the sulphates under investigation.

L. L. BIRCUMSHAW.

Structure of barium sulphate. R. W. JAMES and W. A. WOOD (Mem. Manchester Phil. Soc., 1924—1925, **69**, 39—51).—See preceding abstract.

Crystalline structure of hexachlorobenzene and hexabromobenzene. W. G. PLUMMER (Phil. Mag., 1925, [vi], **50**, 1214—1220).—Hexachlorobenzene and hexabromobenzene have been examined by the powder method of X-ray analysis. Photographs were taken with a Shearer X-ray tube fitted with a copper anticathode, the β-lines of copper being excluded by a nickel filter. The observed spacings are tabulated, and agree with the theoretical spacings assuming 2 mols. per cell. The dimensions of the cell for hexachlorobenzene are $a=8·10$, $b=3·86$, $c=16·68$ Å. These results were later confirmed on a perfect crystal of hexachlorobenzene. Based on these measurements a suggestion is made of the probable arrangement of the atoms in the molecule. The measurements of hexabromobenzene were not so successful, but they prove the general correctness of the structure assumed. A. B. MANNING.

Isomorphism of molybdates of the rare-earth metals with those of calcium, strontium, barium, and lead. F. ZAMBONINI and R. G. LEVI (Atti R. Accad. Lincei, 1925, [vi], **2**, 303—305; cf. A., 1925, ii, 1133).—Tabulated values are given showing that the reflecting planes are essentially the same in crystals of the molybdates of calcium, strontium,

barium, and lead. The following values, based on the values of a determined by X-ray measurements, and on those of the ratios $a : c$ determined by crystallographic methods, are calculated for the elementary cells of these substances. $CaMoO_4$, $a=3{\cdot}67$, $c=5{\cdot}69$ Å.; $SrMoO_4$, $a=3{\cdot}79$, $c=5{\cdot}97$ Å.; $BaMoO_4$, $a=3{\cdot}96$, $c=6{\cdot}43$ Å.; $PbMoO_4$, $a=3{\cdot}80$, $c=6{\cdot}00$ Å. The densities, calculated from these data, are, respectively, 4·28, 4·73, 4·84, 6·95, and agree with experimental values. For the alkaline-earth molybdates, the values of a and c are approximately linear functions of the atomic weights, or atomic numbers, of the cation metals. Since a similar relationship holds for the nitrates of these metals, the possibility is suggested of calculating the dimensions of the elementary cells of isomorphous phases, which are too unstable to be experimentally investigated.

F. G. Tryhorn.

Isomorphism between samarium compounds and the corresponding compounds of calcium, strontium, barium, and lead. G. Carobbi (Rend. Accad. Sci. Fis. Mat. Napoli, 1925, [iii], **31**, 83—95).—The results of the author's investigations on the molybdates and phosphates, together with Zambonini's results (A., 1923, ii, 499, 691), show that certain samarium compounds are capable of forming homogeneous mixed crystals with the corresponding compounds of calcium, strontium, and lead, and that the isomorphism of samarium towards the metals of the isomorphogenic calcium group is more pronounced than that of the other metals of the cerium group.

T. H. Pope.

New magnetic state of the cobalt ion. (Mlle.) A. Serres (Compt. rend., 1925, **181**, 714—715).—Anhydrous amorphous cobalt sulphate has been obtained containing a cobalt ion corresponding with 26 magnetons and possessing a powerful negative molecular field. The magnetic susceptibilities of the salt are recorded over the temperature range 7—422°. (Cf. Foex, A., 1925, ii, 345; Théodoridès, J. Phys. Radium, 1922, [vi], **3**, 1.)

S. K. Tweedy.

Effect of temperature on the paramagnetism of cobalt salts in solution. M. Chatillon (Compt. rend., 1925, **181**, 778—780).—The magnetic properties of solutions of cobaltous chloride, sulphate, and nitrate have been examined at temperatures from 10° to 140°. When the reciprocal of the coefficient of magnetisation, corrected for the diamagnetism of the molecule, is plotted against the absolute temperature, straight lines are obtained which do not pass through the absolute zero, but correspond with a Curie point of −12°, and with a moment of 25·0 magnetons, in contradiction to the value 24·5 found by Brant (Physical Rev., 1921, [ii], **17**, 768). The anhydrous sulphate according to Serres (cf. preceding abstract)) has a moment of 26·0 magnetons, and this value is retained when the anhydrous salt is dissolved in water, the solution giving a Curie point of −33°. But if the solution is crystallised and the crystals are redissolved, the value of 25·0 magnetons is found.

W. Hume-Rothery.

Magnetic susceptibility of rubidium bromide, cæsium iodide, krypton, xenon, [potassium, rubidium, and cæsium]. L. Crow (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 63—70).—The magnetic susceptibilities of krypton and xenon have been determined from observations on rubidium bromide and cæsium iodide, the experimental method of Meyer (A., 1925, ii, 173) being used. The molecular magnetic susceptibilities of rubidium bromide and cæsium iodide are $-62{\cdot}9\times10^{-6}$ and $-77{\cdot}6\times10^{-6}$, respectively. The derived values for the volume susceptibilities at 20° and 760 mm. of krypton and xenon are $-13{\cdot}1\times10^{-10}$ and $-16{\cdot}2\times10^{-10}$. The atomic magnetic susceptibilities of potassium, rubidium, and cæsium are, respectively, $-1{\cdot}9\times10^{-6}$, $-7{\cdot}0\times10^{-6}$, and $-8{\cdot}0\times10^{-6}$.

J. S. Carter.

Magnetic rotatory power of some paramagnetic minerals at very low temperatures. H. K. Onnes, J. Becquerel, and W. J. de Haas (Compt. rend., 1925, **181**, 838—841).—The magnetic rotatory power of certain didymium minerals increases with decreasing temperature down to 4·2° Abs. (A., 1908, ii, 338). The results for tysonite, parisite, and bastnaesite, after a small correction, indicate that Curie's law is followed. Complex results are obtained with xenotime, due to the superposition of two distinct magnetic polarisations; one, generally positive, is due to the Zeeman effect for the absorbed radiations, whilst the other, negative, is peculiar to paramagnetic substances and is due either to orientation phenomena or to distortion in the magnetic field.

S. K. Tweedy.

Absorption spectra of rare-earth crystals in a magnetic field at the temperature of liquid helium. J. Becquerel, H. K. Onnes, and W. J. de Haas (Compt. rend., 1925, **181**, 758—760).—Uniaxial crystals of xenotime (spectrum due to erbium), tysonite, parisite, and bastnaesite (spectrum due to didymium) have been examined. The absorption spectra, which are complex at 80° Abs., become more simple at 14° Abs. At 4·2° Abs., spectra are on the whole even more simple, some bands having disappeared, but others observed only at low temperatures have increased in intensity. The crystals were also examined in a field of 26,170 gauss, the optical axis and beam of light being in the direction of the lines of force. The change of period produced by the magnetic field is independent of the temperature. Great dissymmetry is shown by the intensity of the components corresponding with the absorption of inverse circular vibration, one component sometimes completely disappearing. At 14° Abs., the component displaced towards the violet is reinforced, but this is not always the case at 4·2° Abs.

W. Hume-Rothery.

Effect of the addition of dyes on the crystallisation of calcium carbonate. V. Kohlschütter and C. Egg (Helv. Chim. Acta, 1925, **8**, 697—703; cf. A., 1925, ii, 1035, 1036).—The work on somatoid forms has been extended by an investigation of the effect, on crystallisation of calcium carbonate from solutions of the hydrogen carbonate, of the following dyes: Congo-red, gallacetophenone, ponceau, alizarin

Bismarck-brown, eosin, crystal-violet, fuchsin, tropæolin, and chrysoidine. Congo-red is adsorbed principally by calcite with some deformation of the crystals, whilst aragonite exhibits a smaller tendency to adsorb the dye. The formation of aragonite crystal-nuclei is hindered and sometimes totally inhibited. The importance of colloidal phenomena in the work earlier stressed is now confirmed by the observation that the most effective dyes exhibit an ultramicroscopic effect either alone or in solutions containing the calcium ion. Thus a fresh solution of Congo-red and calcium hydrogen carbonate exhibits an intense light-cone. The colloids are adsorbed on the crystal surfaces and disturbances of crystal-habit and growth ensue which are peculiar to each colloidal dye. Small additions of Congo-red cause the formation of rhombohedra with red cores, suggesting that particles of the calcium salt of the dye serve as a nucleus for crystallisation of calcite. Higher dye concentrations render the crystal surfaces "passive," resulting in deformation or inhibition in crystal-growth.

R. A. MORTON.

Formation of somatoid forms. V. KOHLSCHÜTTER, M. BOBTELSKY, and C. EGG (Helv. Chim. Acta, 1925, **8**, 703—723; cf. preceding abstract).—An attempt is made to define more clearly (cf. A., 1925, ii, 1035) the conditions for the appearance of a whole range of somatoid forms. One type of disc-like bodies only appears in the presence of a colloid. A whole series of somatoid forms designated α is intimately related with the formation of calcite rhombohedra, and the precipitation of these forms occurs only when the ratio of calcium carbonate to colloidal substance comes within a definite range. The particular form is for the α-series largely independent of the chemical nature of the added colloid. By varying the amount of added material, the whole series of α-somatoid forms can be obtained with one and the same substance. More specific effects occur in the formation of β-somatoid forms when aggregations of calcium carbonate and colloidal substance play a dominating part. The investigation concerns crystallisation under conditions approaching those existing in the living organism. R. A. MORTON.

Electrical conductivity of phosphorus pentachloride. G. W. F. HOLROYD, H. CHADWICK, and J. E. H. MITCHELL (J.C.S., 1925, **127**, 2492—2493).—A preliminary paper on the mode of ionisation of phosphorus pentachloride in solution.

R. CUTHILL.

Light scattering of "abnormal" liquids. O. C. H. KITCHING (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 30—31).—The light scattering of aniline, phenol, and acetaldoxime at various temperatures between 20° and 100° has been determined relatively to benzene. With aniline and phenol (normal liquids), the observed temperature coefficients and light scatterings are in fairly good agreement with the calculated values, whilst in acetaldoxime the scattering is more than double and the temperature coefficient less than half the calculated value.

J. S. CARTER.

Light scattering of salt solutions. C. W. SWEITZER (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 31).—A revision of the measurements previously reported (A., 1925, ii, 512) has led to values which approach more closely to those calculated. Methyl alcohol was used in preference to water as the standard of comparison. J. S. CARTER.

Scattering of light by anisotropic liquids. W. H. MARTIN (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 36—38; cf. A., 1925, ii, 90).—The depolarisation factor of the light scattered by *p*-azoxyanisole, rendered dust-free by filtration through a Mandler diatomaceous earth filter, is 0·85. For a liquid composed of molecules in which vibration can occur in only one direction, the calculated value is 0·86. The experimental result hence supports the hypothesis of needle-shaped molecules in this type of liquid crystals. J. S. CARTER.

Dependence of absorption coefficient on the thickness of the absorbing colour layer. A. PREDVODITELEV and W. BLINOV (Z. Physik, 1925, **35**, 38—49).—The absorption coefficients of thin layers of collodion solutions of fuchsin and crystal-violet, of different concentrations, have been determined in a König–Martens spectrometer. The thickness of the films was of the order of 1 μ. The absorptive coefficient was found to be a periodic function of the density distribution of the dye molecules at the surface. It is suggested that this behaviour is due to the transformation into heat of only part of the light energy absorbed, the remainder going to increase the internal energy of the atom or molecule. On this assumption, formulæ have been deduced, and theoretical curves constructed, which are in close agreement with the experimental results.

M. S. BURR.

Specific heat variations in relation to the dynamic action of gases and their equations of state. W. J. WALKER (Phil. Mag., 1925, [vi], **50**, 1244—1260).—Some preliminary experiments on the flow of highly superheated steam through a nozzle are described. The nozzle plate was bolted between two cast-iron boxes of square section and 6 in. internal dimension. The box to which the steam was first admitted contained an electric heater, and the temperature of the steam was measured by an iron–constantan couple placed just behind the nozzle plate and opposite the centre of the nozzle orifice. The pressure was measured by a Bourdon gauge. From the second box, the steam was conducted to a surface condenser, where it was collected and weighed. Results are tabulated giving the observed discharge through a ½ in. nozzle of stream-lined form, for pressures of 26—56 lb. per sq. in. and temperatures of 480—700° Abs. The results suggest an adiabatic relation of the form $pv^n e^{f(T)}$=constant, in which the factor $e^{f(T)}$ involves the variation of specific heat with temperature. This relation is shown to lead to a general equation of state of the Dieterici and Jeans type. A. B. MANNING.

Physical properties of nitromethane. J. W. WILLIAMS (J. Amer. Chem. Soc., 1925, **47**, 2644—2652).—Nitromethane consists of an equilibrium

mixture of the two forms $CH_3{\cdot}NO_2$ and $CH_2{:}NO{\cdot}OH$, and its physical properties may, therefore, be expected to vary irregularly with the temperature. The specific heat, determined as previously described (A., 1924, ii, 589), depends greatly on the method of drying the nitromethane. When dried by distillation from phosphorus pentoxide, the results do not fall on a smooth curve, but there is a minimum at about 30°. Vapour pressures were determined by the method of Ramsay and Young, but no irregularity exists, the logarithm of the vapour pressure varying linearly with the reciprocal of the absolute temperature. The density–temperature curve is also normal, and between 20° and 101° is represented by the empirical equation $d_4^t=1{\cdot}1668-0{\cdot}001358t-0{\cdot}00000055t^2$. Phosphorus pentoxide forms a stable gel with nitromethane in presence of a trace of water. A. GEAKE.

Absolute critical temperatures. M. PRUD'HOMME (Bull. Soc. chim., 1925, [iv], **37**, 1330—1340).—Relations between the absolute critical temperatures (T_c) of substances are pointed out. With simple substances which combine among themselves, the T_c difference of suitably chosen pairs is often equal; thus for carbon dioxide and disulphide, carbon monoxide, and carbonyl sulphide $T_c(CS_2)-T_c(CO_2)=T_c(COS)-T_c(CO)$. For many non-metallic substances, the T_c values are simple multiples or fractions of those for the components. For metallic compounds or carbon compounds containing only one atom of carbon, the metal or carbon atom does not affect the T_c values, which are simple multiples or fractions of the value for the non-metallic element. These multiples are quite arbitrary, and may differ even for analogous substances as cyanogen chloride or bromide. If the linkings between a carbon and a hydrogen atom are considered as one valency, and single, double, and triple linkings between carbon atoms as 2, 4, and 6 valencies, respectively, the absolute critical temperature of aliphatic hydrocarbons is an exponential function of the number of valencies, namely, $T_c=cV^n$, where $n=0{\cdot}489$ and $\log c=2{\cdot}03911$. With the sole exception of ethylene, this rule applies for both saturated and unsaturated hydrocarbons up to hexane. Similar relations exist for saturated alcohols, whilst for esters, ethers, and nitriles the T_c values are additive properties of the different groups present, acetic acid and acetonitrile being exceptions. W. HUME-ROTHERY.

Properties of simple compounds and types of the solid state. E. FRIEDERICH (Z. Physik, 1925, **34**, 637).—Corrections of minor points in an earlier paper (A., 1925, ii, 374). E. B. LUDLAM.

Velocity of sound in mixtures of gases. H. B. DIXON and G. GREENWOOD (Proc. Roy. Soc., 1925, **A**, **109**, 561—569).—The velocity of sound in a number of mixtures of simple gases has been measured, using Kundt's double-tube type of apparatus, the first tube containing dry air, the second the experimental gas or mixture. The method of measuring the dust figures was that used by Partington and Cant (A., 1922, ii, 191). The following were investigated: (1) mixtures with γ practically constant but with varying density (*e.g.*, hydrogen and oxygen); (2) mixtures with both γ and the density variable (*e.g.*, hydrogen and carbon dioxide); (3) a mixture of carbon dioxide, hydrogen, and air; (4) mixtures with both γ and density constant (*e.g.*, carbon dioxide and nitrogen); (5) a single gas (ammonia) with a gas mixture of approximately the same density (*e.g.*, equal volumes of hydrogen and oxygen). In the ammonia experiments, it was necessary to use silica ignited and sieved in place of lycopodium powder, as the latter is attacked by ammonia. In each case, the values found showed satisfactory agreement with those derived from Laplace's formula, $\gamma=(C_pa+C'_pb)/(C_va+C'_vb)$, where a and b are the volumes of the gases in the mixture.

L. L. BIRCUMSHAW.

Compression and decomposition of nitric oxide. E. BRINER, H. BIEDERMANN, and A. ROTHEN (Helv. Chim. Acta, 1925, **8**, 923—928).—The compressibility of nitric oxide has been measured at pressures up to 160 atm. over the temperature range −80° to 10°, and pv values have been plotted against p. The isotherms indicate that nitric oxide is more compressible than the perfect gas, but that when comparison is made with the corresponding data for the non-polymerising gases, nitrogen, oxygen, ethylene, and carbon dioxide, there is no evidence for polymerisation of nitric oxide. The gas exhibits an anomalous temperature-coefficient in the peroxidation reaction which has been explained by polymerisation. Langmuir's octet theory also requires polymerisation of nitric oxide to account for the free valency forces. Both ideas are undermined by the proof that the gas exhibits a normal density.

Nitric oxide under prolonged compression decomposes, yielding a blue liquid which consists of a mixture of nitrous oxide and nitrous anhydride. Nitric oxide decomposes to give nitrous oxide and oxygen, the oxygen reacts with unchanged nitric oxide, yielding the peroxide, which in turn may react with nitric oxide to form the trioxide. The decomposition is very rapid at 700 atm. At lower pressures, the reaction is retarded by corrosion of the glass vessels by nitrogen peroxide. Freshly prepared and condensed nitric oxide is only very faintly blue in colour. Multiple liquefaction does not effect purification, since the blue colour gradually increases in intensity. Liquid nitric oxide is probably colourless and the blue tint is due to nitrous anhydride.

R. A. MORTON.

Assemblies of imperfect gases by the method of partition functions. R. H. FOWLER (Proc. Camb. Phil. Soc., 1925, **22**, 861—885).—A mathematical paper giving a general development of the theory of imperfect gases by means of partition functions. The method allows all the usual results of the theory of mixtures of imperfect gases to be deduced simply. The effects of the inverse square law are discussed in detail and the validity of the combined use of the equations of Boltzmann and of Poisson has been examined with special reference to the theory of strong electrolytes advanced by Debye and Hückel (A., 1923, ii, 459, 724). It is concluded

that this theory is established for small ionic concentrations only. A. E. MITCHELL.

Measurement of vapour tension of "gasoline" and other liquids. H. S. DAVIS (Ind. Eng. Chem., 1925, **17**, 1136—1138).—See B., 1925, 980.

Vapour-composition relationships in the systems phenol–water and phenol–cresol. F. H. RHODES, J. H. WELLES, and G. W. MURRAY (Ind. Eng. Chem., 1925, **17**, 1199—1201).—By distillation of the binary systems phenol–water, phenol–*o*-cresol, phenol–*m*-cresol, and phenol–*p*-cresol, and analysis of the original liquid and distillate in each case, the vapour-composition relationships of the systems were determined at various pressures. The curves for the system phenol–water show that azeotropic mixtures are formed with minimum b. p. The percentage of phenol in the constant-boiling mixture decreases with the pressure, being 9·4 at 760 mm. and 4·4 at 260 mm. The concentration of phenol in the distillate remains nearly constant so long as the concentration in the liquid is below 85%. With each of the three cresols, phenol forms "ideal" liquid mixtures. The results obtained supply the information necessary for the calculation of the theoretical minimum reflux ratio and the minimum number of sections required in the fractionating columns of stills for the separation of phenol from water and from cresol. L. L. BIRCUMSHAW.

Liquid mixed crystals. R. WALTER (Ber., 1925, **58**, [*B*], 2303—2310).—The formation of crystalline liquids from mixtures of substances which themselves do not exhibit crystalline-liquid properties (cf. Vorländer and Gahren, A., 1907, ii, 441) has generally caused the crystalline-liquid phases to be regarded as emulsions. The phenomenon is, however, more readily explained in the following manner. The compounds which yield such mixtures are generally very well crystallised (usually aromatic carboxylic acids) and are not readily supercooled. Consequently, a monotropic, crystalline-liquid phase which may be anticipated for them by reason of their chemical constitution remains latent even when the m. p. is not partly below that of the solid phase. If two chemically similar substances of this type are mixed, it may readily happen that the m. p. of the solid phase, which is generally lower than the m. p. of the individual components, falls below the mixed m. p. of the crystalline-liquid phase which with chemically related substances lies between the two latent crystalline-liquid m. p. of the pure components. Such a mixture exhibits enantiotropic crystalline-liquid properties. The case is realised experimentally with a mixture of anisic and anisylidenepropionic acids. The m. p. of the latent crystalline-liquid phase of these compounds is determined from the behaviour of their mixtures with *p*-methoxycinnamic acid and use of the expression, $t_1=t_2-[100(t_2-t_m):c_1]$, where t_1 is the latent m. p. of a substance, t_2 the known m. p. of an admixed, chemically similar compound, t_m the observed m. p. of the mixture, and c_1 the molecular concentration of the substance under investigation in mol.%. The observed and calculated values are in good agreement. Many other pairs of chemically similar compounds have been investigated. H. WREN.

Viscosity of heated alloys. J. COURNOT and K. SASAGAWA (Compt. rend., 1925, **181**, 661—662).—See B., 1925, 994.

Correlation of the remanent magnetism and specific resistance of some pure iron–carbon alloys. E. D. CAMPBELL (Trans. Faraday Soc., Nov. 1925, advance proof).—The specific resistance and magnetic properties of pure electrolytic iron and a series of iron–carbon alloys containing up to 1·5% of carbon and total elements other than carbon and iron 0·008% have been measured. The magnetic properties were measured using the material as bars with open poles and utilising a special magnetic balance which is described, in which electromagnetic forces were balanced against gravity. For electrolytic iron at 25° slowly annealed in a vacuum the specific resistance is 10·02 micro-ohms/c.c. The increase in specific resistance is almost proportional to the carbide concentration, whilst the magnetic resistance (gilberts required to give 1000 dynes/cm.^{2}) of a bar, magnetised under standard conditions, increases more slowly than the specific resistance up to the eutectoid composition and then more rapidly, indicating that low magnetic resistance is connected with structurally free ferrite. The internal magneto-motive potential (gilberts required to double the dynes) increases to a constant value at 0·6% carbon, whilst the magneto-motive potential (gilberts required to demagnetise) increases continuously, showing that the internal magneto-motive potential of the solvent iron is small compared with that due to dissolved carbides. The force fields of solutes in metallic solution are regarded as transforming electricity into heat, thereby increasing the resistance, whilst the converse transformation is indicated by the thermo-electric potential at solution–solvent junctions. F. G. SOPER.

Absorption of gaseous hydrogen chloride by sulphuric acid. V. CUPR (Publ. Fac. Sci. Univ. Masaryk, 1925, **63**, 1—18; cf. A., 1925, ii, 655).—Further measurements of the absorption of gaseous hydrogen chloride by sulphuric acid solutions of concentrations corresponding approximately with the hydrates $H_2SO_4,2H_2O$ and $H_2SO_4,4H_2O$ at the temperatures 0°, −15·8°, and −25° show that the quantity absorbed diminishes with increasing concentration of sulphuric acid, as was found by Coppadaro (A., 1910, ii, 197) at 17°, 40°, and 70°.

N. H. HARTSHORNE.

Solubility of hydrogen selenide. A. J. MCAMIS and W. A. FELSING (J. Amer. Chem. Soc., 1925, **47**, 2633—2637).—The solubility of hydrogen selenide in water is 0·09611, 0·08415, and 0·07317 mol. per litre at 15°, 25°, and 35°, respectively, and 760 mm. In aqueous hydrogen iodide the solubility is greater, and is 0·11012 mol. per litre in the 2·73*M* acid at 25° and 760 mm. The molal heat of solution in water is calculated to be 2431 cal. at 25°, and the free energy decrease for the reaction $H_2Se(1M)=H_2Se$ (760 mm.) is 1463 cal. for an aqueous solution containing 0·08017 mol. per litre at 25°. A. GEAKE.

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Supersaturation of gases in liquids. N. P. CLARE (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 32—33; cf. Wyatt, A., 1925, ii, 504).—Aqueous solutions of oxygen up to about 250 atm. saturation pressure are being investigated. On the reduction of pressure of such solutions, a cloud of fine bubbles sometimes appears, suggesting the spontaneous formation of bubbles in the liquid away from the walls. J. S. CARTER.

Initiation of bubbles in supersaturated solutions of gases. F. J. FARNCOMB (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 32).—Colloidal arsenious sulphide, colloidal ferric hydroxide, starch, platinum wire, lead chloride crystals, phenol globules, and freshly precipitated silver iodide have no apparent effect on the formation of bubbles in highly supersaturated solutions of oxygen. Paraffin-wax globules, benzoic acid, salicylic acid, phthalide, and iron wire have a small but definite effect. Precipitated silver iodide (24 hrs.' settling), precipitated calcium sulphate, and boric acid have a pronounced effect. It appears that bubbles are initiated by substances which are wetted with difficulty. J. S. CARTER.

Relation between solubility and retention of water of crystallisation in the salts of aromatic sulphonic acids. F. EPHRAIM and E. SEGER (Helv. Chim. Acta, 1925, **8**, 724—739).—Benzenesulphonic acid and naphthalene-1- and -2-sulphonic acids yield a large number of isomorphous, hexahydrated salts of bivalent metals. The loss in weight sustained by each salt in specified times and at definite temperatures in the presence of phosphorus pentoxide has been determined. The solubility at temperatures from 17° to 82° has been determined for each salt of benzenesulphonic acid and naphthalene-2-sulphonic acid, and at 17° only for each salt of naphthalene-1-sulphonic acid. For the first two acids, the solubilities of the salts (expressed by normality) decrease in the order: copper, cadmium, zinc, manganese, nickel, magnesium, cobalt, whilst for the third acid the order is magnesium, cobalt, nickel, copper, cadmium, zinc, manganese. The parallel experiments indicate that the strength of the linkings uniting the salt and its water of crystallisation decreases in the order Co, Ni, Mg, Zn, Mn, Cu, Cd, for the salts of benzenesulphonic acid, and in the order Ni, Co, Mg, Zn, Mn, Cu, Cd for the salts of naphthalene-2-sulphonic acid. Thus in these series it is not the most easily, but the least soluble salts which retain their water of crystallisation most strongly. In the case of the salts of naphthalene-1-sulphonic acid, the water is retained in the order Ni, Co, Mg, Zn, Mn, Cd, Cu. The parallelism therefore breaks down to some extent here, and even when it holds, the connexion between solubility and retention of water is in the sense opposed to that expected. R. A. MORTON.

Vanadium oxytrichloride as a solvent. F. E. BROWN and J. E. SNYDER (J. Amer. Chem. Soc., 1925, **47**, 2671—2675).—The solvent power of vanadium oxytrichloride has been examined. In general the metals are unaffected and inorganic compounds are insoluble, but most of the non-metals are soluble. All the organic substances tested dissolve in or react with the solvent. Organic liquids are miscible in all proportions. The liquid aldehydes react vigorously. The solubility of sulphur increases from 3·3 g. per 100 g. of vanadium oxytrichloride at 0° to 30·7 g. at 65°. A. GEAKE.

Influence of very slight traces of water on solubility equilibrium. I. E. COHEN and W. D. J. VAN DOBBENBURGH (Z. physikal. Chem., 1925, **118**, 37—48).—Determinations of the solubilities of different specimens of salicylic acid in benzene at 30·5° gave values which varied between the limits 1·03—1·36 g. per 100 g. of solution. It is shown that these irregularities are due to the presence of minute quantities of water occluded in the crystals, the solubility of a carefully dehydrated sample of acid being 1·00 g. per 100 g. of solution at this temperature. Data are recorded showing the influence of varying small quantities of water (0·004—0·3%) on the solubility of anhydrous salicylic acid in anhydrous benzene at 30·5°. J. S. CARTER.

Solubility influences. I. Effect of some salts, sugars, and temperature on the solubility of ethyl acetate in water. S. GLASSTONE and A. POUND (J.C.S., 1925, **127**, 2660—2667; cf. Thorne, *ibid.*, 1921, **119**, 262).—The solubility of ethyl acetate has been determined at 25° and 50° in aqueous solutions of varying concentrations of the chlorides, bromides, and iodides of the alkali metals and ammonium, and of dextrose, lævulose, sucrose, and lactose, and the values are used to calculate the hydration of these substances (cf. Philip, A., 1907, ii, 935). The lithium salts and nearly all the iodides give uncertain hydration values, apparently due to the solubility of these salts in the ethyl acetate itself. Since the non-electrolytes reduce the solubility considerably, it appears that molecules as well as ions have considerable salting-out power. No single equation will fit the results over the whole range of concentration.

The solubility of ethyl acetate in water at 0°, 10°, 25°, 37°, and 50° has been measured.

R. CUTHILL.

Relationship of salts in dilute aqueous solution as determined by their influence on the critical solution temperature of the system phenol–water. J. H. CARRINGTON, L. R. HICKSON, and W. H. PATTERSON (J.C.S., 1925, **127**, 2544—2549).—A continuation of the work of Duckett and Patterson (A., 1925, ii, 381). The occurrence of hydrolysis, complex formation, or chemical action causes abnormal results. Otherwise it is found that $e=aC^b$, where e is the elevation of the critical solution temperature caused by C g.-mol. of salt per 1000 g. of total mixture, b is a constant characteristic of the phenol–water system, and a is a specific constant for each salt. From the resemblance between this equation and the Freundlich adsorption isotherm, and between the Hofmeister series and the series representing the order of effectiveness of the anions in raising the critical solution temperature, it seems likely that the last-named phenomenon is associated with adsorption.

R. CUTHILL.

Distribution of pyridine between water and benzene. R. M. WOODMAN and A. S. CORBET (J.C.S., 1925, **127**, 2461—2463).—The ratio of the weight percentages of pyridine in the two layers at 25° is constant at about 2·7 over the range 0—6% pyridine in the total system, then decreases with increasing pyridine concentration to a minimum of 0·8, finally rising again, and reaching unity at the critical point. The results are supported by density data, and may be explained by compound formation between the solute and one of the solvent liquids. R. CUTHILL.

Adsorption of vapours by alumina gel. J. H. PERRY (J. Physical Chem., 1925, **29**, 1462—1468).—The adsorption of the vapours of ten organic substances by alumina gel, prepared from aluminium sulphate, has been studied (cf. Munro and Johnson, A., 1925, ii, 191). The hard, glass-like gel, obtained at 60° and containing 29·98% of water, was activated by passing dry air, free from carbon dioxide and heated at 200°, through it at the same temperature. Air saturated with vapour was then passed over the gel at 25°, and adsorption followed by weighing. The adsorption decreases in the series methylene chloride, ethylene dichloride, carbon tetrachloride, and chloroform. Chlorine derivatives are more or less oxidised in air to acid, which, on a large scale, would destroy the activity of the gel. Methyl ethyl ketone and ethyl formate are readily adsorbed, but a reaction with the gel prevents the recovery of the former; toluene is more efficiently adsorbed than hexane. With methyl acetate the adsorption is nearly complete in the early stages, but decreases rapidly above a certain limit. This substance can only be removed from the gel with great difficulty. Carbon disulphide is satisfactorily adsorbed, but the gel becomes yellow when recovery is attempted. The saturation values for the above-mentioned substances vary between 2·46 g. for methyl ethyl ketone and 3·8 g. for chloroform per 10 g. of gel.

Preliminary experiments show that benzene or ether, adsorbed by alumina gel from mixtures with water vapour, is slowly displaced by the latter on continued passage of the mixed vapour through the gel. L. S. THEOBALD.

Adsorption of dissolved substances. J. BANCELIN (J. Chim. physique, 1925, **22**, 518—555).—Measurements of the amounts of various dyes and salts adsorbed from aqueous solution by glass and silica surfaces at different temperatures gave, in general, results of the order of 10^{-8} g./cm.^{2} of adsorbent. The adsorbed layer is thus not unimolecular, but is of the order of one-tenth saturated. The relationship between the concentration of the solution and the quantity of solute adsorbed is represented, within wide limits, by Perrin's equation; within certain narrow limits of concentration, Freundlich's equation is, however, satisfied. The quantities adsorbed on the free surface of the solution approach a limiting value indicating saturation of the surface and conformity with Perrin's equation. Measurements of the surface tensions of the solutions have been made and, within wide limits, the adsorption at the free surface of the solution and on the surface of mercury is in agreement with Gibbs' equation. When a surface concentrating substance such as saponin is added to the solution, the amount of solute adsorbed at the surface is of the same order as that on the solid surfaces. The degree of precision of the measurements is low. A. E. MITCHELL.

Active charcoal. IV. Binding of chlorine and bromine by wood charcoal and their removal by ammonia and water vapour. O. RUFF, E. RIMROTT, and H. ZEUMER (Kolloid-Z., 1925, **37**, 270—274).—Carefully de-tarred alderwood charcoal takes up chlorine and bromine at a red heat and subsequent evacuation to 1 mm. pressure at the same temperature does not remove any appreciable quantity of these substances. They replace hydrogen which is still present in the charcoal, either (i) on its surface, or (ii) in impurities. Evidence for (i) is given by the fact that a part of the halogen may be made to react with ammonia to give nitrogen and hydrochloric or hydrobromic acid, whilst the variation in the amount of halogen taken up with the experimental conditions, and the somewhat easier introduction of chlorine compared with bromine, point to (ii). The principal reactions of the halogenated charcoals with water vapour and with ammonia lead to the elimination of carbon dioxide and hydrogen cyanide, respectively. The results afford no explanation of the cause of the activity of a charcoal, but rather make this problem more obscure, since it is found that tarry substances in the interior and foreign atoms on the surface do not affect the power of being activated. Further, there is no difference in this respect between the de-tarred charcoals used and a very carefully purified specimen. N. H. HARTSHORNE.

Adsorption. I. Adsorption by coconut charcoal from alcohol–benzene and acetone–benzene mixtures. F. G. TRYHORN and W. F. WYATT (Trans. Faraday Soc., Nov. 1925, advance proof).—The partial vapour pressures of the components of alcohol–benzene and acetone–benzene mixtures have been determined by evaporation of about 5—8% of the binary mixture at 20° and ascertaining the change in composition by measurement of the refractive index of the mixture. The values derived in this way were reproducible to within 2%. The adsorption of the components from these mixtures by specially prepared charcoal was determined by measuring the increase in weight of the charcoal and the change in refractive index of the liquid. The changes of composition of the liquid mixtures when in direct contact with the charcoal are similar to those which are found when adsorption takes place from the vapour phase, and the results support the conclusion that an adsorbed film which is in equilibrium with a saturated vapour must also be in equilibrium with the liquid in contact with that vapour. Alcohol is selectively adsorbed from all mixtures of alcohol and benzene; acetone is selectively adsorbed from mixtures containing up to 72 mol.% of acetone in the vapour phase. These results indicate that the surface of the charcoal is to some extent polar in its action. F. G. SOPER.

Negative adsorption. Surface tensions and activities of some aqueous salt solutions. A. K. GOARD (J.C.S., 1925, **127**, 2451—2458; cf. Goard and Rideal, A., 1925, ii, 510).—The surface tensions of aqueous solutions of varying concentrations of the chlorides of lithium, sodium, potassium, and cadmium, and of silver nitrate have been determined at 20°, and the results used, with the aid of activity data from various sources, to calculate the (negative) surface adsorption of the solutions. The results do not agree with the view that the surface layer of salt solutions consists of a single layer of oriented water molecules. Solutions of cadmium chloride behave anomalously, probably due to the undissociated molecules as well as the ions playing a part in the adsorption.

R. CUTHILL.

Adhesive forces in solution. V. Adsorption of complex compounds. N. SCHILOV and B. NEKRASSOV (Z. physikal. Chem., 1925, **118**, 79—88).—The adsorption phenomena observed when charcoal is brought into contact with aqueous solutions of substances of the type $[(NH_4)_2SO_4,MSO_4,6H_2O]$, cuprammonium compounds, and complex cobalt compounds have been investigated. In all cases, it is found that a disruption of the complex compounds occurs. Although ammonium sulphate is adsorbed to approximately the same extent from all the double sulphates, the order of increasing adsorbabilities of the bivalent metal sulphates is: nickel, zinc, magnesium, manganese, cadmium, cobalt, iron, copper. The complex cobalt ions are reduced to the cobaltous state, the ion $[Co(NH_3)_2]^{\cdot\cdot}$ being adsorbed. In the case of the cuprammonium compounds the ion $[Cu(NH_3)_2]^{\cdot\cdot}$ is adsorbed. Sodium is adsorbed much less than cobalt from solutions of sodium salts containing cobalt as part of the complex anion. Unsymmetrical *cis*-1:2-$[Co(NH_3)_4(NO_2)_2]Cl$ is adsorbed much more readily than the symmetrical *trans*-compound. Maximum adsorption is obtained with the non-ionised compound, $[Co(NH_3)_3(NO_2)_3]$.

J. S. CARTER.

Nature of the interfacial layer between an aqueous and a non-aqueous phase. F. L. USHER (Trans. Faraday Soc., Nov. 1925, advance proof).—The total charge on the particles of an aqueous gamboge suspension has been found by measurement of the quantity of ferric ions associated with the gamboge after coagulation by these ions. The charge per particle, which is $1{\cdot}45\times10^{-3}$ e. s. unit, is 100 times that calculated from the observed migration velocity on the basis of a Helmholtz double layer of molecular dimensions, and 7000 times that calculated assuming the double layer to be diffuse. It is also found that the flocculating power of various cations on a suspension of cupric ferricyanide is proportional to their effect in reducing the concentration of ferricyanide ions by the formation of insoluble ferricyanides. These results support the theory that the surface charge is due to ionisation of molecules furnished by the material itself or adsorbed from the surrounding liquid. The increase of ionisation with dilution explains the increased stability of certain suspensions and their greater adsorption of the flocculating ion in diluted systems. The variation in migration speed with particle size is also satisfactorily explained.

F. G. SOPER.

Attack of hydrogen chloride and ammonium halide on metals. K. A. HOFMANN and F. HARTMANN.—See this vol., 37.

Production of oxide films on copper at the ordinary temperature. U. R. EVANS (J.C.S., 1925, **127**, 2484—2491; cf. A., 1925, ii, 688).—Cathodic treatment of copper in 0·1*N*-sodium hydroxide at the ordinary temperature results in the production of colours similar to those obtained by exposure to air at high temperatures. If the current density is sufficient to cause evolution of hydrogen at the cathode, the colours appear only after the termination of the electrolysis, and when the electrode is allowed to remain in the solution. The effect is destroyed by rubbing or vigorous stirring, but is independent of the current density. Compact copper free from oxide and from porous copper (produced by reduction of oxide) is not easily rendered colourable by cathodic treatment. The phenomenon is probably due to hydrogen stored in the copper, which permits of alternate oxidation and reduction.

If copper is anodically treated in 0·1*N*-sodium hydroxide, it becomes passive at high current density, but at low current densities becomes coated with a black deposit, and if the solution is stirred, bright colours appear on the anode.

Copper is much less readily attacked by silver nitrate solution after considerable exposure to air than when freshly ground; this is presumably due to the presence of an oxide film in the former case.

R. CUTHILL.

Rhythmic reactions. K. SEIDEL (Kolloid-Z., 1925, **37**, 298—299).—The damp root hairs of oat, wheat, rice, and other seedlings develop periodic bands when placed in contact with silver nitrate crystals. Periodic plasmolysis is also observed when glycerol is allowed to diffuse into the roots. The results are discussed. N. H. HARTSHORNE.

Influence of light on lead chromate bands. E. HATSCHEK (Kolloid-Z., 1925, **37**, 297—298).—Polemical, in reply to Dhar and Chatterji (cf. A., 1925, ii, 959). The author's paper on lead chromate bands (cf. Proc. Roy. Soc., 1921, **A**, **96**, 496) has been misunderstood. The reaction between lead acetate and potassium chromate or dichromate in agar gives bands only in the light and not in the dark. No explanation of the screw-like bands was attempted. The author doubts the statement of Dhar and Chatterji that the precipitate is initially of a colloidal nature.

N. H. HARTSHORNE.

Growth of structures formed by reactions at the boundary between solutions of electrolytes in water and those in gels. V. MORÁVEK (Pub. Fac. Sci. Univ. Masaryk, 1925, No. 29).—When a layer of 0·1*N*-lead nitrate solution is placed on a 5% gelatin gel, 0·1*N* with respect to potassium dichromate, fibrous structures, 0·1—0·3 mm. wide, grow from the gel into the nitrate solution. The walls of these are formed by a gelatin membrane coated with

precipitated lead chromate, and growth usually occurs vertically or horizontally, although occasionally in spiral formation. The gelatin membrane is first formed and the lead chromate deposited on it discontinuously. The velocity of growth has a maximum value of 0·16 mm./min. The dimensions, shape, and velocity of growth of the fibres are influenced by the concentration of the gelatin, by substitution of chromate for dichromate ions, addition of foreign ions, and by change of temperature. The nature of the growth of these fibres, and the influence of ions and of temperature on it, resemble in many respects the phenomena of cell-formation. F. G. TRYHORN.

Diffusion experiments in solutions. R. FÜRTH (Physikal. Z., 1925, **26**, 719—722).—The diffusion of a coloured solute in a solution contained in a small cell, about $10\times5\times1$ mm., is followed colorimetrically by comparison with a solution of known concentration in a similar neighbouring cell. The solutions are viewed through a low-power microscope fitted with a micrometer eyepiece, the field being limited to a narrow horizontal strip. The displacement of a band of definite concentration is thus obtained as a function of the time. The method requires only a relatively short time (1—1½ hrs.) for one series of observations, and is capable of considerable accuracy. Fick's law is verified for solutions of picric acid and Congo-red, the respective diffusion coefficients being $6\cdot4\times10^{-6}$ to $6\cdot5\times10^{-6}$ and $1\cdot8\times10^{-6}$ to $1\cdot6\times10^{-6}$. A modification of the method, using the refractive index as a measure of the concentration, has been applied to solutions of sucrose. The results are less accurate, but show that here Fick's law is not applicable, the diffusion coefficient passing through a minimum with increasing concentration. A. B. MANNING.

Specific gravity of concentrated solutions of phosphoric acid. W. H. ROSS and R. M. JONES (Ind. Eng. Chem., 1925, **17**, 1170—1171).—See B., 1925, 987.

Temperature of steam evolved from a [boiling aqueous] solution. E. REISSMANN [with SCHREBER] (Z. angew. Chem., 1925, **38**, 1040—1044; cf. A., 1925, ii, 105).—Experiments were performed using an apparatus similar to that previously described but in which the heating of the steam by radiation from the hot oil-bath is minimised. It is also shown that superheated steam blown into a boiling solution is in equilibrium with the latter if its temperature before entry is the same, but that if cooler it absorbs heat from, and if warmer gives up heat to, the solution. The results are taken by the author [Schreber dissenting], to confirm his previous conclusions. W. T. K. BRAUNHOLTZ.

Viscosity and chemical analogy with reference to the viscosity of aqueous metallic acetate solutions. L.-J. SIMON (Compt. rend., 1925, **181**, 862—864).—The methods previously outlined for determining neutralisation points viscosimetrically are now applied to the mixing of *N*-solutions of some fatty acids with *N*-solutions of sodium and potassium hydroxide. The viscosity–alkali concentration curve is a straight line for acetic acid and is nearly so for propionic acid. The curves for chloro- and trichloroacetic and formic acids show at the neutralisation point the discontinuity previously observed with mineral acids. Solutions of trichloroacetic acid are much more viscous than equivalent solutions of chloroacetic acid; the latter are similarly more viscous than solutions of acetic acid, although the viscosities of their sodium salts in equivalent solution are fairly close. The viscosities of the alkali salts of trichloroacetic acid are very near those of the corresponding propionates in equivalent solution. Comparison of the viscosities of equivalent solutions of the acetates or nitrates of the metals reveals the well-known similarities between, for example, lithium and calcium etc. (cf. A., 1925, ii, 512). S. K. TWEEDY.

Osmotic pressure of hæmoglobin in absence of salts. G. S. ADAIR (Proc. Roy. Soc., 1925, **A, 109**, 292—300).—Osmotic pressures of hæmoglobin determined by previous workers varied from 3·5 to 12·1 mm. per 1% of protein. The high value was accepted as representing hæmoglobin of mol. wt. 16,700 (*i.e.*, the same as the equivalent), whilst the low values were attributed to aggregation. Using the conductivity of the solutions as a test of their freedom from impurities, it has been found that the solution of lowest conductivity gives an osmotic pressure of 3·2 mm. per 1% of protein as the isoelectric point. If the low values were due to aggregation, they should decrease still further at higher concentrations of the protein, but actually the figures indicate a slight increase. It is concluded that the mol. wt. of hæmoglobin is about four times the equivalent. S. BARRATT.

Colloid chemistry of bismuth and its compounds. A. KUHN and H. PIRSCH (Koll. Chem. Beihefte, 1925, **21**, 78—96).—The preparation of sols of bismuth and of some of its compounds is described. Bismuth sols containing 3·5 mg. per c.c. may be prepared by the reduction of bismuth tartrate solutions with sodium hyposulphite in weakly alkaline solution. This shows an improvement on the methods of Lottermoser and Vanino, which with stannic acid as a protective colloid give sols containing only 1·5 mg. per c.c. Bismuth sulphide sols are stable only in the presence of protective colloids. With 1% of gum arabic a sol containing 10 mg. per c.c. may be obtained. Bismuth sulphoiodide sols cannot be prepared without protective colloids. Sols containing 0·3 mg. of bismuth per c.c. with 0·59% of gum arabic, 1·6 mg. with 0·5% of hæmoglobin, and 0·3 mg. with 0·25% of gelatin may be obtained. The gum arabic sol is reversible. By mixing bismuth sulphide, sulphoiodide, or hydroxide with wool fat, subsequent intensive pulverisation of the mixture at the temperature of liquid air, and dissolution of the product in sesamé oil, fairly stable sols result containing 12—16 mg. of bismuth per c.c. for 15—20% of protective colloid. By Bredig's method stable sols of the metal may be prepared containing 8 mg. per c.c. with 5% of wool fat and 0·6 mg. per c.c. with 1% of caoutchouc–ether sol. By Svedberg's protected arc method (Medd. Nobel-Inst., 1910, **5**, No. 10, 4) metal sols cannot be obtained in water even with a protective colloid, but in sesamé oil with at least

5% of wool fat stable sols containing 6 mg. per c.c. are formed. N. H. HARTSHORNE.

Polychrome mercury hydrosols. R. FEICK (Kolloid-Z., 1925, **37**, 257—267).—The theories of the colours exhibited by metal sols are discussed, prominence being given to that of Mie (Ann. Physik, 1908, **25**, 377), in which the colours are stated to be dependent on the optical constants of the dispersed substance (in the massive state) and the degree of dispersion. By the reduction of mercurous nitrate solutions with pyrocatechol, sodium hyposulphite, or quinol, in the presence of gelatin and varying amounts of "nuclear sol," a series of mercury sols of different degrees of dispersion has been prepared, with colours, viewed by reflected light, varying from brownish-black for the coarser suspensions, through browns, reds, and greens to indigo for the most disperse sols. The particle size for each sol was calculated on the basis of Mie's theory and varied from 300 to 80 $\mu\mu$. Within this range, the theory appears to hold satisfactorily for mercury. In a short discussion of the application of the theories of colloidal colours to photohalide effects, it is concluded that the darkening, *e.g.*, of silver chloride, is due to the formation of colloidal silver, and not of a subchloride. N. H. HARTSHORNE.

General colloid chemistry. XVII. Analysis and constitution of colloidal gold. III. L. FUCHS and W. PAULI (Koll. Chem. Beihefte, 1925, **21**, 195—240).—The study of a large number of gold sols has shown that progressive dialysis is accompanied by the formation of hydrogen ions. The concentration of these is the same for sols prepared by reduction both by formaldehyde and by hydrogen, namely, about 1×10^{-5} *N*, measured by microconductometric titration with barium hydroxide. Hydrogen ions derived from carbonic acid in the air, silicic acid from the glass vessels, and organic acids from the parchment paper are shown to be quite insufficient to account for the phenomenon. Further, no other cations can be found in appreciable quantities in the sols. It is therefore concluded that the ions are the partners of the gold particles which are considered to be covered by a layer of the anions of a gold acid. From the titration data and from measurements of the particle number and particle size, it is possible to obtain values for the charge number of the particles, but it is pointed out that the presence of particles invisible under the ultramicroscope may, on account of their relatively large surface, give a quite fictitious value to the result. Bearing this point in mind, the connexion between flocculation and charge values is discussed.

N. H. HARTSHORNE.

Plant colloids. XVI. Behaviour of starch components towards iodine, and their protective colloid action. M. SAMEC and R. KLEMEN (Koll. Chem. Beihefte, 1925, **21**, 55—77).—The colour of starch-iodine complexes is to a large extent independent of the average particle size of the colloid and is not influenced by pairing with phosphoric acid, or substances containing it, or with silicic acid, or by cations bound to amylophosphoric acid. There is no simple relationship between the iodine colour and the protective action towards gold sols. The quantity of iodine taken up by aqueous solutions of single starch components is different for single grain ingredients. With equal potassium iodide concentrations amylo-substances take up more iodine than erythro-substances. The iodine adsorption of amylo-substances increases with increasing potassium iodide concentration up to a maximum, and up to the point of visible coagulation is not appreciably altered by ageing, but falls when the solution is heated to 120°; increase in the degree of dispersion increases the adsorption, and *vice versa*. Amylopectin adsorbs less the longer the period of boiling necessary for the isolation of the sol. The adsorptive power of erythro-amyloses falls with increasing particle size; it is appreciably raised by the presence of potassium iodide, and in contrast with the amyloamyloses excess of the salt does not cause precipitation of the iodine complex. Soluble starch and dextrin generally adsorb less iodine the lower the average particle size. The amyloamyloses have a better protective action towards gold than the erythroamyloses. Generally the protective action increases with increasing dispersity. N. H. HARTSHORNE.

Physical properties of serum on addition of "water-binding" substances. R. FÜRTH and R. PECHHOLD (Biochem. Z., 1925, **164**, 9—17).—See A., 1925, ii, 1056.

Nephelometry of serum. J. KABELIK (Kolloid-Z., 1925, **37**, 274—283).—A review of work on the nephelometry of animal and human sera, carried out by the author and his collaborators [cf. Kabelik and Lednicky, Biol. Listy, 1922, **8**, 212; Kabelik, *ibid.*, 1924, **10**; Centr. Bakt. Ref., 1925, **78**, 185; Loutoucky, *ibid.* (in preparation); Lednicky, Kolloid-Z., 1923, **32**, 12; Stošek, Spisy lék. fak. v. Brně, 1922/23, **18**, A 8; Žak, *ibid.*, 1923/24, II 2, A 12; Trapl, *ibid.*, 1923/24, II 9]. N. H. HARTSHORNE.

Colloidal properties of sericin. G. A. BROSSA (Atti R. Accad. Sci. Torino, 1925, **60**, 231—240).—Extraction of silk cocoons with water in an autoclave for 1½—2 hrs. at 1½ atm. caused a loss of weight equal to 20—22% of that of the cocoons and the production of a turbid, green or yellow liquid. On keeping, flocculation of the liquid occurred. This is promoted by traces of acid, the optimum hydrogen-ion concentration being p_H 4·4—4·6. The precipitate is peptised by heating. By evaporating the extract a product consisting mainly of proteins was obtained. By subjecting the original extract to electro-osmosis an almost colourless suspension was obtained. The clear liquid remaining after the particles were removed by centrifuging gave protein reactions, but, unlike the original extract, did not flocculate spontaneously or on addition of acetic acid. The properties of these two protein products are compared with those of the α- and β-products obtained by Anderlini by the alcoholic extraction of silk cocoons. F. G. TRYHORN.

Action of electrolytes on the stability of disperse sulphur solutions prepared by the mechanical method. P. P. VON WEIMARN and S. UTZINO (Mem. Coll. Sci. Kyōtō, 1925, **A**, 8, 291—306).—Colloidal sulphur solutions have been prepared by grinding sulphur with grape-sugar and treating with water. The suspension carries a negative charge. Stability curves for this sol have been obtained by plotting the concentrations of different electrolytes added, as abscissæ, against the time required for coagulation as ordinates. With sodium, calcium, barium, and cerium chlorides, barium iodide, and hydrochloric acid, the stability rises to a maximum value with increasing concentration of electrolyte, and then decreases to a value considerably below that for the pure sol. The curves for potassium and calcium thiocyanates show two maxima, which is possibly the case for potassium sulphate, but less probable for sulphuric acid. The potassium nitrate curve has no maximum, but indicates instead a continuous decrease in stability with increasing concentration of salt. Salts of tervalent metals display a greater activity than those of bivalent metals, since the first maximum is reached at a lower concentration of the former than of the latter, and has also a higher value. Similarly, salts of bivalent metals are more active than those of univalent metals, and acids are also very active. The coagulating power of an electrolyte appears to be related to its ability to form hydrates, and the double maxima in the case of salts containing sulphur are ascribed to "homo-chemical" action between this combined sulphur and the dispersoid. The results obtained are in agreement with von Weimarn's views on dispersion and aggregation (cf. A., 1925, ii, 969). M. S. BURR.

Influence of electrolytes on glycogen sol, and the origin and inversion of the Hofmeister ion series. S. DOKAN (Kolloid-Z., 1925, 37, 283—296).—The action of electrolytes on glycogen sol increases the sensitiveness of the sol towards dehydrating agents such as alcohol and tannin. The action of different electrolytes under different conditions leads to very varied results. Occasionally only the positive ions (*i.e.*, the ions charged oppositely to the colloid) are effective and their action depends almost entirely on their valency. Under other conditions, both ions appear to come into play, and they act in the order of the well-known lyotrope series, but sometimes in one direction, sometimes in the other. This behaviour is explained as follows. Some of the ions are adsorbed by the colloid and confer on it their tendency to hydrate, whilst the others remaining free tend to dehydrate the colloid. With small ion concentrations, the hydrating action of the ions adsorbed by the colloid exceeds the dehydrating action of the free ions, but with high concentrations the effect is reversed. In the latter case, the dehydrating action of both negative and positive ions is concerned. The total effect on the state of the colloid is the resultant of these factors combined with the effect on the charge of the colloid particles of the adsorbed, oppositely charged ions. The dehydrating action of a substance such as alcohol or tannin affects the colloid first and then the free ions. With alcohol, both these effects may be observed; with tannin, only the former. The explanation may be extended to meet the case of albumin sol. N. H. HARTSHORNE.

Effect of gum arabic and other emulsifiers on the acid hydrolysis of esters in heterogeneous systems. R. C. SMITH (J.C.S., 1925, 127, 2602—2605; cf. Goldschmidt and Messerschmitt, A., 1900, ii, 200; Callow, A., 1916, ii, 94).—Solid insoluble emulsifiers such as kaolin have very little effect on the rate of hydrolysis of ethyl acetate by hydrochloric acid at 25°. Gum dammar and gum tragacanth increase the rate of reaction in the heterogeneous system, but reduce it in the homogeneous system, which indicates that the effect is not due to catalysis. The probable explanation is that the gum produces a change in the partition ratio of the ester between the phases. Similar results are given by other esters. R. CUTHILL.

Influence of duration of dialysis on the ageing of ferric oxide sols. H. HANDOVSKY (Z. physikal. Chem., 1925, 117, 432).—The longer a ferric oxide sol is dialysed the greater is the increase in conductivity on keeping for a long period. This increase in conductivity takes place chiefly in the intermicellary liquid, into which ions move slowly from the micelles. L. F. GILBERT.

Effects of age on soap solutions. (Miss) R. M. COSS (Ind. Eng. Chem., 1925, 17, 1134—1135).—See B., 1925, 998.

Gel of protein type (found) in the kieselguhr stratum of the Lüneburger Heide. F. V. VON HAHN (Kolloid-Z., 1925, 37, 300—303).—A gel with protein properties, to which the name "cornuit" is given, has been found in the kieselguhr of Neu-Ohe. The substance contains about 2·8% of solid and 0·07% of ash, chiefly diatomaceous residue. It shows many of the properties of gelatin. It may be peptised by sodium hydroxide solution and gelatinised again on neutralisation. The jelly so obtained may be used as a medium for Liesegang ring phenomena. The protective action of the sol is 30 times that of gelatin. Boiling lowers the viscosity, but does not cause coagulation. N. H. HARTSHORNE.

[Behaviour of] colloids under an alternating current. O. BLÜH (Kolloid-Z., 1925, 37, 267—270).—A cell is described in which the behaviour of a sol under the influence of an alternating current may be observed ultramicroscopically. In this, the walls are so close together that electro-osmotic oscillation of the liquid is excluded. In experiments with an old vanadium pentoxide sol, it has been found that some of the rod-like particles attach themselves by one end to the walls of the cell and that the application of the current causes the free ends to oscillate. By increasing the applied potential, a point is reached for any particular particle where its amplitude cannot be further increased, since the wall of the cell prevents further movement. This maximum amplitude is equal to the length of the particle, which may thus be measured. N. H. HARTSHORNE.

Influence of adsorption on the colour of sols and of precipitates. N. R. DHAR (J. Physical Chem., 1925, **29**, 1394—1399).—The colours of sols and of freshly-coagulated precipitates are discussed in relation to previous work. They depend on the nature of the material adsorbed. Positively and negatively charged sols of the same substance often differ from each other in colour and from the electrolyte used in the preparation. Yellow silver chromate sol is negative, whilst the red sol is positive (see also Sen and Dhar, Kolloid-Z., 1924, **34**, 270). Negatively charged manganese dioxide sol prepared from permanganate and hydrogen peroxide is deep brown in colour. Addition of a small amount of ferric chloride causes charge reversal and the positive sol is distinctly red. Analysis shows the presence of ferric iron in the coagulum. The colour of hydrated manganese dioxide (prepared from permanganate and manganese sulphate) depends largely on the substance adsorbed during formation of the precipitate. Precipitated in presence of the nitrates of silver, bismuth, mercury, or lead, it is deep black, in the presence of ferric chloride or sulphate, red, and when no electrolyte is added, reddish-brown. Other effects observed with this substance are quoted. The colour of ferric hydroxide precipitated in the presence of potassium dichromate or permanganate or sodium thiosulphate is different from that obtained in their absence. The blue colour of adsorption compounds of iodine with starch, dextrin, basic lanthanum acetate, etc. is due probably to the existence of iodine as the dispersed phase in these media. The colour of complex copper solutions containing alkali and glycerol or sugar is also discussed.

L. S. THEOBALD.

Behaviour of silica gel towards certain alkalis and salts in aqueous solution. W. A. PATRICK and E. H. BARCLAY (J. Physical Chem., 1925, **29**, 1400—1405).—The removal of sodium hydroxide from aqueous solution by silica gel and the subsequent replacement of the "adsorbed" sodium ions by those of silver, copper, and iron (ferric) has been studied. Known weights of gel of definite water-content, between the limits 8% and 11%, were shaken at 20° with solutions of sodium hydroxide of concentrations varying from 0·0127 to 0·1325 mol. per litre. The adsorption of alkali (millimol. per g. of gel) can be represented by $K.c^{1/n}$, in which $K = 0·0171$, $n = 2·56$, and c is the concentration of the solution. The gel containing adsorbed sodium ions was then treated with 0·1*M*-silver nitrate, 0·1036*M*-copper nitrate, and 0·178*M*-ferric sulphate solutions in separate experiments. The sodium ions are replaced stoicheiometrically. With silver and copper solutions, no adsorption occurs with pure silica gel, but with iron, a slight effect was noted.

It is suggested that three types of adsorption should be recognised, viz., (1) chemical, (2) the formation of a molecular layer, and (3) capillary adsorption. With sodium hydroxide, the phenomena partake of the nature of both chemical combination and adsorption, the retention of alkali by the gel being due to chemical forces. The increase in the ratio of alkali taken up to silica with increasing concentration of the former may be due to the peptisation of the gel by alkali and increasing union with the smaller silica particles thus resulting, or the thickness of the alkali "layer" may increase with the amount of alkali in the surrounding solution. If the silica were of true molecular dimensions, the formation of a definite silicate would be expected.

L. S. THEOBALD.

Effect of temperature of formation on the physical character of hydrous aluminium oxide. J. H. YOE (J. Physical Chem., 1925, **29**, 1419—1422).—The adsorptive power of hydrated aluminium oxide for arsenite ions has been shown (A., 1925, ii, 107) to be less the higher the temperature of precipitation, an effect which may be due to the formation of a more compact precipitate at the higher temperature. In order to correlate temperature of formation with size and density of particle, the rates of settling have now been determined. Hydrated aluminium oxide was precipitated from the sulphate at temperatures from 0° to 100° under constant conditions. The velocity of settling, 0·014 cm. per sec. at 20° for the first 50 cm., is, however, approximately the same for all precipitates save that formed at 100° and refluxed for 48 hrs. This last showed a velocity of 0·032 cm./sec. Boiling the precipitate formed at 66° for 62 hrs. did not alter the rate of settling.

The hydrated oxide formed at 0° is very gelatinous, but that formed at higher temperatures is less so, although still voluminous. Contrary to Taylor (A., 1911, ii, 542), aluminium hydroxide, precipitated at 66° by ammonia, and heated to boiling, gives a voluminous, and not a granular, product.

Owing to irregularities in the shape and size of particles of the same specimen, attempts to measure their diameters failed. Staining with 0·01% solution of alizarin was also unsuccessful. L. S. THEOBALD.

Hydrates and hydrogels. VII. Isomeric hydrogels of aluminium hydroxide. VIII. Aluminium hydroxide gel of the formula AlO·OH. R. WILLSTÄTTER, H. KRAUT, and O. ERBACHER. **IX. Silicic acid.** R. WILLSTÄTTER, H. KRAUT, and K. LOBINGER.—See this vol., 34, 35, 36.

Reaction between gaseous methyl ether and hydrogen chloride. J. SHIDEI (Mem. Coll. Sci. Kyōtō, 1925, **9**, 97—119).—An investigation of the reaction $Me_2O+HCl \rightleftharpoons Me_2O,HCl$ previously examined by Friedel (Bull. Soc. chim., 1875, **24**, 160), whose results suggested that the amount of hydrochloride formed is a minimum when the reactants are mixed in equal volumes. Pure anhydrous hydrogen chloride and methyl ether were mixed in varying proportions, and the volume changes were observed. The equilibrium constants, K, in terms of partial pressures at 1°, 5°, 9°, and 19° under a constant pressure of 0·996 atm., were found to be 1·4906, 1·7224, 2·0837, and 3·1744, respectively. In every case, the equilibrium partial pressure of methyl ether hydrochloride was at a maximum when the reactants were mixed in equal volumes, and decreased gradually with increase of excess of one of the components. On plotting $\log K$ against $1/T$, a

straight line is obtained, showing that the heat of reaction at constant pressure is independent of temperature. Substituting the observed values of K and T in the van 't Hoff equation $\log K = 0{\cdot}4343Q/RT + C$, it is found that $Q = -6725$ cal. and $C = 5{\cdot}5373$. The theoretical and experimental values of the equilibrium constants show a satisfactory agreement. L. L. BIRCUMSHAW.

Equilibrium in the system: $CH_3{\cdot}CO_2Me + H_2O \rightleftharpoons CH_3{\cdot}OH + CH_3{\cdot}CO_2H$. G. J. BURROWS (J.C.S., 1925, **127**, 2723—2728; cf. Jones and Lapworth, *ibid.*, 1911, **99**, 1427).—The effect of the addition of water, methyl alcohol, and acetone on the rate of hydrolysis of methyl acetate by hydrochloric acid at 25° has been studied. It is found that the equilibrium constant, K, depends, not only on the ratio $[H_2O] : [HCl]$, but also on the amount of methyl alcohol or acetone present. The addition of acetone reduces the value of K. Increase of the amount of hydrogen chloride relative to the amount of water increases K to an extent which is the greater the greater the amount of methyl alcohol present. It is suggested in explanation that the hydrogen chloride affects the activity of the reactants.

R. CUTHILL.

Colorimetric dissociation constants of 3 : 5-dinitropyrocatechol and 4 : 6-dinitroresorcinol. F. C. LAXTON, E. B. R. PRIDEAUX, and W. H. RADFORD (J.C.S., 1925, **127**, 2499—2501).—The methods used were similar to those previously described by Prideaux and Nunn (A., 1925, i, 24). 3 : 5-Dinitropyrocatechol is colourless in strongly acid solutions, but attains a full yellow colour at p_H 5·34, which beyond p_H 7·6 passes through orange to full reddish-brown at p_H 12·05. This final colour is affected only by the addition of very strong alkali; $p_{K_1} = 3{\cdot}25$, $p_{K_2} = 10{\cdot}35$. 2-Nitroresorcinol shows a pure yellow colour even in acid solution, so that p_{K_1} must be very low. The colour darkens at p_H 5·34, becomes dull reddish-brown at p_H 7·6, and fades to a dull brown at a higher p_H; $p_{K_2} = 6{\cdot}34$. 4 : 6-Dinitroresorcinol is colourless in solutions of p_H below 3·1, and for higher values is yellow, which is constant beyond p_H 6·47; $p_{K_1} = 4{\cdot}22$. R. CUTHILL.

Dissociation constants of organic molecular compounds. H. VON HALBAN and E. ZIMPELMANN (Z. physikal. Chem., 1925, **117**, 461—477).—The dissociation equilibria, in tetrachloroethane solutions, of acenaphthene–*s*-trinitrobenzene, acenaphthene–*m*-dinitrobenzene, and acenaphthene picrate, and of anthracene picrate dissolved in chloroform were investigated by a method involving the photoelectric measurement of the absorption of light at different concentrations. The results agree with the law of mass action. The solubility, at 24·1°, of anthracene picrate in chloroform was determined.

L. F. GILBERT.

Effect of variation in ionic strength on apparent first and second dissociation constants of carbonic acid. A. B. HASTINGS and J. SENDROY, jun. (J. Biol. Chem., 1925, 65, 445—455).—From the investigation of solutions of varying ionic strength, the first dissociation constant of carbonic acid is found to be $k_1 = 4{\cdot}68 \times 10^{-7}$ ($pk_1 = 6{\cdot}33$); the second dissociation constant $k_2 = 6{\cdot}03 \times 10^{-11}$ ($pk_2 = 10{\cdot}22$). The relationships of the apparent dissociation constants, k_1' and k_2', to the ionic strength of the solution (μ) are expressed by the equations $pk_1' = 6{\cdot}33 - 0{\cdot}5\sqrt{\mu}$ and $pk_2' = 10{\cdot}22 - 1{\cdot}1\sqrt{\mu}$. The relationships between the activity coefficients of the hydrogen carbonate and carbonate ions are in good agreement with the theory of Debye and Hückel (A., 1923, ii, 459). C. R. HARINGTON.

Interpretation of neutralisation curves of mixtures of boric acid and polyhydric alcohols. I. M. KOLTHOFF (Rec. trav. chim., 1925, **44**, 974—982).—A method is described whereby the complex constant and the dissociation constant of the complex acid formed by polyhydric alcohols and boric acid can be calculated if the hydrogen-ion concentrations are measured for two solutions containing different amounts of sodium hydroxide. With boric acid and glycerol the reaction is $H_3BO_3 + \text{Alc.} \rightleftharpoons H_3BO_3.\text{Alc.}$, and, from existing data, $K = [H_3BO_3][\text{Alc.}]/[H_3BO_3.\text{Alc.}] = 0{\cdot}9$, where Alc. represents 1 mol. of glycerol. The dissociation constant of the complex acid is about 3×10^{-7}. Mannitol, lævulose, and probably other polyhydric alcohols form polybasic complex acids, in which 1 mol. of alcohol combines with more than 1 mol. of boric acid, but the composition of the complex appears to vary with the ratio of the constituents.

W. HUME-ROTHERY.

Phase diagrams of [binary] alloys where chemical combination occurs. A. MLODZIEJOVSKI (Z. physikal. Chem., 1925, **117**, 361—386).—Theoretical. A comprehensive survey of possible systems, from the point of view of the ζ function.

L. F. GILBERT.

Methods for the investigation of binary systems. I. The "thaw-melt" diagram. H. RHEINBOLDT [with K. HENNIG and M. KIRCHEISEN] (J. pr. Chem., 1925, [ii], **111**, 242—272).—The diagrams obtained by plotting the difference between the temperatures at which a binary mixture begins to melt and is completely molten vary with the type of mixture used. Curves are given for the following 16 pairs of compounds (A in each case represents the substance first mentioned).

Type I (no compound formed): Naphthalene : *p*-nitrophenol (eutectic, 75% A, m. p. 73°); α-naphthol : β-naphthylamine (eutectic, 43·5% A, m. p. 52°); pyrocatechol : naphthalene (eutectic, 18% A, m. p. 72·5°).

Type II (compound formed which melts homogeneously): β-Naphthylamine : *s*.-trinitrobenzene (compound, AB, m. p. 163°; eutectics, 109° and 100°); naphthalene : picric acid (compound, AB, m. p. 150·2°; eutectics, 78° and 111°); β-naphthylamine : nitrosodimethylaniline (compound, A_2B_3, m. p. 86°; eutectics, 81° and 72°); phenol : picric acid [compound, AB, m. p. 86°; eutectics, 36° and 80·5°; no evidence is found for the existence of Goedike's compound, AB_2 (A., 1894, i, 119)]; carbamide : phenol (compound, AB_2, m. p. 61°; eutectics, 60° and 34°); benzamide : nitrosodiethylaniline

(compound, AB_2, m. p. 66·5°; eutectics both melt at 66·5°); *m*-hydroxybenzaldehyde : picric acid (compound of undetermined composition, m. p. 90°; eutectics both melt at 86·5°); antipyrine : quinol (two compounds, A_2B_3, m. p. 130°, and AB_2, m. p. 134°; eutectics, 102·5°, 118·5°, and 120·5°).

Type III (compound formed which decomposes below the m. p.): Acetamide : salicylic acid (compound, AB; eutectic, 53°; transition point, 65°); anthracene : picric acid (compound, AB; eutectic, 110°; transition point, 151·8°); *p*-dinitrobenzene : α-naphthylamine (compound, AB; eutectic, 40°; transition point, 81°); *p*-dinitrobenzene : β-naphthylamine (compound, AB; eutectic, 87°; transition point, 91·2°); carbazole : 2 : 4 : 6-trinitrotoluene (compound, AB; eutectic, 73·5°; transition point, 140°). C. HOLLINS.

System : water and the nitrates of potassium and ammonium at 25°. K. ANDO (Mem. Coll. Sci. Kyōtō, 1925, **8**, 283—286).—The conditions of equilibrium were determined by analysis of the liquid and solid phases. Two series of solid solutions, separated by a considerable gap, are formed. In terms of the formula

$$100m\mathrm{H_2O},x\mathrm{NH_4NO_3},(100-x)\mathrm{KNO_3}$$

the data characteristic of the system are : solid potassium nitrate saturated with ammonium salt, $x=13·5$; solid ammonium nitrate saturated with potassium salt, $x=65·0$; liquid solution saturated with the two salts, $x=79·41$, $m=2·18$.

L. L. BIRCUMSHAW.

Equilibrium in the system potassium sulphate, potassium nitrate, water at 25°. R. INOUYE (Mem. Coll. Sci. Kyōtō, 1925, **8**, 287—290).—The equilibrium conditions were deduced from analyses of both the liquid and solid phases. The solubilities of potassium sulphate and potassium nitrate are, respectively, 11·98 and 38·19 g. of salt in 100 g. of water. The solution saturated with respect to both salts contains 3·95 g. of potassium sulphate and 25·37 g. of potassium nitrate per 100 g. of water. L. L. BIRCUMSHAW.

Equilibria in the system mercuric chloride, ammonium chloride, potassium chloride, and water at 25°. Y. OSAKA and K. ANDO (Mem. Coll. Sci. Kyōtō, 1925, **9**, 81—95).—The conditions of equilibrium were deduced from analyses of both liquid and solid phases. The results show the existence of the following double salts and solid solutions :

$HgCl_2,KCl,H_2O$	$HgCl_2,NH_4Cl,H_2O$	$HgCl_2,(K,NH_4)Cl,H_2O$ (complete)
$HgCl_2,2KCl,2H_2O$	$HgCl_2,2NH_4Cl,H_2O$	$HgCl_2,2(K,NH_4)Cl,H_2O$ (complete)
$2HgCl_2,KCl,2H_2O$	—	$2HgCl_2,(K,NH_4)Cl,2H_2O$ (a gap)
—	$3HgCl_2,2NH_4Cl,H_2O$	$3HgCl_2,2(K,NH_4)Cl,H_2O$ (gaps)
—	$9HgCl_2,2NH_4Cl$	—
—	—	$(K,NH_4)Cl$ (a gap)

The solubility data for the double salts and their solid solutions are recorded, and the equilibrium relations represented graphically. A graphical method is described for finding the composition of solid solutions when two solid solutions are present which cannot be completely separated from each other.

L. L. BIRCUMSHAW.

System silver sulphate–aluminium sulphate–water at 30°. R. M. CAVEN and T. C. MITCHELL (J.C.S., 1925, **127**, 2550—2551).—Mixtures of solutions of the two salts yield no crystalline compound at 30°. R. CUTHILL.

Equilibrium in the systems aluminium sulphate–copper sulphate–water and aluminium sulphate–ferrous sulphate–water at 25°. V. J. OCCLESHAW (J.C.S., 1925, **127**, 2598—2602; cf. Caven and Mitchell, A., 1925, ii, 396).—No double salt is formed in the copper sulphate system. From the other system a double salt, $Al_2(SO_4)_3,FeSO_4,24H_2O$, has been isolated. R. CUTHILL.

Equilibrium in systems of the type $Al_2(SO_4)_3$–$M''SO_4$–H_2O. II. Aluminium sulphate–nickel sulphate–water at 30°. R. M. CAVEN and T. C. MITCHELL (J.C.S., 1925, **127**, 2549—2550; cf. A., 1925, ii, 396).—No double salt is formed in solution. R. CUTHILL.

Ternary systems. III. Silver perchlorate, toluene, and water. A. E. HILL and F. W. MILLER (J. Amer. Chem. Soc., 1925, **47**, 2702—2712; cf. A., 1922, ii, 555).—Of the three binary systems silver perchlorate–water, water–toluene, and silver perchlorate–toluene, the first has already been investigated, whilst the second is difficult to study on account of the extremely low mutual solubility of the components. The third has now been investigated over the range −73·5° to 75°. At the lower temperature, the solubility of the salt is too small for detection; at 25° the saturated solution contains 50·3% of silver perchlorate and is thus unique for the combination of a highly polar solute with a non-polar solvent. Below 22·6°, the solid phase is the compound $AgClO_4,C_7H_8$, and the solubility falls very rapidly with falling temperature.

The ternary system has been studied from the ternary eutectic at −94° up to 91·75°. In ascertaining the composition of the liquid phases, the salt was determined directly and the water by an indirect method. The data show the existence of seven quintuple points, each of which was characterised, and twenty 4-phase equilibria. In addition to the solubility curves for silver perchlorate, its hydrate, and its toluene compound, there are two binodal curves. One of these is submerged and does not reach any of the two-component axes at any temperature. The other binodal curve shows an abnormal distribution of silver perchlorate between the toluene and water phases, the salt being present almost entirely in the latter up to high concentrations, in spite of its great solubility in toluene. This may be due to complete dissociation in concentrated aqueous solution, but it is probable that compound formation and chemical affinities play a large part in all cases of distribution. The intersection of the two binodal curves at points other than their plait points gives rise to a three-liquid system, which is stable from −24·1° to 90°. A. GEAKE.

System Na_2SO_4–Na_2Cl_2–$MgSO_4$–$MgCl_2$–H_2O. H. J. ROSE (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 33).—The composition of the solution saturated with respect to thenardite, mirabilite, and astrakanite

at 25° is: (mols./1000 mols. of water) $MgSO_4$, 11·6; Na_2SO_4, 26·0; Na_2Cl_2, 26·3. Diverse numbers obtained by other investigators are quoted.

J. S. CARTER.

Thermal decomposition of chloro-salts of metals of the platinum group. Univariant systems. G. GIRE (Ann. Chim., 1925, [x], **4**, 183—221).—The univariant systems $M_2M'Cl_6$ solid $\rightleftharpoons$ M′ solid+2MCl solid+$2Cl_2$ gas $-Q$, where M=Na or K and M′=Pt, Ir, or Rh, have been studied by measurements of the dissociation pressures of the salts over wide ranges of temperature. All the reactions are shown to be completely reversible within the temperature limits of the investigation. The dissociation of potassium chloroplatinate becomes apparent at about 600°, the curve (log p–$1/T$) consisting of two straight lines intersecting at 774°, the latter portion of the curve being inclined at a greater angle to the abscissæ axis, due to the heat of fusion of the potassium chloride (m. p. 774°), the system above this temperature being of the type solid $\rightleftharpoons$ solid+liquid+gas$-Q'$. The values for the heats of reaction Q and Q' determined from the curve are 38·6 Cal. and 46·0 Cal., respectively, whence the value of the molecular heat of fusion of potassium chloride ($Q'-Q=S$) is 7·4 Cal. This is higher than the value determined directly (cf. Schemtschuschny and Rambach, A., 1910, ii, 204), the difference being due to the heat of solution of the potassium chloroplatinate, which is found to dissolve in fused potassium chloride. The dissociation pressure of potassium chloroplatinite (cf. Vezes, A., 1899, ii, 492) is initially much higher than that of the chloroplatinate at the same temperature, but rapidly approximates to the latter. The dissociation of sodium and barium chloroplatinates (cf. Gire, A., 1922, ii, 551) was not investigated up to the m. p. of the chlorides, and hence the curves are straight lines. Dissociation is apparent at about 500° and 400°, respectively, the pressure reaching 1 atm. at 717° and 676°, respectively. The curve for potassium chloroiridate resembles that for the chloroplatinate, since the liquid phase is again introduced. Dissociation is observed at 575°, and intersection of the two portions of the curve occurs at 774°, the values of Q, Q', and S being 36·1, 41·2, and 5·1 Cal., respectively. Measurements of the dissociation pressures of an intimate mixture of potassium chloroiridate and potassium chloride corresponding with $2K_2IrCl_6+2KCl \rightleftharpoons 2K_3IrCl_6+Cl_2$ gave 764° as the m. p. of potassium chloride in this system, whence the values for Q, Q', and S are 32·1, 23·3, and 4·4 Cal., respectively, the low value for S being due to the negative heat of solution of the chloroiridite in the fused potassium chloride. Sodium chlororhodate shows measurable dissociation at 600°; the two portions of the curve intersect at 790°. The heating curve of the mixture shows a second arrest at 904°, the m. p. of the sodium chlororhodate, whence Q, Q', and S have the values 35·3, 46·0, and 45·35 Cal., respectively.

J. W. BAKER.

Thermal decomposition of chloro-salts of metals of the platinum group. Calorimetric investigations. G. GIRE (Ann. Chim., 1925, **4**, 370—409).—Measurements have been made of the heats of solution of various salts of the type $M_2M'Cl_6$, the thermal decomposition of which has been already studied (cf. preceding abstract), and of the heats of the reactions $M_2M'Cl_6+2Co=M'+2CoCl_2+2MCl+q$, whence, since the heat of the reaction $2Co+2Cl_2=2CoCl_2+q$ is 94·8 Cal. (Thomsen, J. pr. Chem., 1877, **15**, 435; Pigeon, A., 1894, ii, 455), the heats of formation of $M_2M'Cl_6$ could be determined. The heats of solution, obtained by direct measurement, for potassium, sodium, and barium chloroplatinates (anhydrous) are, respectively, −12·15, +7·10, and +9·05 Cal. (−1·06 Cal. for the hexahydrate of the barium salt), and the corresponding molecular heats of formation of the solid salts, +91·2, +79·6, and +82·1; and for the dissolved salts, +88·7, +90·50, and 88·70 Cal., respectively. The hypothesis of Thomsen and Pigeon (*loc. cit.*) that the heats of formation in solution of all the chloroplatinates from the chlorides are the same is thus verified, but the mean value obtained is 89 Cal. instead of the value 85 Cal. given by the earlier investigators. Sodium chlororhodate crystallises with 12 mols. of water, thus confirming the formula $Na_3RhCl_6,12H_2O$ assigned to it by Gutbier and Hüttlinger (cf. A., 1908, ii, 200). The heats of solution of the hydrated and anhydrous salts are, respectively, −20·56 and +7·70 Cal. and the heat of formation of the solid salt is 74·4 Cal. The heats of solution of potassium chloroiridate and chloroiridite, K_3IrCl_6, are −13·12 and −7·90 Cal., respectively. Reduction of the chloroiridate either with cobalt or chromous chloride occurs in two stages: $2K_2IrCl_6+2KCl=2K_3IrCl_6+Cl_2-Q$ and $2K_3IrCl_6=2Ir+6KCl+3Cl_2+Q$, the second stage being too slow to permit of calorimetric measurements. An approximate value, −29 to 30 Cal. (low) for the heat of the first reaction was obtained by the addition of 5% of potassium chloride to the solution to suppress the second reaction. The solubility of potassium chloroiridate is 0·66 g. and 1·12 g. per 100 g. of water at 0° and 20°, respectively. From the dissociation curves obtained (cf. preceding abstract) the value of Q/T is deduced for each of the systems studied, a mean value of 0·0325 being obtained (that for sodium chlororhodate is slightly lower). Similar calculations applied to the published data for a large number of other univariant systems give $Q/T=0·032$ for compounds of the type MCl,xNH_3, 0·028 for the dissociation of hydrates, and values varying between 0·028 and 0·034 for other systems, whilst the dissociation of auric chloride, a reaction similar to those studied, gives a value 0·0326: hence for each group of similar reactions Q/T has a definite value which, in disagreement with Nernst's hypothesis, seems to be independent of temperature. The application of the results to the constitution of the salts on Werner's theory is discussed.

J. W. BAKER.

Thermal decomposition of metallic sulphates. (MLLE.) G. MARCHAL (J. Chim. phys., 1925, **22**, 493—517).—The thermal decomposition of anhydrous magnesium sulphate can be detected at about 880°; from this temperature to beyond the m. p. (1155°), the total pressure of the dissociation products follows the normal logarithmic law. At 1190°, the total

pressure is 212·6 cm. of mercury. From the sulphur dioxide partial pressures at equilibrium the mean value of the heat of dissociation into magnesia and sulphur trioxide over the range 1000—1100° has been calculated as 66·07 cal., whilst that obtained from thermochemical measurements is 65·6 cal. Beryllium sulphate dissociates appreciably at 565° and the dissociation follows the reaction $5BeSO_4=SO_3,5BeO+4SO_3$. Up to 785°, the sulphur trioxide equilibrium pressure is represented closely by the equation $\log p_{SO_3}=-14{\cdot}907/T-14{\cdot}10 \log T+57{\cdot}97$, whence the calculated values for the heat of decomposition over the range 700—800° has a mean value of 41 cal. compared with 49·8 cal. given by thermochemical measurements for the direct decomposition to the oxide. The fact that over the temperature range 590—775° the dissociation pressure of aluminium sulphate is considerably higher than that of beryllium sulphate suggests a possible method for the separation of the two metals. The double sulphate of potassium and magnesium melts at 750°, but does not commence to dissociate appreciably until 895°; this agrees with the thermodynamic deduction that its dissociation pressure should be considerably lower than that of magnesium sulphate. The double salt of potassium and beryllium melts at 900°. Dissociation can be detected at 700—710° and the dissociation curve is normal up to about 975°, but at higher temperatures, owing to the solution of potassium sulphate in the fused double salt, the pressure is diminished. The calculated mean value of the heat of decomposition up to the m. p. is 65·2 cal., above which temperature it is 58·8 cal. The value obtained from thermochemical measurements is 58·5 cal., from which it follows that the value 6·4 cal. does not necessarily correspond with the heat of fusion of the salt. A. E. MITCHELL.

Thermochemistry of beryllium. C. MATIGNON and (MLLE.) G. MARCHAL (Compt. rend., 1925, **181**, 859—861).—The heats of solution of some beryllium compounds in water and in solutions of hydrogen chloride, hydrogen fluoride, and sodium hydroxide are recorded. The following heats of formation are given: beryllium oxide, 137·4 cal.; hydroxide, 209·3 cal.; sulphate, 276·9 cal. The results obtained illustrate the close chemical analogy between beryllium and aluminium. S. K. TWEEDY.

Heats of combustion of normal substances. P. E. VERKADE and J. COOPS (Z. physikal. Chem., 1925, **118**, 123—128).—A reply to the criticisms of Jaeger and von Steinwehr (A., 1925, ii, 126) that undue weight has been given to Dickinson's value for the heat of combustion of benzoic acid in view of the results obtained by other observers. Recent accurate determinations (Verkade and Coops, A., 1923, ii, 294; Schläpfer and Fioroni, A., 1923, ii, 832; Swientoslawski and Starezewska, A., 1922, ii, 616) are in agreement with Dickinson's value, and it is claimed that the results quoted by Jaeger and von Steinwehr are less trustworthy. In particular, the electrical method of determining heat values involves a systematic error.
J. S. CARTER.

Calorimetric researches. IX. Heat of combustion of *d*- and *meso*-tartaric acids, racemic acid, and some derivatives. J. COOPS and P. E. VERKADE (Rec. trav. chim., 1925, **44**, 983—1011; cf. A., 1925, ii, 490).—*Ammonium hydrogen* meso-*tartrate* (m. p. 167°) is prepared by adding solid *meso*-tartaric acid to concentrated ammonia until neutral to methyl-orange; the same amount of the acid is then added and the solution evaporated and crystallised. meso-*Tartramide* (m. p. 187—187·5° with slight decomposition) separates slowly from a solution of ethyl *meso*-tartrate saturated with ammonia at 0°. The molecular heats of combustion at constant pressure (mol. wt. in mg.; 15° cal.) are: *d*-tartaric acid, 275·1; racemic acid, 273·0; *meso*-tartaric acid, 275·7; ammonium hydrogen *d*-tartrate, hydrogen racemate, and hydrogen *meso*-tartrate, 341·7, 339·5, and 341·2, respectively; methylammonium hydrogen *d*-tartrate and hydrogen racemate, 508·0 and 506·0, respectively; ethylammonium hydrogen *d*-tartrate and hydrogen racemate, 665·4 and 663·1, respectively; aniline hydrogen *d*-tartrate and hydrogen racemate, 1079·3 and 1077·3, respectively; benzylamine hydrogen racemate and hydrogen *meso*-tartrate, 1229·9 and 1231·5, respectively; *d*-tartramide, 427·0; *meso*-tartramide, 426·4; *d*-tartaric diethylamide, 1064·1; racemic acid diethylamide, 1064·3; *meso*-tartaric diethylamide, 1065·3. The heat of racemisation of solid *d*-tartaric acid is thus $2{\cdot}1\pm0{\cdot}1$ Cal. Both in the crystalline state and in dilute aqueous solution, the symmetrical intramolecular inactive acid has a greater free energy content than the asymmetrical optically active isomeride. *meso*-Tartaric acid has a larger heat of combustion, but a smaller dissociation constant than *d*-tartaric acid, in contradiction to the rule of Stohmann (J. pr. Chem., 1889, **40**, 357). The heats of combustion of succinic, *l*-malic, and the tartaric acids show that replacement of a hydrogen atom by a hydroxyl group does not produce a constant difference, and hence the heat of combustion is not an additive quantity. Both racemic acid and hydrogen racemates are racemic compounds.
W. HUME-ROTHERY.

Calorific value and constitution. M. F. BARKER (J. Physical Chem., 1925, **25**, 1345—1363).—Previous empirical expressions for calculating the calorific values of carbon compounds take little or no account of constitutive effects. The contributions of like atoms and of the CH_2-group have been taken as constant, which, except in the case of hydrogen, is not permissible. The molecular calorific value of an organic compound depends on its constitution; that of carbon varies and becomes less as the disposition of valency bonds approaches that in the symmetrical tetrahedral positions. The thermal effects accompanying oxidation of the carbonyl group and the combination of a hydrogen atom with a hydroxyl group, deduced from the calorific values of diphenyl, benzil, and benzoin, are 60·7 Cal. and 12·9 Cal., respectively. The combustion of diatomic hydrogen is similar to that of hydrogen in a hydrocarbon, and since the calorific value of hydrogen is the same in all the organic compounds studied, it is adopted as the basis of calculation.

The heat of combustion deduced for the carbon atom in methane (normal case) is 75·5 Cal.; for each of those of ethane, 83·1 Cal. This increase is ascribed to a decrease in the angle between the valency bonds accompanying the change from methane to ethane. In ascending an homologous series, this increase becomes less. Replacement of the four hydrogen atoms in methane by the same group (*e.g.*, in tetramethylmethane) restores symmetry to the molecule and the central carbon atom attains the original value. The value of the change $-C:C- \longrightarrow CO_2$ is 97·7 Cal., of the same order of magnitude as the combustion of elementary carbon: similarly with "benzenoid" carbon. The linking $-C:C-$ has a value 120·5 Cal. in acetylene to 124·5 Cal. in dipropargyl.

The contribution of the carboxyl group is not equivalent to one carbonyl plus one hydroxyl group. Results point to mobility of a hydrogen atom giving rise to an additional potential hydroxyl, thus $X<^{H}_{COOH} \longrightarrow X{\cdot}C<^{OH}_{OH}$, and favouring association. Discrepancies between calculated and observed values disappear when calorific values of the vapours of the acids are taken. The aldehydic group is equivalent to one carbonyl and one hydrogen group. Among the simpler aromatic hydroxy-compounds, only the dihydroxybenzenes are anomalous, possibly because of tautomeric effects. The results of various observers indicate that the benzene molecule is best represented by Ladenburg's prism formula. L. S. THEOBALD.

Heat of solution of gypsum at the maximum solubility. E. LANGE and F. DÜRR (Z. physikal. Chem., 1925, **118**, 129—139).—The heat of solution in water of gypsum has been determined at 22·5°, 27·8°, 33·4°, and 37·6°, the values for the molecular heats of solution being −590, −300, ±0, and 230 cal., respectively. Contrary to the statement of Colson (A., 1925, ii, 37), the zero value for the heat of solution occurs at a temperature which, within the limits of experimental error, is that at which the solubility is a maximum. J. S. CARTER.

Calculation of some characteristic constants of free ammonium. A. BALANDIN (Z. physikal. Chem., 1925, **118**, 114—118).—According to formulæ derived by the author (A., 1924, ii, 719; 1925, ii, 637) the heat of formation of ammonium is −17,800 cal., the molecular volume, 47·9 cm.^{3}, and the density in the solid state, 0·356. J. S. CARTER.

Analogies and differences in behaviour of the various forms of energy in reversible and irreversible transformations. E. DENINA (Gazzetta, 1925, **55**, 638—645).—A mathematical paper, in which the various formulæ derived from the second law of thermodynamics are reduced to the same type independent of the form of energy involved. T. H. POPE.

Vapour-pressure lowering as a function of the degree of saturation. I. I. BENCOWITZ (J. Physical Chem., 1925, **29**, 1432—1452).—A relation expressing the vapour pressure of aqueous solutions of non-volatile solutes as a function of temperature and solubility has been deduced, using the degree of saturation as a fundamental method of expressing concentration. The equation has the form $\log \Delta P = K[1/T - a(1 - \log S/b)]$, where ΔP is the lowering of the vapour pressure, T the absolute temperature, and S the degree of saturation, *i.e.*, the ratio of the number of g. or mols. of solute in solution to the number present at saturation, in a given weight of solvent. K, a, and b are constants. The three postulates used in deducing this relationship are as follow: (1) the coefficient $[(\partial P \log \Delta P)/\{\partial(1/T)\}]_S$ is constant (equals K), and (2) is independent of S, and (3) the coefficient $[(\partial K \log S)/\{\partial(1/T)\}]_{\Delta P=1 \text{ mm.}}$ is constant.

Existing data are used to verify these. The relation is shown to hold for 31 salts, which include the commoner salts of the alkali metals and ammonia, the chlorides and bromides of the alkaline earths, and the sulphates of beryllium, nickel, copper, and zinc. The values of the constants, K, a, and b are also given for these salts. The value of a is the reciprocal of the absolute temperature at which a saturated solution has a vapour pressure lowering of 1 mm.

From the above equation, there follow two generalisations, (1) the ratio of the lowering of the vapour pressure, at any degree of saturation, to that of a saturated solution, at a given temperature, is independent of temperature, and (2) the value of this ratio is a simple function of the degree of saturation, *i.e.*, $\Delta P/\Delta P_S = S^{Ka/b}$. L. S. THEOBALD.

Free energy of ions measured by capillary electrode. P. B. TAYLOR (Physical Rev., 1924, [ii], **23**, 556).—Using a cell with one mercury electrode contained in a capillary and completely polarisable, the other being reversible to the anion of the electrolyte, it is shown that $T = T_0 + Cf(V - V_0)$, where V is the fall of potential across the cell, V_0 the *E.M.F.* of the reversible electrode, T the surface tension of the polarised electrode, T_0 a constant, whilst C depends only on the concentration of the electrolyte. Curves may be constructed yielding values of the difference in free energy of the anion at two concentrations. The ratio of the change in free energy of the anion to that of the electrolyte is 0·50 for potassium and sodium chlorides, but 0·85 for potassium hydroxide above 0·1*N*. A. A. ELDRIDGE.

Electrical conductivity in benzene solutions. S. JAKUBSOHN (Z. physikal. Chem., 1925, **118**, 31—36).—The electrical conductivity of solutions of aluminium bromide monothiohydrate ($AlBr_3,H_2S$) over the concentration range 20—54% by weight increases with increasing concentration of solute; the values of the specific conductivities at 25° of the 20% and 54% solutions are $0{\cdot}81 \times 10^{-6}$ and $3{\cdot}54 \times 10^{-4}$, respectively. The mol. wt. as determined by the cryoscopic method over the concentration range 1—22·5% increases with increasing concentration, being 271 in the 1% solution and 359 in the 22·5% solution. Electrolysis results in the cathodic liberation of hydrogen and the anodic deposition of bromine which reacts with the solvent to form bromine

derivatives. The decomposition voltage at 25° for a 45% solution is 0·74 volt. J. S. CARTER.

Pseudo-acids. G. B. SEMERIA and A. PICHETTO (Atti R. Accad. Sci. Torino, 1925, **60**, 241—250).—Measurements have been made of the equivalent conductivities of aqueous solutions of camphoroxime, of its sodium salt, and of the sodium salt of nitrocamphor, at a series of temperatures between 25° and 50°. The conductivity of the sodium salt of camphoroxime increases between 25° and 35° with dilution more rapidly than that of the other sodium salt, but between 40° and 50° the relation is reversed, For the former temperature range, the degree of ionisation of the nitrocamphor salt is greater, and for the latter range, lower, than that of the camphoroxime salt. The pseudo-acid character of the two compounds is confirmed by the gradual neutralisation which their salts exhibit with hydrochloric acid, which has been followed by conductivity measurements. Equilibrium between the two forms is reached in the shorter time by nitrocamphor. Refractometric measurements with the two salts lead to nearly equal values for the molecular refractivities, the small differences being attributed to the difference in structure. Camphoroxime $[R_L]_D^{25}$ 60·5499, sodium salt of camphoroxime $[R_L]_D^{25}$ 62·2605, sodium salt of nitrocamphor $[R_L]_D^{25}$ 62·9818. The difference between the molecular refractivities of the two sodium salts is 1·7, in conformity with the rule of Muller and Bauer (A., 1903, ii, 705). F. G. TRYHORN.

Conductivity and electrolysis of iodine trichloride in acetic acid. B. P. BRUNS (Z. physikal. Chem., 1925, **118**, 89—98).—Iodine trichloride dissolves in anhydrous acetic acid to give a clear solution. In the moist solvent some iodic acid is precipitated as a result of the reaction: $3ICl_3 + 6H_2O = 9HCl + HI + 2HIO_3$. Conductivity measurements at 18° show that the value of the molecular conductivity passes through a minimum at a dilution, $v=10$ litres. The irregularities in the temperature-conductivity curves in the region 20—30° are regarded as furnishing evidence of the existence of complexes in solution. Electrolysis results in the liberation of chlorine in double the amount anticipated on the basis of Faraday's law. A decomposition potential either does not exist or is extremely small. It is suggested that iodine trichloride forms complexes with the solvent and that the ionic dissociation is: $ICl_3,n(CH_3{\cdot}CO_2H) \rightleftharpoons ICl_3'' + (CH_3{\cdot}CO_2H)_n^{\cdot\cdot}$. J. S. CARTER.

Concentration *E.M.F.* in solutions containing acid. A. R. GORDON and C. WEBER (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 26—27).—The *P.D.* across a liquid surface separating two air-free solutions of copper sulphate in maximum conducting sulphuric acid, when current is flowing, is given by the equation $P.D. = CR + B \log_n c_1/c_2$, where c_1 and c_2 are the copper concentrations in the two solutions and B is the Nernst factor for bivalent ions ($RT/2F$). Experiments with cuprous chloride in 3*N*-hydrochloric acid and with silver sulphate in *N*-sulphuric acid give $B=RT/F$. The transport number of silver in these solutions is 0·023 for *N*/40 solutions and 0·011 for *N*/80-solutions. J. S. CARTER.

Thermodynamic potential difference at the boundary of two liquid phases. II. S. WOSNESSENSKY (Z. physikal. Chem., 1925, **117**, 457—460).—Cells similar to those previously studied (A., 1925, ii, 673) have been examined, amyl alcohol being used as non-aqueous solvent. With electrolytes consisting of mixtures of potassium hydroxide and phosphoric acid, or of potassium hydroxide and citric acid, singular points were obtained in the *E.M.F.*–composition curves corresponding with the formation of the primary, secondary, and tertiary salts of the respective acids. When *N*-potassium chloride was used as the electrolyte in a cell of zero *E.M.F.* and butyric acid was added to the half-cell containing the aqueous solution, no change of *E.M.F.* was observed until the concentration of the acid was about 0·5*N*. Valeric acid produced no change in the concentration range investigated (up to about 0·1*N*). These effects seem to be connected with the surface activity of the acids. L. F. GILBERT.

Electromotive behaviour of aluminium. C. J. DE GRUYTER (Rec. trav. chim., 1925, **44**, 937—969).—The freezing-point diagram of the system aluminium–mercury has been determined. No compounds or transition points exist, the liquidus falling from the m. p. of aluminium, at first gradually and later very rapidly, to an eutectic of practically pure mercury. A solid solution of mercury in aluminium, containing approximately 8 atoms % of mercury, exists at the ordinary temperature. The *P.D.* of aluminium–mercury alloys in contact with dry alcoholic solutions of aluminium chloride and with solutions containing both mercury and aluminium salts has been measured. The *P.D.* for pure aluminium in aqueous salt solutions has been determined in the absence of oxygen. For amalgamated aluminium in normal salt solutions it is 1·590 volts, relative to the calomel electrode. The influence of different salts and of hydrogen-ion concentration on the potential of aluminium has been examined, and the complex results interpreted in reference to Smit's theory of allotropy. Mercury is a positive and aluminium hydroxide or oxygen a negative catalyst for the internal reaction $Al_{solid} \rightleftharpoons Al_{solid}^{+++} + 3\ominus_{solid}$, and the passivity of aluminium is due to the slowness of the (—) reaction. W. HUME-ROTHERY.

Pseudohalogens. II. (I) The fulminic residue. (II) Equilibrium between iodine, selenocyanogen, and the corresponding silver salts. (III) Polypseudohalides. L. BIRCKENBACH and K. KELLERMANN (Ber., 1925, **58**, [*B*], 2377—2386; cf. A., 1925, ii, 568).—I. Comparison of the decomposition potentials of mercury fulminate and mercury cyanate shows the fulminic to be slightly more strongly electronegative than the cyanic residue. The decomposition potential of potassium fulminate could not be measured, since the product of the action of potassium amalgam on mercury fulminate could not be purified completely from potassium hydroxide.

II. The equilibrium between silver iodide, silver selenocyanide, selenocyanogen, and iodine in the presence of ether (cf. *loc. cit.*) is established for mixtures in stoicheiometric proportions when 86%

of the iodine is present as silver iodide and 14% remains in the ethereal solution.

III. The tendency of the alkali halides to yield polyhalogen salts can be measured by potentiometric titration. Standard ethereal solutions of halogens are added to standard alcoholic solutions of halides and the changes of potential against an unattackable electrode are measured in the usual manner. Potassium iodide and potassium selenocyanide are thus titrated with iodine and selenocyanogen solution and sudden alterations of potential are observed corresponding with the formation of the salts KI_3, $K(SeCN)I_2$, $K(SeCN)_2I$, $K(SeCN)_3$. The tendency to form such compounds attains its maximum in the case of cæsium; *cæsium triselenocyanide* has been isolated.

The simple halogen atoms appear univalent, since the periphery contains seven electrons and by the addition of a further electron yield the complete octet. The idea is extended to the pseudohalogens, and it is pointed out that the azide residue has fifteen electrons, eight of which surround and hold together the complex and are externally inactive chemically, whereas the remaining seven condition the halogen-like behaviour of the group. Similarly, the sum of the electrons in the cyano-, thiocyano-, selenocyano-, and telluracyano-residues is fifteen and a similar arrangement may be assumed. H. WREN.

Decomposition potentials and polarisation of certain heavy metallic chlorides dissolved in anhydrous pyridine. R. B. MASON and J. H. MATHEWS (J. Physical Chem., 1925, **29**, 1379—1393; cf. Müller, A., 1923, ii, 287; 1925, ii, 133, 134).—The decomposition potentials and polarisation curves of certain metallic chlorides in anhydrous pyridine have been studied in order to test the behaviour of the reference electrodes, which consisted of an amalgam covered with a paste of the salt of the metal contained in the amalgam. The reference electrodes Hg–Cd,$CdCl_2$ and Hg–Zn,$ZnCl_2$ are the most satisfactory. The decomposition potentials of saturated solutions of zinc, cadmium, cuprous, and mercuric chlorides at 30° are, respectively, 1·75, 1, 0·5, and 0·65 volts. The curves for lead chloride and for mercuric sulphate in pyridine show no changes in direction. Solutions of cupric chloride were difficult to work with owing to low solubility and low conductance, and the results obtained depend on the method of preparation of the anhydrous salt. The cuprous chloride solution conducts well, but the formation of a compound at the anode makes polarisation difficult to follow. Where possible, both total polarisation and polarisation at either electrode have been followed. The solutions of lead, mercuric, and cuprous chlorides behave as if a depolariser for small amounts of chlorine is present. Cadmium and zinc chlorides in pyridine give results which are similar to those obtained with water as solvent.

L. S. THEOBALD.

Effect of variation of current and concentration on polarisation in a lead cell. J. T. BURT-GERRANS and H. R. HUGILL (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 26).—Two co-axial lead cylinders were used as electrodes, the arrangement of the apparatus affording a uniform electric field between the cylinders. With acid more dilute than 0·05*N* as electrolyte the fall in *E.M.F.* during the discharge is due to depletion of acid in the electrolyte, but with maximum conducting sulphuric acid the fall is due to exhaustion of active material on the electrodes. Polarisation, which occurs at the cathode only with currents down to 0·03 amp., is manifested by a sudden increase in the voltage. The time from the beginning of the charge to the rise in polarisation voltage varies inversely as the current, and changes in a regular manner with the previous history of the cell (preliminary charging and discharging in preparation for test charge). Polarisation effects can only be observed separately from other changes in potential difference with acids which are more dilute than 0·5*N*. No regular variation with acid concentration was observed. J. S. CARTER.

Photomicrographic study of the evolution and disappearance of gas during the passage of electricity through glass. J. B. FERGUSON and O. W. ELLIS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 34).—Photographs which illustrate the points stressed by Rebbeck and Ferguson (A., 1924, ii, 840) have been obtained. With the reappearance of gas the presence of a brown colour in the glass was noted. The colour may be made to come and go by proper regulation of the direction of the electrolysing current. Photographs show that the colour originates in minute circular spots with dark centres which later grow and spread over the glass. The colour is not attacked by concentrated nitric acid. Microscopical examination shows the coloured spots to be in the same plane and very thin. The discontinuous nature of the coloration and the way in which gas bubbles form in different tubes indicate that glass does not behave as a homogeneous medium when electrolysed.

J. S. CARTER.

Electrolysis of soda-lime glass. M. J. MULLIGAN (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 35—36).—In an extension of the work of Schulze (Ann. Physik, 1913, **40**, 335) the electrical migration of silver into glass from anodes of metallic silver and of aqueous solutions of silver nitrate at 100° has been observed. Silver was also found to diffuse into glass at 100° from an aqueous solution of silver nitrate without the use of the current. J. S. CARTER.

Dialysis and ultrafiltration, electrodialysis, and electroultrafiltration. A comparison. E. HEYMANN (Z. physikal. Chem., 1925, **118**, 65—78).—The kinetics of the removal of crystalloids from sols by dialysis, ultrafiltration, electrodialysis (Freundlich and Loeb, A., 1925, i, 96) and electroultrafiltration (Bechhold and Rosenberg, A., 1925, ii, 668) are considered and expressions for the rate of removal under ideal conditions are derived. Strong electrolytes are removed from sols by electrodialysis or electroultrafiltration about 10 times more rapidly than by ultrafiltration and about 100 times more rapidly than by dialysis. Where weak electrolytes are concerned, as in the separation of gelatin from its degradation products (amino-acids etc.) (Knaggs, Manning, and Schryver, A., 1923, i, 1144), the advantages of the electrical method are nullified and ultrafiltration is

most suitable. Removal of non-electrolytic crystalloids by ultrafiltration is considerably influenced by the mol. wt. of the crystalloid and by the nature of the dispersed phase. With hydrophobic colloids (rapidly removed by ultrafiltration) and crystalloids of high mol. wt. (100—400) complete separation is attained 20—50 times as rapidly by ultrafiltration than by dialysis. With hydrophilic colloids (slowly removed by ultrafiltration) separation is attained about 5—15 times as rapidly. If it is necessary to free a protein solution from electrolytes and also from non-ionised degradation products of high mol. wt., recourse must be had to electroultrafiltration.

J. S. CARTER.

Rate of unimolecular reactions. D. ALEXIEV (Z. physikal. Chem., 1925, **118**, 119—122).—A theoretical paper in which the importance of collision as a factor in unimolecular gas reactions is emphasised. A reaction mechanism is suggested which leads to an expression for the reaction velocity involving concentration to the first power only. J. S. CARTER.

Derivation of the equation for the effect of temperature on reaction rate. R. C. TOLMAN (J. Amer. Chem. Soc., 1925, **47**, 2652—2661).—The equation, $-dC/dt=ke^{-(E/RT)}C$, connecting the rate of a first order unimolecular reaction with the temperature and the energy of activation (E) is derived without making any specific assumption as to either the rate or the mechanism of activation, and is thus shown to be at least approximately valid under a wide variety of conditions. The energy of activation is the excess per mole in the energy of the molecules that react over the average energy of the unactivated molecules. The corresponding equation, $-dC/dt=kT^{1/2}e^{-[(E+E')/RT]}CC'$, for a second order bimolecular reaction is derived both on the assumption that the reacting molecules have received their energies of activation preceding the collision that leads to reaction, and on the assumption that the processes of activation and reaction are merged in one collision.

A. GEAKE.

Influence of inflammable and other gases on the explosibility limits of mixtures of gas and air. XI. Graphical representation. W. P. JORISSEN (Rev. trav. chim., 1925, **44**, 1039—1047).—See B., 1925, 980.

Thermal decomposition of nitrogen pentoxide at low pressures. H. S. HIRST and E. K. RIDEAL (Proc. Roy. Soc., 1925, **A**, **109**, 526—540).—The results of several investigators agree in showing that the thermal decomposition of nitrogen pentoxide satisfies the usual criteria of a unimolecular reaction. Observations have been made both on the gaseous system, and on solutions of the pentoxide in organic solvents. The surface of the glass containing vessel, the presence of inert gases and of the products of reaction, are factors which do not disturb the unimolecular law. The heat of activation, calculated in the normal manner, is about 24,700 cal. per g.-mol. The high velocity of the reaction precludes the possibility of this large activation energy being supplied either by inelastic thermal collisions, or by "black-body" radiation, unless some "chain" mechanism is called into play. Such mechanisms have been suggested. One depends on the passage of a radiation quantum through a chain of successive molecules, each one re-emitting the quantum after reaction. The other supposes that an activated form of nitrogen dioxide is produced by the decomposition, and that such molecules, on collision, may cause further reaction. Both these theories would predict a diminution in the velocity of reaction at low pressures, owing to the greater probability of the rapid failure of a "chain." This point has now been tested experimentally. The rate of decomposition of gaseous nitrogen pentoxide has been measured at pressures as low as 0·01 mm. of mercury. The procedure was to measure the pressure of oxygen resulting from the reaction by a platinum Pirani gauge, after removing the other gases into a cooled side-tube. No retardation of the decomposition was observed, but below a critical pressure of the total gaseous constituents in the reaction vessel—about 0·25 mm. of mercury—the reaction velocity began to increase, finally, at the lowest pressures, attaining five times its normal value and becoming approximately constant at this value. Possible disturbing factors such as the presence of impurities are carefully considered, but it is decided that the observed velocity increase is of real significance. All "chain" mechanisms are irreconcilable with the phenomenon. The results are interpreted by the assumption that a definite fraction of the activated molecules always undergoes decomposition irrespective of pressure, but that a larger fraction (about four-fifths) does not decompose if it collides within 10^{-6} sec. after activation, but is deactivated by collision. Calculations on this basis are in good agreement with experiment. A possible explanation of the two different types of activated molecules is offered, based on the fact that there are four NO linkings, and only one shared NO linking in the molecule of the pentoxide. Activation of one linking causes decomposition, activation of the shared linking invariably so; activation of the others, only after a time interval and if collisions do not intervene.

S. BARRATT.

Rate of reaction of bromine with aqueous formic acid. D. L. HAMMICK, W. K. HUTCHISON, and F. R. SNELL (J.C.S., 1925, **127**, 2715—2720).—The reaction between bromine and formic acid has been studied in dilute aqueous solution, using the Ostwald isolation method. The formic acid is completely oxidised to carbon dioxide. The reaction is of the second order, but the rate is retarded by the hydrobromic acid produced. From a study of the separate effects of the hydrogen and bromine ions, it is deduced that the reaction takes place between the formyl ions and free bromine molecules, *i.e.*, those molecules of bromine which are not combined with bromine ions to give the complex ions Br_3'. In order to obtain agreement with theory, it is necessary to assign to the constant for the equilibrium between bromine molecules, bromine ions, and tribromide ions a value considerably higher than that found by Jakowkin (A., 1896, ii, 514). This is justified by the fact that this author's experiments were carried out with higher concentrations and his constants

showed a regular increase with decreasing concentration of bromine. E. E. WALKER.

Velocity of the reaction between hydrogen peroxide and iodine ions. J. A. CHRISTIANSEN (Z. physikal. Chem., 1925, **117**, 433—447).—The influence of neutral salts on the velocity of this reaction was investigated, potassium iodide being used as a source of iodine ions. Potassium chloride, bromide, and nitrate cause a slight acceleration, potassium sulphate, oxalate, and chromate a slight retardation, and the alkaline-earth chlorides a marked acceleration. The temperature coefficient, between 0° and 25°, of the acceleration of the reaction by hydrogen ions (supplied by hydrochloric acid) was also determined. L. F. GILBERT.

Mechanism of the reaction between iodine, iodine ions, and hydrogen peroxide. J. A. CHRISTIANSEN (Z. physikal. Chem., 1925, **117**, 448—456).—Theoretical. A mechanism is suggested which is in harmony with Abel's data (A., 1921, ii, 180). The observations of Bray and Livingstone (A., 1923, ii, 473) on the course of the reaction between hydrobromic acid, bromine, and hydrogen peroxide are similarly explained. L. F. GILBERT.

Dependence of the rate of alkaline hydrolysis on the constitution of the alcohol. II. L. SMITH and H. OLSSON (Z. physikal. Chem., 1925, **118**, 99—106; cf. A., 1922, ii, 701).—The kinetics of the bimolecular reaction in aqueous solution between sodium hydroxide and *n*- (3·93), *iso*- (3·54), *sec*.- (0·816), and *tert*.-butyl acetates (0·081), *n*- (44·7) and *sec*.-propyl glycollates (13·8), have been investigated at 20°. The numbers in parentheses represent the values of the velocity coefficients at this temperature. The rate of hydrolysis varies with the nature of the alkyl radical and of the acid. When the alkyl acetates investigated in this and previous researches are arranged in the order of decreasing reactivities, the series obtained is identical with the corresponding series for the rate of ester formation from alcohols and acetic anhydride (Menschutkin, A., 1888, 901) and for the rate of formation of the corresponding ethyl alkyl ethers (Sagrebin, Z. physikal. Chem., 1900, **34**, 149). J. S. CARTER.

Dependence of the rate of alkaline hydrolysis on the constitution of the alcohol. III. Temperature coefficients. H. OLSSON (Z. physikal. Chem., 1925, **118**, 107—113).—The velocity coefficients for the reaction between sodium hydroxide and the two propyl acetates, the four isomeric butyl acetates, *iso*amyl acetate, and the two propyl glycollates in aqueous solution at 0·2°, 10°, 20°, 30°, and 40° have been determined. The temperature coefficients (10° intervals) decrease with increasing temperature according to Arrhenius' formula, there being no maximum value in the region 10—20° as recorded by Trautz and Volkmann (A., 1908, ii, 824).

J. S. CARTER.

Effect of differential aëration on corrosion. Electrode potential measurements. A. L. MCAULAY and F. P. BOWDEN (J.C.S., 1925, **127**, 2605—2610).—The four zones distinguished by Evans (A., 1925, ii, 688) in a sheet of metal partly immersed in water have been investigated by means of electrode potential measurement using 0·1*N*-sodium chloride as electrolyte. Iron and zinc surfaces tend to exist in one of two normal states, one a more electro-negative state characteristic of pure metal and corroded regions, and the other a less electro-negative state characteristic of aërated regions. For zinc, the difference in single electrode potential between these states is about 75 millivolts, for iron it is about 200 millivolts. These differences may be increased if the oxidation and corrosion respectively are very drastic. Experiments with drops of electrolyte on metal plates have shown that surfaces having a clean, bright appearance may be in either of these two states and then change rapidly from one state to the other with changing conditions. E. E. WALKER.

Mechanism of reduction. V. H. J. PRINS (Rec. trav. chim., 1925, **44**, 1051—1055; cf. A., 1925, ii, 1169).—Measurements of the rate of dissolution of lead in acetic acid in presence of nitromethane show that the reaction is much slower than in presence of nitrobenzene and that it is a true reaction velocity which is observed, not a velocity of diffusion. The critical concentration is calculated to be a 1·125*M* solution of nitromethane. The reactivity of the nitro-group in nitrobenzene is about 65 times that of the nitro-group in nitromethane, the difference being attributed to the positively charged carbon atom of the benzene nucleus. The mechanism of the reduction is discussed in detail.

G. M. BENNETT.

Catalytic combustion. I. Union of carbon monoxide and oxygen in contact with a gold surface. W. A. BONE and G. W. ANDREW (Proc. Roy. Soc., 1925, **A, 109**, 459—476; cf. A., 1906, ii, 434).—The rate of combination of a moist, theoretical mixture of carbon monoxide and oxygen, in contact with a gold surface at about 300° in a "normal" state of activity (*i.e.*, the maximum reached after a period of use), is always directly proportional to the pressure of the mixture. The catalysing power of the surface may be much reduced by cooling to the ordinary temperature over a period of days, or by prolonged evacuation. The reattainment of "normal" activity takes many hours. The catalysing power of the surface, when in "normal" activity, can be highly stimulated by previous exposure to either carbon monoxide or oxygen at the experimental temperature. When either of the two reacting gases was present in excess, the rate of combination was proportional to the partial pressure of the carbon monoxide, which was thus the controlling factor.

The rate of reaction depends on the presence of moisture in the gases. It is concluded that both combining gases are activated by the surface, and that the activation is not confined to a unimolecular adsorbed layer, but extends to more deeply occluded gas. Structural changes in the metal probably play a part in the phenomena, although no change in the surface could be detected microscopically. The gold was introduced in the form of a gauze.

S. BARRATT.

Sulphuric acid from a quadruple mixture. R. SAXON (Chem. News, 1925, **131**, 372—373).—Electrolysis in series of solutions of ferrous ammonium sulphate and of equimolecular mixtures of copper and ferrous ammonium sulphate yields a 9% solution of sulphuric acid in the first case and a 12% solution in the second case in 3 hrs. After 7 hrs.' electrolysis, a ferrous ammonium sulphate solution will contain 14% of free sulphuric acid, whilst an equimolecular solution of nickel, copper, ammonium, and ferrous sulphates electrolysed in series with the ferrous ammonium sulphate solution will contain 19% of free acid. A. R. POWELL.

Surface catalysis in photochemical processes. H. S. HIRST and E. K. RIDEAL (Nature, 1925, **116**, 899—900).—It is improbable that the diverse results obtained by various investigators for the rate of combination of gases irradiated in silica tubes by a mercury-vapour lamp can in general be attributed either to an inhibiting factor or to the propagation of chains. A mercury surface illuminated at the ordinary temperature with radiation, including strong emission of the resonance line, 2537 Å., promotes combination in various mixtures of gases, but no catalytic effect has yet been observed with other metals. In the absence of hydrogen, ozone can be identified by the tailing of the mercury, but in presence of hydrogen, mercuric oxide is formed on the mercury surface and the walls of the vessel. Condensation of formaldehyde and its polymerides from carbon monoxide and hydrogen is accompanied by auto-retardation of the rate of reaction. This catalytic effect is believed to account for the high rates of combination frequently recorded.
A. A. ELDRIDGE.

Decomposition of ozone in red light. G. KISTIAKOVSKI (Z. physikal. Chem., 1925, **117**, 337—360).—An apparatus is described which has been used for the investigation of the decomposition of ozone at high concentrations in red light. Empirical equations are derived with which the observed course of decomposition is in agreement. The apparently contradictory results obtained by previous workers (von Bahr, A., 1910, ii, 949; Warburg, A., 1913, ii, 652; Weigert, A., 1915, ii, 813; Griffith and others, J.C.S., 1923, **123**, 2752, 2767) are due to erroneous interpretation of the experimental data, which agree approximately with those of the author. Helium, argon, nitrogen, carbon monoxide, carbon dioxide, and oxygen retard the reaction, the retarding influence increasing from left to right of the series.
L. F. GILBERT.

Mechanism of the photochemical reaction between hydrogen and chlorine. II. A. L. MARSHALL (J. Physical Chem., 1925, **29**, 1453—1461).—The amount of photochemical reaction between hydrogen and chlorine increases with the total pressure (A., 1925, ii, 883). A preliminary study of the effect of pressure over the range 0·001—6·0 em. has now been made by a method in which a mixture of the two gases is drawn through a quartz vessel illuminated by a quartz mercury arc. After exposure, the chlorine and hydrogen chloride are removed by liquid air and the pressure of the hydrogen is measured. The results are accurate only when this pressure greatly exceeds that of the chlorine.

The number of molecules of hydrogen chloride formed per quantum of light absorbed increases rapidly with pressure; over the above range the quantum yield increases from 20 to 25,000 mols. (approx.). At a constant total pressure of 5·9 cm., the quantum yield is unchanged when the light intensity is increased twenty times, a result not in agreement with Baly and Barker (J.C.S., 1921, **119**, 653; cf. also Chapman, A., 1924, ii, 668).
L. S. THEOBALD.

Microbalance. II. Photochemical decomposition of silver chloride. E. J. HARTUNG (J.C.S., 1925, **127**, 2691—2698).—The action of light on silver chloride has been investigated gravimetrically by the same method as that employed for silver bromide (A., 1925, ii, 57). Films of silver weighing less than 0·5 mg. were deposited on vitreous silica, ignited, chlorinated, and then weighed on a Steele-Grant microbalance. The film was chlorinated by exposure to chlorine diluted with air, concentrated chlorine being found to act more slowly. The silver chloride film was sealed up and insolated as described for the bromide (*loc. cit.*) in the presence of air, nitrogen, or hydrogen at low pressure (0·001 or 10 mm.), copper or potassium hydroxide being present to absorb the chlorine evolved. The maximum percentage loss of chlorine on insolation was 91·1% in air, 89·9% in nitrogen, and 94·8% in hydrogen. It is shown that silver and chlorine are the only products of decomposition, there being no evidence of the formation of subchloride. In the chlorination of silver deposits, optimum concentrations of chlorine were found to exist both for fresh and for previously chlorinated deposits. E. E. WALKER.

Nature of the photohalides and related substances. R. FEICK and K. SCHAUM (Z. wiss. Phot., 1925, **23**, 389—412).—See B., 1925, 1013.

Behaviour of silver iodide in the photovoltaic cell. A. GARRISON (J. Physical Chem., 1925, **29**, 1406—1407).—A reply to the criticism of Price (A., 1925, ii, 680). L. S. THEOBALD.

Selective action of polarised light on starch grains. E. C. C. BALY and E. S. SEMMENS (Nature, 1925, **116**, 817).—Polemical against Jones (Ann. Bot., 1925, **39**, 651). When starch grains in water are placed in a Petri dish or a flask and illuminated with a strong beam of polarised light they are hydrolysed. A. A. ELDRIDGE.

[Group of volatile hydrides.] F. PANETH and E. RABINOVITSCH (Ber., 1925, **58**, [*B*], 2446—2448; cf. A., 1925, ii, 760).—A reply to Hantzsch and Carlsohn (A., 1925, ii, 1043) and Carlsohn (*ibid.*, 1044). H. WREN.

Hydrates and hydrogels. VII. Isomeric hydrogels of aluminium hydroxide. R. WILLSTÄTTER, H. KRAUT, and O. ERBACHER (Ber., 1925, **58**, [*B*], 2448—2458; cf. A., 1924, ii, 767, and previous abstracts).—*Aluminium hydroxide-α* is prepared as a white, somewhat plastic gel when a solution of ammonium alum is precipitated with an excess of

ammonia and the precipitate rapidly washed with water containing ammonia and subsequently dried with acetone; the success of the method depends entirely on rapidity of manipulation and exact observance of conditions completely specified in the original memoir. The compound, which has the composition $Al(OH)_3$, readily passes within a few hours or a day into *aluminium hydroxide-β*, which is converted by 10% ammonia at 100° into a gel poorer in water, whereas the α-compound is only transformed into a coarsely disperse condition. The second modification is likewise unstable, but several months are required for its conversion into *aluminium hydroxide-γ*. The composition of the latter compound, which behaves towards ammonia in the same manner as the α-compound, is sometimes exactly, sometimes approximately, that of an orthoanhydride. The hydrogels-α and -β behave as distinct chemical compounds, the second of which is much less basic than the first. Hydrogel-α dissolves in cold 0·1% hydrochloric acid within 20 min., immediately in cold 2% or hot 0·5% acid, whereas hydrogel-β is not noticeably soluble in cold 5% acid. Both basic and acidic properties are lost in hydrogel-γ, which does not dissolve in cold dilute or moderately concentrated hydrochloric acid or in 0·1*N*- or *N*-sodium hydroxide. These properties are not in any way connected with the degree of dispersion of the colloid, since a typical γ-preparation absorbs invertase more freely than good specimens of the α- and β-gels. The differences between the α- and γ-compounds are therefore due either to isomerism or to polymorphism.

The transformation of aluminium hydroxide-α into the β-compound is invariably accompanied by a diminution in the proportion of combined water in the product (after treatment with acetone). The product reabsorbs moisture in the course of a few days, and its composition thereby gradually approximates to that of aluminium orthohydroxide. It appears most probable that the β-compound is a polyaluminium hydroxide, $4Al(OH)_3—H_2O$, which is converted by ammonia into the hydroxide, $4Al(OH)_3—3H_2O$.

Aluminium hydroxide-*C*, prepared according to the method of Willstätter and Kraut (A., 1923, ii, 493), is frequently used for the absorption of enzymes, but, as now shown, the process may lead to the formation of either the α-, β-, or γ-modifications; the nature of the product is most readily established by its behaviour towards ammonia. H. WREN.

Hydrates and hydrogels. VIII. Aluminium hydroxide gel of the formula, AlO·OH. R. WILLSTÄTTER, H. KRAUT, and O. ERBACHER (Ber., 1925, **58**, [*B*], 2458—2462).—Aluminium hydroxide-α gradually loses water when heated in a current of dry air, but the composition of the residue remains constant between 212° and 239°, 16·6% H_2O being present. The mineralised hydroxide-α loses water without break at 150—250°. Aluminium hydroxides-β and -γ have constant compositions in the temperature intervals 214—239° and 242—272°, the water content being 19·1—19·5% and 14·5—15·4%, respectively. In these cases, the product appears to consist mainly of aluminium metahydroxide, AlO·OH, mixed with aluminium oxide or polyaluminium hydroxide. Homogeneous *aluminium metahydroxide* is obtained when any of the aluminium hydroxide gels is heated rapidly in a sealed tube with 10% ammonia to 250°, maintained at this temperature for 8—9 hrs., and subsequently treated with acetone. The new product retains the gel structure and is without basic or acidic properties. Its chemical individuality is established by its stability over a range of 200°. The selective adsorptive capacity of aluminium metahydroxide for enzymes is remarkable. Thus from yeast autolysates the invertase is adsorbed one twenty-fifth, the maltase one-fifth, as much as by the customary aluminium hydroxide gels, so that from such mixtures it is possible to adsorb two-thirds of the maltase without the passage of invertase into the solid phase; the homogeneous enzyme is obtained by elutriation with diammonium hydrogen phosphate. Since the most markedly selective action is exhibited by the aluminium hydroxide gel which reacts least readily with acids or alkali hydroxide, it is no longer possible to consider adsorption as an effect of the opposed electrochemical nature of enzyme and adsorbent. The result cannot be ascribed to surface action, but must be attributed to affinity relationships which cannot yet be defined exactly. H. WREN.

Calcium "phosgeno-aluminate" [chloroaluminate]. A. F. O. GERMANN and C. R. TIMPANY (J. Physical Chem., 1925, **29**, 1423—1431).—The existence of the compound $COAl_2Cl_8$, which behaves as a weak acid and is designated "phosgeno-aluminic acid," has been previously postulated (Science, 1925, **61**, 71). The present investigation is to test the theory put forward. Calcium "phosgeno-aluminate" [chloroaluminate], $CaAl_2Cl_8$, prepared as described by the authors (A., 1925, ii, 1085), is the salt used. The vapour pressures, densities, and electrical conductivities at 25° and 0° for solutions in carbonyl chloride varying in concentration up to supersaturation at 35% (approx.) have been measured by methods previously used (cf. A., 1925, ii, 196, 288, 1066). The complete vapour-pressure curve for the system $CaAl_2Cl_8$–$COCl_2$ at 25° is given. The composition of the crystals which commence to separate when the solution contains 33·5% of the compound $CaAl_2Cl_8$ corresponds with the formula $CaAl_2Cl_8,2COCl_2$. The mol. wt. of the solute, using values from the curve in the usual vapour-pressure formula, is 766 ($Ca_2Al_4Cl_{16}$=756).

The molecular conductivity of calcium chloroaluminate in carbonyl chloride is greater than that of aluminium chloride in carbonyl chloride ("phosgeno-aluminic acid") at all concentrations. The conception, based on chemical grounds, of the latter as a weak acid is thus supported, although, it is pointed out, additional evidence for the theory is still required. The data for the physical properties mentioned above are tabulated. L. S. THEOBALD.

"Phosgeno-aluminates" [chloroaluminates] of sodium, strontium, and barium. A. F. O. GERMANN and D. M. BIROSEL (J. Physical Chem., 1925, **29**, 1469—1476; cf. Germann and Timpany, A., 1925, ii, 1085, and preceding abstract; Kendall, Crittenden, and Miller, A., 1923, ii, 387).—Some new

" phosgeno-aluminates " [chloroaluminates] have been prepared by allowing carbonyl chloride and aluminium chloride to react in a sealed tube with metallic chlorides. The solution was decanted and fractionally crystallised from carbonyl chloride. The vapour-pressure curves at 25° have been determined and are discussed in the systems formed by the chloroaluminates of barium, strontium, and sodium, respectively, with carbonyl chloride. The data also are tabulated. The m. p. of the *salts* $BaAl_2Cl_8$, $CaAl_2Cl_8$, $SrAl_2Cl_8$, and $NaAlCl_4$ are 295°, 280° (with loss of aluminium chloride), 325°, and 155·5°, respectively; the solubilities in carbonyl chloride (omitting the calcium salt), 52·5%, 52·3%, 36·5% at 25°. *Compounds* of the following composition have been identified: $3BaAl_2Cl_8,8COCl_2$; $BaAl_2Cl_8,COCl_2$; $5SrAl_2Cl_8,9COCl_2$; and $SrAl_2Cl_8,COCl_2$. The sodium salt forms no such compound at 25°. Calculations of mol. wt. from the lowering of the vapour pressure indicate 15—20 atoms of metal in the strontium and sodium compounds. L. S. THEOBALD.

Solid hydrides of arsenic, antimony, and bismuth. E. J. WEEKS and J. G. F. DRUCE (Rec. trav. chim., 1925, **44**, 970—974; cf. A., 1925, ii, 700).—Amorphous arsenic dihydride, As_2H_2, is formed as a brown powder when a solution of alkali hydroxide is electrolysed with an arsenic cathode and a platinum anode, the electrodes being separated by a porous pot. It is also produced when a solution of arsenic trichloride in dilute hydrochloric acid is added to an ethereal solution of stannous chloride; $2AsCl_3+4SnCl_2+2HCl=As_2H_2+4SnCl_4$. Solid antimony dihydride is similarly prepared by electrolysis, and also by the reduction of antimony salts by zinc in acid solution. Solid *bismuth dihydride*, Bi_2H_2, is prepared by adding a solution of bismuth trichloride in hydrochloric acid to a mixture of zinc and acid while the latter is evolving hydrogen. It is a grey powder which decomposes when heated in a vacuum, and reacts violently with fused potassium nitrate. W. HUME-ROTHERY.

Hydrates and hydrogels. IX. Silicic acid. R. WILLSTÄTTER, H. KRAUB, and K. LOBINGER (Ber., 1925, **58**, [*B*], 2462—2466; cf. Mylius and Groschuff, A., 1906, ii, 160).—Solutions of monosilicic acid are not suitably prepared by the interaction of sodium silicate and hydrochloric acid, since the subsequent dialysis is too slow and is accompanied by great loss. It is preferable to add silicon tetrachloride slowly to a well-stirred mixture of ice and water or to pass the vapours from the boiling chloride by a rapid current of air into water at 0° to −3°. The bulk of the hydrochloric acid is immediately removed by precipitation with silver oxide at 0°, whereby about 10% of the silicic acid passes to the precipitate. Very cautious addition of the final quantities of silver oxide permits the removal of 99% of the hydrochloric acid, but the remainder cannot easily be eliminated in this manner owing to the solvent action of silicic acid on silver oxide; it is removed by dialysis. Solutions of α-silicic acid, free from chloride, can be rapidly concentrated at 15° in the high-vacuum distillation apparatus until they contain 5—7% SiO_2; they are completely transparent and mobile. Rapid evaporation without gelatinisation has not been effected with solutions containing more than 7—10% SiO_2. Precipitation of gels from these solutions is best effected by ammonia and much ammonium chloride. The water content of the gels which have been treated with acetone never exceeds 22% (calculated on SiO_2) and generally lies between the values required for $H_2Si_2O_5$ and $H_4Si_3O_8$. Dialysis experiments establish the existence of at least two forms of α-silicic acid, one of which readily, the other slowly, passes through a diaphragm. They are regarded as monosilicic acid and oligosilicic acids formed from a few molecules of the former; in contrast with them are the polysilicic acids of the β series formed by further condensation. The latter acids readily precipitate egg-albumin, whereas the former do not. It is remarkable that α-silicic acid is somewhat volatile with steam. H. WREN.

Bismuth nitrates. M. PICON (Bull. Soc. chim., 1925, [iv], **37**, 1365—1375).—The water content of basic bismuth nitrates cannot be accurately determined from the loss of weight at 110°, but only by decomposition by heat in the presence of copper, and absorption of the water formed. The nitrate content is not accurately determined by boiling with sodium hydroxide or by the oxalic acid method, but results correct to 1% are obtained by boiling with a ferrous salt solution in an atmosphere of carbon dioxide, followed by titration with permanganate. The effect of conditions of formation on the composition of the medicinal compounds is determined. When the salts concerned are kept in a vacuum at 15° in the presence of phosphoric oxide, the following changes take place: (1) $Bi(NO_3)_3,5H_2O \longrightarrow Bi_2(NO_3)_6,3H_2O$;
(2) $Bi(OH)_2(NO_3) \longrightarrow (NO_3BiO)_{12},5H_2O$;
(3) $(NO_3)_{18}Bi_{20}O_{21},7H_2O \longrightarrow (NO_3)_{18}Bi_{20}O_2,6H_2O$;
(4) $(NO_3)_{10}Bi_{12}O_{13},8H_2O \longrightarrow (NO_3)_{10}Bi_{12}O_{13},4H_2O$.
The action of heat on these salts is complex and pure bismuth trioxide is not obtained below 425°.
W. HUME-ROTHERY.

Additive compounds of hydrogen chloride and sulphates of the heavy metals. F. EPHRAIM (Ber., 1925, **58**, [*B*], 2262—2267).—Attempts to prepare anhydrous " chloro-acids " by the action of dry hydrogen chloride on lead, silver, cadmium, nickel, cuprous, cupric, mercurous, or mercuric chloride over a wide temperature interval were unsuccessful. On the other hand, hydrogen chloride readily combines with certain metallic sulphates, yielding compounds of the type $\left[X^{SO_4}_{Cl_2}\right]H_2$ or $\left[X^{SO_4}_{(2HCl)}\right]$. Addition of hydrogen chloride occurs readily with the sulphates of metals of which the chlorides do not readily evolve hydrogen chloride when treated with concentrated sulphuric acid, and the temperature at which evolution of the gas commences is very approximately the dissociation temperature of the complex. The evolution of hydrogen chloride from sulphuric acid and a chloride appears, therefore, not to be an ionic reaction. The additive products generally lose about 1·5HCl at the temperature of dissociation, whereas the

remainder is evolved only at a gradually increasing temperature; the production of additive compounds containing 0·5HCl is not definitely established. The following *compounds* are incidentally described and the temperatures of dissociation for the mean pressure of 713 mm. are recorded: $PbSO_4$,2HCl (32°); $CdSO_4$,2HCl (128—135°); $CuSO_4$,2HCl (83°); $HgSO_4$,2HCl; Ag_2SO_4,2HCl, which does not exhibit a definite temperature of dissociation, but yields a series of solid solutions when heated until it ultimately becomes converted into a mixture of silver chloride and silver hydrogen sulphate. Zinc sulphate and hydrogen chloride appear to yield only a series of solid solutions; the temperature of dissociation of the adduct lies below that of the customary freezing mixture. H. WREN.

Conditions underlying the attack of hydrogen chloride and ammonium halide on metals. K. A. HOFMANN and F. HARTMANN (Ber., 1925, **58**, [*B*], 2466—2475; cf. A., 1925, ii, 685).—The greater readiness with which copper is attacked by ammonium chloride vapour than by hydrogen chloride is explicable on thermochemical grounds, but the magnitude of the superiority of the former over the latter can be accounted for only if the much greater adsorption of ammonium chloride vapour is taken into account. In every case, the evolution of hydrogen from ammonium chloride is preceded by vaporisation of the latter and adsorption of the vapour. The previous view (*loc. cit.*) that copper reacts with undissociated ammonium chloride molecules is therefore abandoned in favour of the hypothesis that the reactive system is an adsorbate, Cu . . . NH_3,HCl. All those conditions which increase the adsorption of hydrogen chloride or of hydrogen chloride and ammonia within the temperature range 270—330° facilitate the reaction, which yields hydrogen in a remarkable manner. Thus the presence of carbon dioxide increases the yield of hydrogen from copper gauze of limited surface, whilst aniline hydrochloride and, in particular, dimethylaniline hydrochloride are more active than ammonium chloride, since the bases are less readily carried away by the gases than ammonia. Under like conditions, hydrogen chloride gives only a very small yield of hydrogen, which, somewhat unexpectedly, is lowered by the presence of water vapour. The reaction is not facilitated by mixing the hydrogen chloride with methyl alcohol, ethyl alcohol, ether, or diphenylamine. The activity of hydrogen chloride can be increased, not only by the presence of substances which facilitate adsorption, but also by increase of the adsorbing surface, which is most readily effected by substituting copper powder for the gauze. Under these conditions, the difference between the activity of ammonium chloride vapour and hydrogen chloride may be reduced to such an extent that the ratio of the amounts of hydrogen evolved is only 1·8 : 1 (instead of 140 : 1); this order of magnitude is in agreement with that expected on thermochemical grounds. The superiority of ammonium chloride vapour over hydrogen chloride in chemical activity towards copper depends therefore mainly on its much greater adsorption, and is more pronounced as the surface of the copper is reduced. The decomposition of ammonium chloride vapour by tin is much less marked than by copper, since tin has but little affinity for ammonia.

If the conditions are sufficiently favourable for adsorption the chemical energy of the system is a measure of the extent of the change. Thus, ammonium bromide gives 1·7 times as much hydrogen with copper powder as does ammonium chloride, whilst ammonium iodide and copper gauze yield 2·6 times the amount of hydrogen obtained with ammonium chloride; these amounts agree with those expected from the heats of formation of cuprous bromide and cuprous iodide. H. WREN.

Different states of beryllium oxide. H. COPAUX and C. MATIGNON (Bull. Soc. chim., 1925, [iv], **37**, 1359—1365).—See A., 1925, ii, 1192.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. V. DOLEJŠEK and J. HEYROVSKÝ (Nature, 1925, **116**, 782—783).—An examination of the polarograph curves obtained in investigations of the electrolytic deposition potentials of manganous solutions, particularly when prepared from potassium permanganate, reveals humps which cannot be due to the presence of zinc, nickel, cobalt, or iron, but may be due to that of eka-manganese (atomic number 43) and dvi-manganese ("rhenium," atomic number 75). Manganese amalgam in contact with platinum foil was immersed for several days in a nearly saturated solution of manganous sulphate, the deposit removed from the platinum with concentrated hydrochloric acid, and, after dilution, neutralisation with sodium carbonate, and acidification with acetic acid, the solution was treated with hydrogen sulphide; the solution then contains manganese with about 2% of dvi-manganese. One of the humps is due to the element 75, but it could not be determined whether the other is caused by the element 43. Concentrated acidic solutions containing the element 75 are green, and the dry green chloride becomes black on keeping. Neutral solutions yield a yellowish-brown precipitate, probably by oxidation. Apparently higher valency compounds of the element 75 are more stable than those of manganese. Provisional spectroscopic results were obtained as follows: $L\alpha_1$, 1430X., $L\beta_1$, 1235·3X., $L\beta_2$, 1204·3X., $L\gamma_1$, 1059 X., the copper $K\beta$ line being used as reference. The results of Noddack, Tacke, and Berg (Naturwiss., 1925, **26**, 567) are inconclusive, their observed lines agreeing better with those of thallium than those of the element 75. A. A. ELDRIDGE.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. A. N. CAMPBELL (Nature, 1925, **116**, 866).—The second hump in the potential-current curve obtained by Dolejšek and Heyrovský (preceding abstract), and ascribed by them to the discharge of dvi-manganese, may represent the potential of incipient discharge of hydrogen. A. A. ELDRIDGE.

Complex compounds of ruthenium chlorides. R. CHARONNAT (Compt. rend., 1925, **181**, 866—867).—Observations are recorded confirming the co-ordin-

ation number six for tervalent ruthenium in its chloro-salts (cf. Briggs, A., 1925, ii, 703; Charonnat, *ibid.*, 586). The *salts* $[RuCl_6]M_3,H_2O$, where M=K and NH_4 were prepared by saturating with hydrogen chloride a cooled 10% solution of the salt $[RuCl_5(H_2O)]M_2$. The potassium salt forms orthorhombic plates which lose their water at 120°. Howe's method of preparing the salts $[RuCl_5(H_2O)]M_2$ was found to yield the *salt* $[RuCl_6]Na_3,12H_2O$ when M=Na, which crystallised from acid-free solutions in soluble, efflorescent, dark red, rhombohedric crystals. The water of crystallisation is lost at 130°. Five ruthenium chloro-salts are thus known, completely analogous to the corresponding iridium and rhodium salts in which the metals have almost certainly a co-ordination number of six. Dark red, deliquescent needles of the *acid* $RuCl_3,HCl,2H_2O$ were also prepared; this substance is considered to be $[RuCl_4(H_2O)_2]H$ rather than $[RuCl_4]H,2H_2O$, because no salt of the latter constitution is known. S. K. Tweedy.

Properties of active hydrogen. K. F. Bonhoeffer (Z. Elektrochem., 1925, **31**, 521—522).—Monatomic hydrogen can be produced, by means of suitable apparatus, in a concentration of approximately 20%. Its life is about ⅓ sec., as measured by chemical methods. Towards elements, oxides, and reducible organic compounds it is very active, but it does not react with nitrogen to form ammonia. The blue glow which active hydrogen emits on contact with mercury contains, in addition to mercury hydride bands, a resonance line at 2537 Å., which requires 112,000 cal. for excitation and for which no simple explanation is apparent. W. A. Caspari.

Preparation of an ash-free wood charcoal. L. H. Reyerson (Ind. Eng. Chem., 1925, **17**, 1114).—See B., 1925, 979.

Hydrogen electrode for flowing liquids. A. H. W. Aten and P. H. J. van Ginneken (Rec. trav. chim., 1925, **44**, 1012—1038).—See B., 1925, 1014.

Colorimetric p_H test of water or unbuffered solutions. H. T. Stern (J. Biol. Chem., 1925, **65**, 677—681).—In order to convert bromothymol-blue into a suitable indicator for unbuffered solutions in the region of the neutral point, it is necessary to adjust the indicator to a pure dark green colour by the addition of alkali; such adjusted solutions are not stable, and a neutral solution of *p*-nitrophenol forms a more satisfactory indicator, being also apparently not affected by atmospheric carbon dioxide. C. R. Harington.

Use of the Lehmann micro-electrode. G. E. Vladimirov and M. J. Galvialo (Biochem. Z., 1925, **160**, 101—104).—Lehmann's micro-electrode gives good results in the case of liquids free from carbon dioxide. In presence of carbon dioxide, the method is inferior to others in both accuracy and rapidity. The method is especially applicable to very viscous liquids, jellies, and tissues.
P. W. Clutterbuck.

Argentometric titration of iodides. I. M. Kolthoff (Pharm. Weekblad, 1925, **62**, 1309—1312; cf. A., 1921, ii, 517).—In slightly alkaline solutions, iodides may be titrated with silver nitrate solution, after addition of a trace of iodate, with very fair accuracy even in presence of large quantities of bromides or chlorides. A suitable degree of alkalinity is obtained by the addition of ammonium carbonate. In 0·1*N*-solutions the results are about 0·6% too low.
S. I. Levy.

Volumetric determination of soluble sulphates by means of barium chloride and potassium stearate. H. Atkinson (Analyst, 1925, **50**, 590—600).—Barium chloride solution reacts with the alkaline (to B.D.H. universal indicator) solution of potassium stearate to form a neutral solution when the whole of the stearate is precipitated, and it is therefore possible to determine sulphates volumetrically under certain conditions. A comparison of the solution of unknown concentration with a standard solution of approximately the same concentration is necessary because the end-point of the titration is reached before the theoretical quantity of barium chloride has been added, and this discrepancy is constant for equal concentrations. In order to obtain a sharp end-point, the concentration of the solution should be of the order of 0·05*N* or less, and the barium chloride solution should be added in excess and titrated back with standard potassium stearate solution. Aluminium, zinc, calcium, and magnesium are quantitatively precipitated by the potassium stearate solution, but their presence is not a serious drawback. The standard potassium stearate solution is prepared by adding 22—23 c.c. of 0·5*N*-alcoholic potassium hydroxide solution and 100 c.c. of neutral 95% alcohol to 3 g. of pure stearic acid, and boiling. A few drops of phenolphthalein are added and either more alcoholic potassium hydroxide solution or stearic acid, until the pink colour is just discharged. The solution is made up to 450 c.c. with neutral alcohol, and 50 c.c. of distilled water are added, the flask corked, and the liquid cooled. This solution is standardised against 0·1*N*-barium chloride solution, of which 5·5 c.c. in 50—60 c.c. of water are used, and 25 c.c. of the stearate solution are added, or more, until the end-point is passed at the development of a greenish-blue colour. Barium chloride solution is again added until the true yellowish-green end-point is reached. The limit of error of this method is of the order of 1 drop of 0·01*N*-solution.
D. G. Hewer.

Splash-head for Kjeldahl apparatus. H. Lowe (Analyst, 1925, **50**, 605).—The tube from the tap funnel passes through the centre of the bulb of the splash-head. The whole is sealed together and requires only one hole in the cork of the digestion-distilling flask. D. G. Hewer.

Determination of nitrogen by Acél's method. F. Himmerich (Biochem. Z., 1925, **160**, 105—112).—A number of modifications and improvements of Acél's method are suggested (cf. A., 1922, ii, 225).
P. W. Clutterbuck.

Determination of arsenic. I. BANG (Biochem. Z., 1925, **161**, 195—209).—The material is incinerated with sulphuric acid and nitric acid is dropped in from a special container. After driving off excess of the latter, reduction is effected by ferrous ammonium sulphate in the presence of potassium bromide and chloride, followed by distillation into sodium hydroxide. To the distillate are added sodium hydrogen carbonate and a crystal of potassium iodide and the solution is titrated with 0·005*N*-iodine.

C. RIMINGTON.

Azido-dithiocarbonic acid. II. Determination of the azido-dithiocarbonate radical. A. W. BROWNE and G. B. L. SMITH (J. Amer. Chem. Soc., 1925, **47**, 2698—2702).—The azido-dithiocarbonate radical resembles the halogenoid radicals and may be determined by titration of the free acid with alkali, by precipitating and weighing the silver salt, by converting this into silver chloride and weighing, by titrating with silver nitrate solution by Gay-Lussac's or by Volhard's method, or by titration with alcoholic iodine. These all give slightly low results, the best being Volhard's method.

A. GEAKE.

Micro-determination of sodium. E. TSCHOPP (Helv. Chim. Acta, 1925, **8**, 893—900; cf. A., 1921, ii, 655; 1924, ii, 123, 413, 500).—Volumetric, colorimetric, and electrolytic methods for micro- and semi-micro-analysis of biochemical products are described in detail. The complex sodium cæsium bismuth nitrite, $6NaNO_2,9CsNO_2,5Bi(NO_2)_3$, may be precipitated under suitable conditions. A solution of the complex on electrolysis deposits the bismuth quantitatively at the cathode. R. A. MORTON.

Electrometric study of the separation of silver iodide, bromide, and chloride. H. T. S. BRITTON (Analyst, 1925, **50**, 601—604).—Since the solubility products of the iodide, bromide, and chloride of silver are of the order 10^{-16}, 10^{-13}, and 10^{-10}, electrometric titrations of ammoniacal solutions of the three halides with silver nitrate solutions, in which the concentrations of the ammonia and silver nitrate are suitably varied, enable the continuous change in silver-ion concentration to be made sufficiently gradual to permit of the complete precipitation of one halide before the separation of the next begins. A silver electrode placed in the beaker containing the ammoniacal halide solution was connected through a salt bridge of saturated potassium nitrate solution with a normal calomel electrode. The *E.M.F.* of this combination were measured after the addition of each amount of silver nitrate. Using 3·37*N*-ammonia solution and 0·5*N*-silver nitrate solution, the bromide and chloride were separated quantitatively from the bromide, but not the iodide. With 0·1*N*-silver nitrate solution and (i) 18*N*-, (ii) 8*N*-, and (iii) 4*N*-ammonia solution it was possible with (i) and (ii) completely to separate the silver iodide (by filtration through a Gooch crucible), but not with (iii). The experiments are illustrated by means of curves. The following mean values at 18° were found, $[Ag^{\cdot}][I'] = 7 \times 10^{-17}$; $[Ag^{\cdot}][Br'] = 2{\cdot}8 \times 10^{-13}$; $[Ag^{\cdot}][Cl'] = 1{\cdot}8 \times 10^{-10}$.

D. G. HEWER.

Micro-determination of calcium and magnesium in organic liquids. L. CONDORELLI (Rend. Accad. Sci. Fis. Mat. Napoli, 1925, [iii], **31**, 73—83).—When precipitated from an albuminous solution, calcium oxalate is included in a gelatinous envelope which resists the action of water and should be washed with dilute ammonia solution. The micro-methods developed by the author for determining calcium and magnesium in organic liquids are as follows: 1 c.c. of the blood or other liquid is evaporated to dryness and ashed in a platinum crucible. The ash is dissolved in 0·5 c.c. of *N*-hydrochloric acid and the solution transferred, by means of a thin pipette bent at right angles, to a 12 c.c. centrifuge tube, the crucible being washed successively with 0·5 c.c. of the acid, and 0·5 c.c. of water, and twice with 0·5 c.c. of 3% oxalic acid solution, and the wash liquors also placed in the centrifuge tube. After addition of a drop of methyl-red solution, the tube is immersed in a boiling water-bath and the solution neutralised by slow addition of *N*-ammonia solution from a micro-burette. Next 1 c.c. of ammonium chloride solution and 1 c.c. of 9% ammonium oxalate solution are added and the liquid is stirred well with a small glass rod, which is then washed into the tube with sufficient water to bring the total volume to 6 c.c. After 24 hrs., the liquid is centrifuged for 20 min., the clear solution being pipetted into a dry test-tube and replaced by 5 c.c. of water, which is removed after a brief centrifuging; this operation is repeated with two further quantities of water. Five c.c. of *N*-sulphuric acid are then added and, with the tube immersed in a boiling water-bath, the solution is titrated with 0·01*N*- or 0·005*N*-permanganate. With a liquid such as blood which contains iron, care must be taken that this is not precipitated with the calcium. To this end, the acid with which the ash is treated is introduced into the bottom of the centrifuge tube and centrifuged rapidly for 1—2 min., the clear liquid being then pipetted off into the precipitation tube; each of the washing liquids is treated similarly, the subsequent operations being as described above.

In an aliquot part of the liquid decanted from the calcium precipitate, the magnesium is precipitated as magnesium ammonium phosphate by addition of 1 c.c. of 2·5% ammonium phosphate solution and 2 c.c. of 10% ammonia solution. After 24 hrs., the crystalline precipitate is washed with three separate quantities of 5 c.c. of 10% ammonia, which are pipetted off after centrifugation. About 3 c.c. of the last wash water are neutralised with dilute sulphuric acid and treated with 1 c.c. of molybdic acid solution (50 g. of pure ammonium molybdate dissolved in 1000 c.c. of cold *N*-sulphuric acid) and 2 c.c. of quinol solution (20 g. dissolved in 1000 c.c. of water and 1 c.c. of concentrated sulphuric acid added); if no blue or green colour develops in 5 min., the washing is complete. The precipitate is then dissolved in 1 c.c. of *N*-sulphuric acid, which, together with five or six quantities of 1 c.c. of wash water, is transferred to a 25 c.c. flask, the whole being treated with 1 c.c. of the molybdic acid solution and 2 c.c. of the quinol solution, and, after 5 min., with 10 c.c. of a solution prepared by filtering a mixture of 2000 c.c. of 20% sodium carbonate solution with 500 c.c. of 15% sodium

sulphite solution. The solution is made up to 25 c.c. with water and mixed, the colour being compared in a Duboscq colorimeter with that obtained similarly from 10 c.c. of $N/5000$-potassium dihydrogen phosphate solution, which corresponds with 0·04864 mg. of magnesium. These methods yield highly accurate results. T. H. POPE.

Equilibrium between metal chloride, hydrogen sulphide, metal sulphide, and hydrogen chloride and its use in separating metals. Cadmium, bismuth, and lead. W. MANCHOT [with G. GRASSL and A. SCHREEBERGER] (Z. anal. Chem., 1925, **67**, 177—195).—The maximum quantity of hydrogen chloride that may be present in a solution for complete precipitation of cadmium by hydrogen sulphide at 20° is about 5 g. per 100 c.c., and of bismuth, 14·5 g. per 100 c.c. No precipitation at all occurs when the hydrogen chloride exceeds 9·5 g. per 100 c.c. in the case of cadmium, 16·5 g. per 100 c.c. in the case of bismuth, or 7·2 g. per 100 c.c. in the case of lead. With hot solutions, these values are considerably reduced, so that by regulation of the temperature and acidity it is possible to separate cadmium from antimony and mercury, and bismuth and lead from mercury by treatment of the solution with hydrogen sulphide. As cadmium sulphide has a tendency to be carried down by mercury sulphide, it is advisable to use an acidity of 19 g. of hydrogen chloride per 100 c.c. Antimony is separated from cadmium by treating a hot solution containing 8 g. of hydrogen chloride per 100 c.c. with the gas so as to obtain a black, crystalline antimony sulphide, adding an equal volume of hot water, filtering hot through a Gooch crucible, and washing the precipitate with hot water containing 4·5 g. of hydrogen chloride per 100 c.c.
A. R. POWELL.

Iodometric micro-determination of copper. N. SCHOORL and H. BEGEMANN (Rec. trav. chim., 1925, **44**, 1077—1086).—A micro-determination of copper by the ordinary iodometric method is described, the titration being carried out with a $0·001N$-thiosulphate solution, and the end-point observed in a dark room with special white illumination and a comparison solution. Liberation of iodine by atmospheric oxidation is prevented by the use of acetic acid for acidification. The titration is satisfactory in presence of iron salts if sodium phosphate or fluoride is added. The separation of the copper by electrodeposition on the microanalytical scale is also described, the metal being then dissolved in nitric acid, the solution evaporated to dryness, and the copper determined by titration. Amounts of 0·05—0·5 mg. of copper are determined with an accuracy of 1%.
G. M. BENNETT.

Determination of traces of mercury. I. Sensitive qualitative test for mercury. H. S. BOOTH and N. E. SCHREIBER (J. Amer. Chem. Soc., 1925, **47**, 2625—2629).—The usual qualitative tests for mercury are not sensitive to less than 5 mg. per litre. A new test is described in which the tip of a finely-pointed copper wire is used as the cathode for the electrolysis of one drop of the liquid, acidified with nitric acid. The anode is a platinum wire, and the passage of a current of 1·3—1·5 milliamp. at 1·5—2·0 volts for a few minutes is sufficient to produce a silver-white amalgam on the cathode. This is examined microscopically, and 0·5 mg. of mercury per litre can be detected. By evaporating 25—30 c.c. of the test solution to a few drops in a vacuum desiccator over sulphuric acid, the sensitivity of the test is increased a thousandfold. A. GEAKE.

Volumetric determination of iron in hydrochloric acid solution. W. MANCHOT and F. OBERHAUSER (Z. anal. Chem., 1925, **67**, 196—197).—The ferric chloride solution is reduced with sulphur dioxide or with metallic cadmium and after removal of the excess of reducing agent, 1 g. of potassium fluoride and 20 c.c. of 15% hydrochloric acid are added, followed by an excess of $0·1N$-bromine in N-potassium bromide solution. The excess of bromine is determined by titration with arsenious acid. Phosphoric acid may be used as a decolorising agent in place of potassium fluoride. A. R. POWELL.

Determination of ferrous oxide in insoluble silicates. O. HACKL (Z. anal. Chem., 1925, **67**, 197—204).—Decomposition of silicates by means of sulphuric and hydrofluoric acids in a neutral atmosphere and titration of the ferrous sulphate solution obtained gives low results for ferrous oxide. It is suggested that more accurate values would be obtained by the addition of a known weight of potassium dichromate during the decomposition, followed by a gravimetric, volumetric, or colorimetric determination of the excess. Preliminary tests indicate that fluorides do not affect the precipitation of ferric hydroxide by ammonia or potassium carbonate, the reaction between chromate and silver nitrate in acetic acid solution, or the colorimetric determination of chromium. Ammonia precipitation of the iron, however, results in a slight loss of chromate, but potassium carbonate yields a good separation of ferric hydroxide and chromate. A. R. POWELL.

[Detection of nickel.] L. A. TEST and D. L. SCOLES (Proc. Indiana Acad. Sci., 1924, **34**, 163—164).—The test for nickel dependent on the retardation of the change to pink cobaltous hydroxide of the blue basic cobalt compound obtained on addition of excess of sodium hydroxide to a solution of a cobalt salt is not trustworthy unless the sodium hydroxide solution is freshly prepared or free from silicate.
CHEMICAL ABSTRACTS.

Determination of uranium. G. E. F. LUNDELL and H. B. KNOWLES (J. Amer. Chem. Soc., 1925, **47**, 2637—2644).—See B., 1925, 1016.

Delicate colour reactions for zirconium, hafnium, and fluorine by means of hydroxyanthraquinones. J. H. DE BOER (Rec. trav. chim., 1925, **44**, 1071—1076).—The colour test for zirconium (or hafnium) with alizarinsulphonic acid (A., 1924, ii, 705) depends on the formation of a complex of 1 atom of zirconium to 1 mol. of the sulphonic acid. Addition of an excess of hydrochloric acid does not discharge the colour, but the resulting solution is a sensitive reagent for fluorides, detecting as little as 10^{-6} g. of fluoride ions in 1 c.c. of water, the reddish-

violet colour being turned yellow by removal of the zirconium as a complex fluoride. A method is described, based on these facts, for the volumetric determination of zirconium by titration with a fluoride solution, using alizarinsulphonic acid as indicator. Fairly accurate results are obtained by an empirical comparative method, the titration being carried out side by side with a solution of a known amount of zirconium having a similar concentration of hydrochloric acid. The results are independent of the presence of titanium, cerium, erbium, yttrium, manganese, or aluminium. Ferric salts must be reduced before titration by addition of an excess of stannous chloride.

The reactions of a number of other hydroxyanthraquinone derivatives with zirconium are described; colorations are produced wherever the substance contains two hydroxyl groups in the 1 : 2-positions. Hafnium gives similar reactions, but a slight difference is detected in the reaction with rufigallic acid (1 : 2 : 3 : 5 : 6 : 7-hexahydroxyanthraquinone), the colour developed being somewhat more easily discharged by hydrochloric acid with hafnium than with zirconium. G. M. BENNETT.

Crystalline digallic acid as a precipitant. M. NIERENSTEIN (Analyst, 1925, **50**, 604—605).—Since all recent work goes to show that gallotannin is a mixture, and even when purified by the usual methods contains free gallic acid, its replacement in analysis is suggested by such a trustworthy crystalline reagent as digallic acid, which possesses all the properties of gallotannin and is readily prepared from gallotannin or gallic acid.

D. G. HEWER.

Improved form of electric vacuum furnace. J. R. PARTINGTON and N. L. ANFILOGOFF (Trans. Faraday Soc., Nov. 1925, advance proof).—Full details and working drawings are given for the construction of a hot carbon tube furnace. The furnace is designed for work at high temperatures in a vacuum or in an atmosphere of an inert or a reacting gas.

F. G. SOPER.

Precision *X*-ray spectrometer for chemical investigations. G. L. CLARK, H. C. WEBER, and R. L. HERSHEY (Ind. Eng. Chem., 1925, **17**, 1147—1150).—A description is given of the source of power, tube housing, spectrometer, make-and-break switch, auxiliary shielding, ionisation chamber, and potentiometric control of the installation. Current delivered from a transformer at 240,000 volts is rectified by a rotating full-wave synchronous rectifier. The tube used is a 140,000-volt Coolidge tube with a tungsten target; interchangeable with this is a water-cooled molybdenum target tube operated at 35,000 volts. Angles can be read to 0·2 sec. The quadrant electrometer needle is charged to 45 volts, and the ionisation chamber to 90—200 volts.

L. L. BIRCUMSHAW.

Laboratory production of pure magnesia ware. R. F. MEHL, J. L. WHITTEN, and D. P. SMITH (Ind. Eng. Chem., 1925, **17**, 1171—1172).—See B., 1925, 992.

Precise automatic pressure regulator. L. E. DAWSON (J. Physical Chem., 1925, **29**, 1408—1414).—The regulator differs slightly in form from that previously described by the author (A., 1924, ii, 246), but the same principle is involved. The regulator may now be used for pressures greater, as well as less, than atmospheric. Improvements in adjustment give a high degree of accuracy in regulation. No adjustment of the apparatus is needed to compensate differences in atmospheric pressure when the pressure is measured with a manometer which has one end open to the air and the other connected with the system to be maintained under constant pressure. This only holds, however, when the latter is mechanically produced; in distillation processes, for example, changes in atmospheric pressure must be counterbalanced by changes in the setting of the regulator. Pressures approximately 100—250 cm. of water up to 50 cm. of mercury above atmospheric can be maintained with no fluctuation in the manometer levels.

A system for the regulation of pressure when the source of pressure fluctuates is also described.

L. S. THEOBALD.

Viscosity measurements by means of Mohr's balance. C. STICH (Pharm. Zentr., 1925, **66**, 781—783).—A simple method of measuring relative viscosities is described, in which the rate at which a horizontal plate, suspended in the liquid from one arm of the balance, is displaced by a suitable weight on the opposite pan, is determined.

N. H. HARTSHORNE.

Analytical crucible. J. D. M. SMITH (J.S.C.I., 1925, **44**, 539—540T).—Practically all the disadvantages of ordinary crucible methods of analysis result directly from the exterior-fitting lids. These disadvantages are all simultaneously overcome by the use of a lid having the vertical flange serrated instead of entire, the lid fitting wholly inside the crucible. Used with squat-shape crucibles of silica or platinum, this completely obviates the usual losses due to decrepitation of solids, spurting of liquids and pasty masses, and the "creeping" of heated volatile liquids over the outside of the crucible. Details are given of the application of such crucibles to the determination of nearly all the known metals as anhydrous sulphates, oxides, or free elements, whether in the form of pure compounds or as undried precipitates obtained by wet processes of separation.

Circulation apparatus for gases. N. G. CHATTERJI and G. I. FINCH (J.C.S., 1925, **127**, 2464—2466).—An improvement of the apparatus described by Bone and Wheeler (*ibid.*, 1903, **83**, 1074). It may also be used for the circulation of liquids. R. CUTHILL.

Mechanism of chemical gas reactions. M. KRÖGER (Z. physikal. Chem., 1925, **117**, 387—431).—Apparatus is described for volatilising solids and for obtaining part of the vapour in "unidimensional" streams, *i.e.*, in which no collisions of the molecules take place, either between themselves or between the molecules and the walls of the containing vessels. Such a stream of iodine, passed through a platinum

cylinder heated at 1100°, was found, within the limits of experimental error, to have suffered no decomposition into atoms. It would appear generally that a unimolecular reaction cannot take place if collisions cannot occur. Arrangements are described by which streams of two different vapours may be made to impinge on one another and the products examined. Preliminary experiments have been made with the vapours of cadmium and iodine, cadmium and sulphur, and cadmium and selenium.

L. F. GILBERT.

Apparatus for demonstrating thermal transformations of steels and anomalies in special alloys. P. CHEVENARD (J. Phys. Radium, 1925, [vi], **6**, 264—272).—Apparatus has been designed primarily for illustrating lecture courses in metallurgy. The experiments include a neat method for demonstrating recalescence, using a series of rings of ferronickel (25% Ni) mounted alternately with steel rings on a spindle; the whole is first heated to redness and on cooling there is a very decided difference in brilliancy between the alternate rings. A wire dilatometer enables an audience to follow the change in volume of an alloy. The polymorphic transformations of a specimen are contrasted with the expansion of baros (10% chromium, 90% nickel). This alloy has no thermal anomaly, and its expansion is optically compared with that of the specimen and anomalies indicated on a screen. The apparatus is suitable for quantitative investigations on the mechanism of the tempering process. Another instrument, the thermomagnetic tracer, records the magnetisation–temperature curve of a ferromagnetic substance. The thermo-elastic oscillometer and a galvanoscope for wires under torsion exhibit in a striking manner the positive thermo-elastic anomaly of certain ferronickel alloys. In certain iron–nickel alloys such as "invar" the form which is stable in the heated state is not only more dense but also more rigid than the form stable in the cold. Whilst in "invar" the anomalous contraction due to the magnetic transformation scarcely compensates for the normal expansion, the anomalous increase in rigidity is much greater than the normal decrease. Thus the elastic modulus may increase with temperature. This phenomenon is ingeniously demonstrated. In "elinvar," the anomaly has been modified by suitably changing the alloy so that no indication of its existence is found by using this new alloy with the apparatus devised. None of the devices is unduly complicated. R. A. MORTON.

Mineralogical Chemistry.

Meteorite (eucrite) fallen in the Haute-Volta on June 27th, 1924. A. LACROIX (Compt. rend., 1925, **181**, 745—749).—The meteorite, belonging to the eucrite class, was practically unbroken by the fall, and weighed 18 kg. It contained 3·48% of free silica; 34·93% of total felspars (orthose 1·11%, albite 1·57%, anorthite 32·25%); 57·94% of total pyroxenes ($CaSiO_3$, 9·40%, $MgSiO_3$, 16·20%, $FeSiO_3$, 32·34%); 0·46% of magnetite; 1·22% of ilmenite; 0·57% of pyrrhotite; 1·25% of chromite; 0·34% of apatite. The general composition agrees closely with that of the eucrite type of meteors which have occasionally fallen elsewhere. W. HUME-ROTHERY.

Chlorite in Transvaal marundite. J. ORCEL (Compt. rend., 1925, **181**, 795—797).—Particulars are given of the analysis of optically active lamellar chlorite of greyish-green colour, found in marundite corundum-bearing rock, near Mays Kraal (East Transvaal). The specimen was of the grochauite type, of formula $4SiO_2,2Al_2O_3,7MgO,6H_2O$, but with 9·42% of ferrous oxide in place of magnesia. The composition agreed closely with that of a chlorite from North Carolina, but with the ratio MgO : FeO lower in the Transvaal specimen, indicating the existence of a ferrous grochauite intermediate between true grochauite (MgO : FeO=10 approximately) and the ripidolites or perromagnesium perchlorites (MgO : FeO<3). W. HUME-ROTHERY.

Identity of fibrillar limonite with goethite. R. GAUBERT (Compt. rend., 1925, **181**, 869—872).—Investigation of the effect of temperature on the variation of the dispersion of the optical axes of goethite and of limonite and also of the action of hydrochloric and hydrofluoric acids on these minerals indicates that fibrillar limonite is impure goethite. The former phenomenon also serves to distinguish between goethite and lepidocrocite.

S. K. TWEEDY.

Variation with depth of certain salts utilised in plant growth in the sea. W. R. G. ATKINS and H. W. HARVEY (Nature, 1925, **116**, 784—785).—There is a marked decrease in p_H value (8·35—7·87) with increasing depth (0—3000 m.), due mainly to the removal of carbon dioxide by the phytoplankton, but partly to the high surface temperature altering the equilibrium between hydrogen carbonate and atmospheric carbon dioxide. Phosphate first appears at a depth of 50—75 m. and increases to 88 mg. per $m.^3$ Nitrate nitrogen varies from 15 mg. per $m.^3$ at the surface to 6 mg. at 75 m. and 265 mg. at 3000 m.; silica varies from 220 mg. at the surface to 1200 mg. at 3000 m. A. A. ELDRIDGE.

Sulphoselenium from Vulcano (Aeolian Islands). E. QUERCIGH (Rend. Accad. Sci. Fis. Mat. Napoli, 1925, [iii], **31**, 65—69).—Amorphous vitreous specimens of sulphoselenium from the fumaroles of Vulcano have d below 4 and n_D between 2·544 and 2·675, corresponding with 83—95% Se (cf. Merwin and Larsen, Amer. J. Sci., 1912, **34**, 43); they begin to soften below 100° and become gradually pasty and then liquid. Unlike the material described by Stromeyer (Pogg. Ann., 1824, ii, 410), they are free

from ammonium chloride. Crystalline sulphoseleniums, containing 98·71—99·06% S, 0·83—1·03% Se, and traces of tellurium and arsenic, are also found, and probably consist of mixed rhombic crystals (cf. Ringer, A., 1902, ii, 651; Pellini, A., 1909, ii, 805).
T. H. POPE.

Relationships between radioactivity, density, helium content, and hafnium content in certain zircons. A. PIUTTI (Rend. Accad. Sci. Fis. Mat. Napoli, 1925, [iii], **31**, 72—73).—No relationship is apparent between the hafnium contents and densities of zircons from different localities containing comparatively small proportions of hafnium, but the author's results confirm von Hevesy's observation that a connexion exists between the percentages of hafnium present and the radioactivities of the minerals. Vesuvian zircon contains about 0·7% HfO_2.
T. H. POPE.

Structure of α- and β-quartz. W. H. BRAGG and R. E. GIBBS.—See this vol., 13.

Barytes, cellestine, and anglesite. R. W. JAMES and W. A. WOOD.—See this vol., 13.

Magnetic rotatory power of paramagnetic minerals. H. K. ONNES and others.—See this vol., 14.

Gel of protein type (found) in the kieselguhr stratum of the Lüneburger Heide. F. V. VON HAHN.—See this vol., 23.

Organic Chemistry.

***X*-Rays and the constitution of the hydrocarbons from paraffin wax.** S. H. PIPER, D. BROWN, and S. DYMENT (J.C.S., 1925, **127**, 2194—2200).—The distances apart of the main cleavage planes of the crystals of seven hydrocarbons, isolated from Scotch paraffin wax by Francis (*ibid.*, 1922, **121**, 1529), have been determined by *X*-ray examination. The reflexion spectra (from specimens melted on glass strips) yielded by iron *K*-rays from a Shearer tube were photographed on a Müller spectrograph. Comparative photographs were obtained from synthetic triacontane, dotriacontane, and tetratriacontane. With these as standards, values were obtained graphically for the number of carbon atoms in the molecule of each unknown hydrocarbon. These were found to be whole numbers, indicating that the paraffin wax hydrocarbons are of normal constitution, without side-chains. The respective numbers obtained were: 22, 24, 25, 26, 28, 29, and 31. The mol. wts. of the seven hydrocarbons, determined by the ebullioscope method of Menzies and Wright (A., 1921, ii, 622), indicated the following numbers of carbon atoms in the respective hydrocarbon molecules: 23, 24, 26, 26, 28, 29, 31.
A. DAVIDSON.

Hydrogenation of ethylene in presence of metallic calcium. R. N. PEASE and L. STEWART (J. Amer. Chem. Soc., 1925, **47**, 2763—2766).—Reaction between ethylene and hydrogen was not observed when the mixed gases were bubbled through liquid sodium–potassium alloy at 300°. Hydrogen is adsorbed by metallic calcium at 200°, formation of the hydride apparently not taking place at this temperature. When a mixture of equal volumes of hydrogen and ethylene is passed, at 200°, over metallic calcium which has been previously saturated with hydrogen, rapid combination takes place and the resultant gas contains up to 92·7% of ethane. Ethane is also formed, but at a much slower rate, when ethylene alone is passed, at 200°, over the metal saturated with hydrogen, and a portion of the gases remains adsorbed on the catalyst. On treating the gas-saturated catalyst with hydrogen, a small proportion of a hydrocarbon, apparently methane, was obtained. The reaction appears to be of zero order, and it is concluded that the intermediate formation of calcium hydride is improbable.
F. G. WILLSON.

Stability of hexa-substituted ethanes. A. E. GRAY and C. S. MARVEL (J. Amer. Chem. Soc., 1925, **47**, 2796—2802).—*Di*cyclo*hexylphenylchloromethane*, m. p. 122°, obtained by the action of acetyl chloride in benzene on di*cyclo*hexylphenylcarbinol (cf. Godchot, A., 1910, i, 104), yields *s.-tetra*cyclo*hexyldiphenylethane*, b. p. 170—171°/1·75 mm., n_D^{23} 1·6710, when treated with molecular silver in toluene. This hydrocarbon is not oxidised when heated in air at 330° for 30 min. Reaction between ethyl hexahydrobenzoate and excess of magnesium *cyclo*hexyl bromide affords a product, b. p. 130—133°/2 mm., presumably impure di*cyclo*hexylcarbinol. *Tri-γγ-dimethyl-Δ$^{\alpha}$-butinenyl chloride*, m. p. 170—171°, obtained by the action of phosphorus trichloride on the corresponding carbinol in toluene, darkens on keeping, even in absence of light. When heated in toluene, it is converted into a yellow, crystalline *solid*, m. p. 210—220°, which contains chlorine. The chloride does not react with metals at the ordinary temperature, except with partial conversion into the above solid. When heated on the steam-bath with molecular silver in toluene for 15 hrs., the resulting mixture absorbs oxygen corresponding with the production of the free radical *tri-γγ-dimethyl-Δ$^{\alpha}$-butinenylmethyl* in 50% yield, the oxidised mixture containing the above solid, m. p. 210—220°, and a resinous, non-purifiable material. The existence of this purely aliphatic, free radical, as well as the stability of the above tetra*cyclo*hexyldiphenylethane, are in accord with Lewis' explanation of the existence of free radicals.
F. G. WILLSON.

Preparation of hexachloroethane by the chlorination of ethylene. G. E. MILLER (Ind. Eng. Chem., 1925, **17**, 1182—1183).—See B., 1925, 1011.

Electropyrogenetic decomposition of ethyl alcohol. F. G. MÜLLER (Helv. Chim. Acta, 1925, **8**, 821—825).—When an electric arc is maintained

beneath the surface of ethyl alcohol, the products are: amorphous carbon, graphite, acetaldehyde (1·5%), acetylenes condensed at −40° to −80° (0·3%), and a gaseous mixture of the composition: acetylene, 7—9·9%; ethylene, 6·0—9·6%; carbon monoxide, 20—24%; hydrogen, 46—50%; paraffins, 20·4—6·8%. Traces of diacetylene are also present (see following abstract). G. M. BENNETT.

Diacetylene [butadi-inene]. F. G. MÜLLER (Helv. Chim. Acta, 1925, **8**, 826—832; cf. Baeyer, Ber., 1885, **18**, 2272; A., 1925, i, 626).—The gases evolved in the electropyrogenetic decomposition of ethyl alcohol (preceding abstract) are cooled to −30° to −40° and from the liquid thus condensed the diacetylene is removed as silver salt and preserved under water (0·5—1 g. from 1000 c.c. of alcohol). The gas liberated from this salt by concentrated hydrochloric acid is fractionated first at the ordinary pressure and then in a vacuum with liquid air cooling. The pure butadi-inene has m. p. −36° to −37°, b. p. +13·6°. Earlier observations are confirmed as to its copper salt, silver salt, conversion by bromine into a hexabromide, m. p. 181°, and by iodine into a di-iododiacetylene, m. p. 93°, exploding at 95°. The liquid polymerises very rapidly at the ordinary temperature to an insoluble, amorphous, dark brown solid not melted at 350°, but exploding at a red heat.

G. M. BENNETT.

Symmetrical substitution derivatives of trimethylene dibromide and pentamethylene dibromide. W. H. MILLS and L. BAINS (J.C.S., 1925, **127**, 2502—2507).—Hydratropaldehyde reacts with formaldehyde and potassium carbonate to give *β-phenyl-β-methylpropane-αγ-diol*, m. p. 88°, b. p. 184°/17 mm. Prolonged action of hydrogen bromide on the *diacetate* (b. p. 179°/20 mm.) yields *αγ-dibromo-β-phenyl-β-methylpropane*, b. p. 143—146°/12 mm. From the glycol, *α-bromo-γ-hydroxy-β-phenyl-β-methylpropane*, b. p. 173°/15 mm., and *α-chloro-γ-hydroxy-β-phenyl-β-methylpropane*, b. p. 117—118°/15 mm., were also prepared, and from the diacetate *α-bromo-γ-acetoxy-β-phenyl-β-methylpropane*, b. p. 174—174·5°/18 mm., was obtained. Hydrogen bromide reacts with αγ-diacetoxy-β-phenylpropane to form *αγ-dibromo-β-phenylpropane*, b. p. 152°/14 mm., which, like the previous dibromide, has a strong geranium-like odour. Di-β-phenoxyethylacetic acid treated with hydrogen bromide yields *ethyl αε-dibromopentane-γ-carboxylate*, b. p. 166—167°/19 mm., which combines with piperidine to form *4-carbethoxybispiperidinium-1 : 1′-spiran bromide*,

$$\left[CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>CH\cdot CO_2Et\right]Br$$

(hygroscopic crystals, *picrate*, m. p. 130°). This passes on hydrolysis into *4-carboxybispiperidinium-1 : 1′-spiran bromide*, m. p. 289—290° (decomp.); *picrate*, m. p. 169—170°. B. W. ANDERSON.

Action of sodium on bromoethylenes. A. KIRRMANN (Compt. rend., 1925, **181**, 671—673).—Ground sodium reacts with solutions of bromoethylene derivatives to form hydrocarbons, without the liberation of hydrogen. With compounds of the type CHR:CHBr and CRBr:CH_2, the substances CHR:CH_2 and CR:CH are produced, the latter only in traces in the case of the second compound, together with small quantities of certain condensation products which are not formed by Wurtz' syntheses. Derivatives of the type CRR′:CHBr yield diolefinic hydrocarbons (cf. Pogorželsky, A., 1899, i, 785). Delacre's interpretation of the reaction (cf. A., 1906, i, 476) is untenable, since, among other things, the presence of water is unnecessary and intermediate hydrocarbons are not formed. The exact course of the reaction is unknown, but a tentative explanation is offered.

S. K. TWEEDY.

Formation of nitrosates from olefines. F. W. KLINGSTEDT (Ber., 1925, **58**, [*B*], 2363—2370; cf. Schaarschmidt and Hofmeier, A., 1925, i, 877).—The formation of solid compounds by addition of nitrogen peroxide appears to be in general a property of such ethylenic compounds as contain the double linking between a secondary and tertiary or two tertiary carbon atoms. The yield of such compounds is invariably far below that expected on theoretical grounds. Attempts to base a method for the determination of ethylenic compounds on this reaction are unsuccessful, since the yield of solid bisnitrosate is dependent, not only on temperature, time, and composition of the reaction mixture, but also on the absolute quantity, so that reproducible results cannot be obtained. The yield of β-methyl-Δ^{β}-butene bisnitrosate from the hydrocarbon and nitrogen tetroxide in ether or light petroleum is about one-tenth that from the same weight of hydrocarbon, amyl nitrite, and nitric acid. The yield of β-methyl-Δ^{β}-pentene bisnitrosate from the hexene and nitrogen tetroxide in light petroleum appears to increase up to a certain point with increasing temperature (cf. Schaarschmidt and Hofmeier, *loc. cit.*). Maximal yields are obtained only when a certain time is given for the process of polymerisation and the temperature of the mixture is not allowed to exceed 0° greatly. Sooner or later secondary changes commence in the bluish-green liquid portions of the mixture, which may ultimately cause the complete disappearance of the solid bisnitrosate.

Further attempts to obtain a quantitative method for the determination of olefines are based on the assumption, as recorded in the literature, that the bluish-green liquid portions consist mainly of the unimolecular form of the nitrosate, which might possibly be combined with a suitable base and weighed as the solid nitrolamine. The solid bisnitrosates react readily with aniline, for example, giving the corresponding nitrolamine in a uniform yield of 70—80%. The liquid products, however, do not yield similar products and are therefore regarded as containing for the most part compounds which differ in constitution or configuration from the readily polymerised nitrosate. This supposition is in harmony with the observation that the process of polymerisation in the original mixtures occurs with comparative rapidity and that the bulk of the liquid products possesses no tendency to polymerise to the bisnitrosate. Similarly, the addition of nitrogen trioxide, nitrosyl chloride, or nitrosyl bromide to ethylenic compounds appears generally to give a mixture of products.

The following compounds are incidentally described: β-methyl-Δ^{β}-pentene nitrosate, m. p. 116° (corr.); *β-methyl-Δ^{β}-pentene nitrolaniline*, $C_{12}H_{18}ON_2$, m. p. 86°. H. WREN.

Dehydration of primary alcohols containing tertiary radicals. A. FAVORSKI and (MME.) J. ZALESSKI-KIBARDINE (Bull. Soc. chim., 1925, [iv], **37**, 1227—1234).—The dehydration of primary alcohols containing a tertiary carbon atom, and in which two of the groups attached to the latter are similar, when effected by treatment of the chlorohydrin with alcoholic potassium hydroxide or pyridine, yields olefines in which the two identical groups are symmetrical with respect to the double linking, one of these groups migrating: $CR_2R'\cdot CH_2\cdot OH \rightarrow CRR':CHR$ (cf. Haller and Bauer, A., 1913, i, 168; Favorski, J. Russ. Chem. Soc., 1918, **50**, 63). Blondeau's deduction that in the dehydration reaction the relative migratory powers of the phenyl, methyl, ethyl, and benzyl groups decrease in the order given applies only to particular experimental conditions examined by him.

The *chlorohydrin* of methyl ethyl ketone, b. p. 85°/280 mm., 111°/761 mm., when heated successively with magnesium and gaseous formaldehyde yields hexane, hexylene, and *β-methyl-β-ethylbutanol*, b. p. 111°/145 mm., 155°/738 mm., d_4^{ν} 0·8407, n_D^{20} 1·4253 (*allophanate*, m. p. 102°, *phenylcarbamate*), which on oxidation with chromic acid yields a mixture of an acid (*silver* salt, $C_7H_{13}O_2Ag$) and an aldehyde (*semicarbazone*, $C_8H_{17}ON_3$, m. p. 174°). Hydrogen iodide at 0° converts the alcohol into the iodohydrin, which with alcoholic potassium hydroxide affords γ-methyl-Δ^{γ}-hexene, b. p. 93·8—94·2°/755 mm.

R. BRIGHTMAN.

Transformation of alkylvinylcarbinols into β-alkylallyl alcohols. R. DELABY (Compt. rend., 1925, **181**, 722—724; cf. Baudrenghien, A., 1922, i, 710; Delaby, A., 1923, i, 753).—Ethylvinylcarbinol when treated with bromine yields αβ-dibromo-*n*-pentan-γ-ol, which with sodium formate gives the αβ-diformate; this when heated and subsequently treated with potassium hydroxide yields Δ^{β}-penten-α-ol, the yield of the last-named from ethylvinylcarbinol being 20%. L. F. HEWITT.

Catalytic hydrogenation under reduced pressure. R. ESCOURROU (Chem. et Ind., 1925, **14**, 519—529).—See B., 1925, 1011.

Substitution by halogen of the hydroxy-group of secondary alcohols. P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1925, **65**, 507—513).—The halogenation, whether by means of hydrogen iodide, thionyl chloride, or phosphorus pentachloride, of butan-β-ol, δ-methylpentan-β-ol, and αβ-diphenylethanol, resulted in all cases in a reversal of the optical rotation. d-δ-*Methylpentan-β-ol*, prepared from the racemic compound by the method of Pickard and Kenyon (J.C.S., 1907, **91**, 2058), had $[\alpha]_D^{20}$ +22·38° and gave, with hydrogen iodide, the *iodide*, $[\alpha]_D^{20}$ −18·08°; l-δ-*methylpentan-β-ol*, $[\alpha]_D^{20}$ −7·63°, with thionyl chloride in pyridine gave the *chloride*, $[\alpha]_D^{20}$ +20·41°; *d-αβ-diphenylethanol*, $[\alpha]_D^{20}$ +16·73°; with phosphorus pentachloride gave *αβ-diphenylethyl chloride*, $[\alpha]_D^{20}$ −2·13°, whilst the *l*-isomeride with thionyl chloride gave a chloro-derivative having $[\alpha]_D^{20}$ +7·36°. The chlorination of these compounds was attended with difficulties and was probably accompanied by some racemisation.

C. R. HARINGTON.

Aliphatic nitro-alcohols. E. SCHMIDT, A. ASCHERL, and L. MAYER (Ber., 1925, **58**, [*B*], 2430—2434; cf. A., 1923, i, 288).—The conditions under which aliphatic nitro-alcohols can be reduced to the corresponding hydroxylamines without simultaneous formation of the amines have been determined. The success of the method appears to depend on the maintenance of a suitable hydrogen-ion concentration in the solution.

The preparation of *α-nitropentan-β-ol*, b. p. 87—88°/3 mm., d_4^{20} 1·0847, n_D^{20} 1·4421, α-nitro-γ-methylbutan-β-ol, b. p. 83—84°/4 mm., and α-nitro-δ-methylpentan-β-ol, b. p. 90—91°/2 mm., 99—100°/6 mm., d_4^{20} 1·0519, n_D^{20} 1·4433, is described in detail. Reduction is effected with hydrogen in the presence of palladised barium sulphate. Nitromethane and α-nitropropan-β-ol in aqueous solution in the presence of oxalic acid give *hydroxylaminomethane oxalate* $(NHMe\cdot OH)_2,C_2H_2O_4$, m. p. 158° (decomp.), and *α-hydroxylaminopropan-β-ol oxalate*, m. p. 111° (decomp.). In 96% alcoholic solution, α-nitrobutan-β-ol and α-nitropentan-β-ol similarly afford *α-hydroxylaminobutan-β-ol oxalate*, m. p. 100—101° (decomp.), and *α-hydroxylaminopentan-β-ol oxalate*, m. p. 99° (decomp.), whereas for the production of *α-hydroxylamino-δ-methylpentan-β-ol oxalate*, decomp. 144—145°, the addition of acetic acid is necessary. α-Nitro-γ-methylbutan-β-ol is hydrogenated in aqueous alcoholic solution in the presence of oxalic acid to *α-hydroxylamino-γ-methylbutan-β-ol oxalate*, m. p. 106—108° (decomp.), whereas the production of *α-hydroxylamino-octan-β-ol oxalate*, decomp. 142—143°, requires the simultaneous presence of acetic acid.

H. WREN.

Catalytic preparation of ethyl ether from ethyl alcohol by means of aluminium oxide. R. H. CLARK, W. E. GRAHAM, and A. G. WINTER (J. Amer. Chem. Soc., 1925, **47**, 2748—2754).—By passing ethyl alcohol vapour over aluminium oxide at 250°, an 80·8% conversion into ethyl ether and water was obtained (cf. Pease and Yung, A., 1925, ii, 37) and the reversibility of the reaction confirmed by demonstrating the formation of alcohol when ether and water are passed in equimolecular proportions over the catalyst at the same temperature. The catalysts were prepared (*a*) by precipitating aluminium hydroxide slowly from an 8% solution of sodium aluminate ($Al_2O_3 : Na_2O = 1 : 2$) with 0·25*N*-sulphuric acid, washing the precipitate free from sulphate with cold water, washing again with hot water, and drying by heating gradually to 400°; (*b*) by precipitating a 10% solution of the same salt slowly with carbon dioxide and drying the washed precipitate at 350°; and (*c*) by allowing a similar 10% solution to deposit alumina by hydrolysis on keeping. Catalysts prepared by the last two methods gave yields of ether lower than 50% unless complete removal of alkali was effected by repeated heating to 400° and washing in hot water. Catalyst (*c*), when free from alkali, gave the highest

yields. No diminution in activity of the catalysts was observed after the conversion of 1500 c.c. of alcohol. A corrected table and chart are given for the determination of ether in mixtures of ether, alcohol, and water by the method of Pease and Yung (*loc. cit.*). F. G. WILLSON.

Preparation of aliphatic ethers. J. B. SENDERENS (Compt. rend., 1925, **181**, 698—700; cf. A., 1923, i, 432; 1924, i, 638; 1925, i, 113).—Four more ethers have been obtained by heating the corresponding alcohol with the proportion (by volume) of sulphuric acid mentioned at the temperatures given: n-*heptyl ether*, b. p. 261·5°/745 mm., with 3% of concentrated sulphuric acid at 145°; *cetyl ether*, m. p. 55°, decomp. about 300°, with 4% of sulphuric acid trihydrate at 145°; sec.-*amyl ether*, b. p. 162° (corr.)/748 mm., d_4^{15} 0·775, with 2·5% of concentrated sulphuric acid at 120°; allyl ether, with 20% of sulphuric acid trihydrate at 105°. With increase in mol. wt. less acid is required to accomplish etherification and secondary require less acid than primary alcohols. L. H. HEWITT.

Organic phosphoric acid derivatives. I. Formation of primary phosphoric esters. F. ZETZSCHE and M. NACHMANN (Helv. Chim. Acta, 1925, **8**, 943—945).—Monoalkyl phosphates have been obtained, in 9—17% yield, as barium salts by interaction of organic halides with an aqueous-alcoholic solution of silver dihydrogen phosphate in presence of an excess of phosphoric acid to prevent the formation of the di-silver salt. The following are described: *barium benzyl phosphate*, $CH_2Ph{\cdot}O{\cdot}PO_3Ba$; *barium allyl phosphate*, $+H_2O$; *barium* β-*bromoethyl phosphate*, +EtOH+H_2O; *barium* γ-*iodo*-β-*hydroxypropyl phosphate*, +EtOH, from di-iodo-*n*-propyl alcohol, and *barium* γ-*bromo*-n-*propyl phosphate*, +EtOH, from trimethylene dibromide. G. M. BENNETT.

Oxidation of secondary mercaptans. P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1925, **65**, 515—518).—*l*-β-Iodo*iso*hexane was converted (with some racemisation) into the corresponding *mercaptan*, the least racemised preparation of which had $[\alpha]_D^{20}$ +21·21°; on oxidation with nitric acid this yielded *l-iso*hexane-β-sulphonic acid, $[\alpha]_D^{20}$ −6·68°; αβ-*diphenylethyl mercaptan*, $[\alpha]_D^{20}$ +8·56°, gave, on oxidation, αβ-*diphenylethylsulphonic acid*, $[\alpha]_D^{20}$ −36·40°. This reversal of rotation on oxidation is similar to that observed in the case of other mercaptans (A., 1924, i, 940) and resembles that accompanying the halogenation of secondary alcohols (cf. this vol., 45). The latter fact suggests that the stereochemical relationships between the mercaptans and the sulphonic acids are similar to those between the alcohols and their halogen derivatives. C. R. HARINGTON.

Occurrence of free radicals in chemical reactions. IV. Decomposition by iodine of silver salts of organic acids. H. WIELAND and F. FISCHER (Annalen, 1925, **446**, 49—76).—By the interaction of iodine with the silver salts of organic acids, the complex substances described by Simonini (A., 1893, i, 391) can be isolated. The formula $\left[Ag{<}\begin{matrix}OOCR\\OOCR\end{matrix}\right]I$ is preferred to that suggested by Simonini. The decomposition of these complexes by water and by heat has been studied for the following acids: acetic, hexoic, phenylacetic, triphenylacetic, cholic, crotonic, cinnamic, phenylpropiolic, benzoic, glycollic, lactic, mandelic, benzilic, oxalic, succinic, tartaric, glutaric, adipic, phthalic, hexahydrophthalic, maleic, and fumaric, and for ethyl hydrogen succinate. With water they all react thus: $3(R{\cdot}CO_2)_2AgI+3H_2O \rightarrow 6R{\cdot}CO_2H+2AgI+AgIO_3$, the complex taking up hydrogen with the formation of silver hypoiodite, which passes into the iodide–iodate mixture. The thermal decomposition of the complex in the fatty acid series leads to the formation of esters: $(R{\cdot}CO_2)_2AgI \rightarrow R{\cdot}CO_2R+CO_2+AgI$ (cf. Heiduschka and Ripper, A., 1923, i, 894) and the same occurs to a less extent in the aromatic series (except phthalic acid, cf. Birnbaum and Reinherz, A., 1882, 970). The complexes from many acids evolve only a small amount of carbon dioxide and the acid is largely regenerated, hydrogen being withdrawn from a part of the substance thus: $2(RH{\cdot}CO_2)_2AgI \rightarrow 2RH{\cdot}CO_2H+(R{\cdot}CO_2)_2AgI+AgI$. Far more than half the original acid is regenerated, showing that a complex which has once lost hydrogen tends to lose more. The complex from succinic acid yields maleic acid (cf. Birnbaum and Gaier, A., 1880, 801), that from glutaric acid yields γ-butyrolactone (cf. Windaus and Klänhardt, A., 1921, i, 392) and that from ethyl hydrogen succinate yields *ethyl* β-*carbethoxyethyl succinate*, b. p. 166—171°/12 mm. In no case could a hydrocarbon be isolated during the decomposition of the complex and hence, contrary to the statement of Birnbaum and Gaier (*loc. cit.*), the mechanism cannot be similar to those of the Kolbe electrolysis or the decomposition of diacyl peroxides (cf. Fichter and Fritsch, A., 1923, i, 438). It is concluded that the free radical $R{\cdot}CO_2$ does not take part in any of the reactions, but that the complex as a whole is always involved. R. W. WEST.

Do free alkyl radicals occur in the Kolbe electrochemical synthesis of hydrocarbons? H. ERLENMEYER (Helv. Chim. Acta, 1925, **8**, 792—797).—The production of methyl bromide or iodide, when the Kolbe electrolysis of potassium acetate is carried out in presence of sodium bromide or iodine, which has been cited as evidence for the transitory existence of free radicals, has now been shown to occur only to the extent of a 0·5% current yield, whereas the figure for by-products normally present is 2—3%. Moreover, the usual yield of ethane is still obtained in these experiments. The formation of methyl halide is accounted for on the assumption that peracetic acid occurs at the anode, and reacts as follows: $Me{\cdot}CO_3H+HX=MeX+CO_2+H_2O$, this reaction having been found to occur with synthetic peracetic acid. G. M. BENNETT.

Action of phenylhydrazine and hydrazine on fats and fatty acids. J. VAN ALPHEN (Rec. trav. chim., 1925, **44**, 1064—1070).—The observations of Falciola (A., 1920, i, 476) as to the action of hydrazine

on fats have been repeated, using an absolute methyl-alcoholic solution of hydrazine, and the direct formation of the hydrazides of the fatty acids has been confirmed. Not only oleic acid, but also the unsaturated acids of linseed oil are reduced in the process, yielding stearylhydrazide. The substitution of phenylhydrazine for hydrazine leads to the production of phenylhydrazides of each acid without any reduction of the unsaturated acids. The fatty acids are isolated from the hydrazides by heating with dilute sulphuric acid and benzaldehyde. *Palmitylphenylhydrazide*, m. p. 110·5°, is prepared by heating the acid or its esters with phenylhydrazine at 130—150°; its m. p. is not depressed by admixture of stearylphenylhydrazide. *Ricinoleylphenylhydrazide*, m. p. 63°, is obtained in a similar manner from castor oil. Stearylhydrazide reacts with aldehydes to yield stearylhydrazones; *benzylidenestearylhydrazone*, $C_{17}H_{35}$·CO·NH·N:CHPh, m. p. 83°, and *o-nitrobenzylidenestearylhydrazone*, m. p. 97·5°, are described.

G. M. BENNETT.

Action of halogens on acraldehyde in dilute aqueous solution. Trihalogenated propionic acids. A. BERLANDE (Bull. Soc. chim., 1925, [iv], **37**, 1385—1394).—α-Monosubstituted acraldehydes are readily obtained by the action of halogens on acraldehyde in dilute aqueous solution. It is improbable that hypochlorous or hypoiodous acid plays any part in the reaction, since under the conditions described these acids yield only traces of the α-halogenated acraldehyde. Thus acraldehyde with 1 mol. of 2·67% bromine water gives an 80% yield of α-bromoacraldehyde, n_D^{25} 1·501, d 1·67 when freshly distilled, increasing to 1·90 after 15 days at 25°. Bromine in ethereal solution converts it into ααβ-tribromopropaldehyde, oxidised by fuming nitric acid (cf. Moureu and Chaux, A., 1924, i, 1281) to ααβ-tribromopropionic acid, m. p. 94° (yield 70%). The *ethyl* ester has d^{23} 2·084, n_D^{23} 1·532, b. p. 140—142°/30 mm. Similarly, chlorine in carbon tetrachloride gives (yield 75%) *αβ-dichloro-α-bromopropaldehyde*, b. p. 81°/45 mm., d^{23} 1·83, n_D^{23} 1·511, oxidised to *αβ-dichloro-α-bromopropionic acid*, m. p. 61—62° (*ethyl* ester, b. p. 132—133°/45 mm., d^{23} 1·161, n_D^{23} 1·482). α-Chloroacraldehyde, obtained in 50% yield, similarly yields *ααβ-trichloropropaldehyde*, b. p. 63°/42—45 mm., d^{25} 1·470, n_D^{25} 1·473, oxidised to *ααβ-trichloropropionic acid*, m. p. 50—52° (*ethyl* ester, b. p. 121°/55 mm., d^{25} 1·36, n^{25} 1·458), and *α-chloro-αβ-dibromopropaldehyde*, b. p. 105°/55 mm., d^{20} 2·17, n_D^{20} 1·548. *α-Chloro-αβ-dibromopropionic acid*, m. p. 73°, its *calcium* salt (+2H_2O, lost at 110°), and *ethyl* ester, b. p. 142—143°/45 mm., d^{25} 1·84, n_D^{25} 1·504, are described. *α-Iodoacraldehyde*, b. p. 37°/8—9 mm., d^{23} 1·82, is obtained in 25% yield by the action of iodine in aqueous potassium iodide. The product rapidly becomes very viscous, probably through polymerisation, as the analytical figures remain unchanged.

R. BRIGHTMAN.

***iso*Oleic acid and other unsaturated fatty acids formed by distillation of ι-hydroxystearic acid.** V. VESELY and H. MAJTL (Chem. Listy, 1925, **19**, 345—356).—Pure ι-hydroxystearic acid yields on distillation a solid consisting of a eutectic mixture of Δ^4-elaïdic and Δ^9-elaïdic (*iso*oleic) acids, and a liquid containing ordinary oleic acid and its Δ^4-*isomeride*.

B. W. ANDERSON.

Structure of chaulmoogric and hydnocarpic acids. R. L. SHRINER and R. ADAMS (J. Amer. Chem. Soc., 1925, **47**, 2727—2739).—Chaulmoogric acid is reduced rapidly by hydrogen in alcoholic solution in presence of platinum oxide to dihydrochaulmoogric acid, m. p. 71—72° (cf. Barrowcliff and Power, J.C.S., 1907, **91**, 557), hydnocarpic acid yielding similarly dihydrohydnocarpic acid, m. p. 64—65° (cf. Dean and Wrenshall, A., 1921, i, 91; U.S. Pub. Health Bull., 1924, **141**, 25). Methyl chaulmoograte and methyl hydnocarpate are reduced analogously, with formation of methyl dihydrochaulmoograte, m. p. 27°, b. p. 204—205°/10 mm., d_{25}^{30} 0·9018, n_D^{30} 1·4356, and *methyl dihydrohydnocarpate*, b. p. 187—188°/10 mm., d_{25}^{25} 0·9057, n_D^{30} 1·4523. Bromodihydrochaulmoogric acid (cf. Power and Gornall, J.C.S., 1904, **85**, 838, 851), m. p. 37—38°, is converted by the action of alcoholic potassium hydroxide into a mixture containing 22% of chaulmoogric acid. Ethyl bromodihydrochaulmoograte, $[\alpha]_D$ +7·1°, obtained by the action of hydrogen bromide on ethyl chaulmoograte in light petroleum, yields similarly a mixture containing 5·4% of chaulmoogric acid. Oxidation of this mixture with dilute aqueous potassium permanganate at 18—20°, followed by esterification of the product with methyl alcohol, affords a methyl ester, m. p. 64—65°, b. p. 220—250°/9 mm., which, on hydrolysis, yields the corresponding acid, m. p. 125—126°, previously designated by Barrowcliff and Power (*loc. cit.*) as γ-keto-β-methyl-*n*-pentadecane-αα′-dicarboxylic acid. On reduction with amalgamated zinc and hydrochloric acid, however, this ketonic acid affords *n*-hexadecane-αα′-dicarboxylic acid, m. p. 118°, which was synthesised by the electrolysis of potassium ethyl sebacate, and is therefore δ-keto-*n*-hexadecane-αα′-dicarboxylic acid, its derivation from chaulmoogric acid being formulated as follows:

$$\begin{matrix}CH{=}CH\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!CH{\cdot}[CH_2]_{12}{\cdot}CO_2Et \xrightarrow{HBr}$$

$$\begin{matrix}CH_2{\cdot}CHBr\\ CH_2{-}CH_2\end{matrix}\!\!>\!CH{\cdot}[CH_2]_{12}{\cdot}CO_2Et \xrightarrow{KOH}$$

$$\begin{matrix}CH_2{-}CH\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!C{\cdot}[CH_2]_{12}{\cdot}CO_2H \xrightarrow{KMnO_4}$$

$$CO_2H{\cdot}[CH_2]_3{\cdot}CO{\cdot}[CH_2]_{12}{\cdot}CO_2H.$$

On treatment with ozone in glacial acetic acid solution, followed by decomposition of the ozonide according to the method of Helferich and Schäfer (A., 1925, i, 7), chaulmoogric acid yields a vitreous solid, which, when treated with dry ammonia in ether, yields *ammonium αγ-dialdehydo-n-pentadecane-α′-carboxylate*, and, when oxidised with chromic acid in glacial acetic acid, followed by esterification with methyl alcohol, affords trimethyl *n*-pentadecane-αα′γ-tricarboxylate, m. p. 37—38°, identical with that obtained by esterification of the acid produced by direct oxidation of chaulmoogric acid with potassium permanganate (cf. Power, *loc. cit.*). Methyl chaulmoograte yields, similarly, a liquid, non-purifi-

able product, from which, on treatment with hydroxylamine, the *dioxime* of *methyl* αγ-*dialdehydo*-n-*pentadecane*-α′-*carboxylate*, m. p. 93—94°, was obtained. An isomeric *dioxime*, m. p. 102—103°, was produced under different conditions. Consideration of the above reactions, and a review of other transformations of chaulmoogric acid, lead to the conclusion that the *cyclo*pentene form of Power's suggested tautomeric structure gives adequate representation of the structure of chaulmoogric acid, and that it is not actually a tautomeric substance.

F. G. Willson.

Action of ethyl acetopyruvate on diazonium hydroxides. Favrel and C. H. R. Z. Jean (Bull. Soc. chim., 1925, [iv], **37**, 1238—1241).—The sodium derivative of ethyl acetopyruvate reacts readily with diazonium compounds either in acetic acid or in the presence of a large excess of hydrochloric acid, yielding crystalline substances which are soluble in alkali and are provisionally regarded as hydrazones of the type $CO_2Et{\cdot}CO{\cdot}C(COMe){:}N{\cdot}NHAr$. Benzenediazonium chloride in acetic acid gives 96% of the theoretical yield of the γ-*phenylhydrazone* of ethyl acetopyruvate, m. p. 111—112°; in hydrochloric acid the yield is 78%. The γ-o-*tolylhydrazone*, lemon-yellow needles, m. p. 67—68°; γ-p-*tolylhydrazone*, green, m. p. 113—114°; γ-o-*nitrophenylhydrazone*, yellow, m. p. 144—145°; γ-m-*nitrophenylhydrazone*, m. p. 106—107°; γ-p-*nitrophenylhydrazone*, m. p. 137—138°; γ-m-*chlorophenylhydrazone*, yellow, m. p. 91—92°, and the γ-m-*bromophenylhydrazone*, m. p. 99—101°, are similarly obtained in yields varying from 73% to 99% of theory.

R. Brightman.

Oxidation of oxalic acid with potassium permanganate. G. Scheff (Biochem. Z., 1925, **160**, 390—397).—When potassium permanganate in excess reacts with oxalic acid in the presence of sulphuric acid at 70°, the reduction is greater than that calculated from the equation $2KMnO_4+3H_2SO_4+5C_2H_2O_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O$. If the reaction time is constant, the permanganate reduced is proportional to the oxalic acid present. The secondary reaction, which is not completed in 30 min., is thought to be $2KMnO_4+3MnSO_4+2H_2O=K_2SO_4+2H_2SO_4+5MnO_2$.

E. C. Smith.

Configuration of αα′-dibromodibasic acids. IV. αα′-Dibromoglutaric acids. H. R. Ing and W. H. Perkin, jun. (J.C.S., 1925, **127**, 2387—2399; cf. *ibid.*, 1921, **119**, 1393; A., 1924, i, 1039, 1162).—Dibromination of glutaric acid yields a mixture of *meso*-αα′-dibromoglutaric acid, m. p. 170°, and the *dl*-acid, m. p. 142°. The methyl and ethyl esters have been prepared by Ingold's method (*ibid.*, 1921, **119**, 316). *Ethyl* αα′-*dibromoglutarate*, b. p. 162°/14 mm., is an inseparable mixture of the two isomerides. *Methyl* meso-αα′-*dibromoglutarate*, m. p. 45°, was obtained by boiling the *meso*-acid in methyl alcohol containing 10% of sulphuric acid, while the dl-*ester*, obtained similarly from the *dl*-acid, forms an oil, b. p. 143—145°/10 mm. By heating the dibromoesters in methyl alcohol with sodium iodide, a solid *methyl* αα′-*di-iodoglutarate*, m. p. 75°, and a liquid ester were obtained.

Methyl and ethyl dibromoglutarates were condensed with the sodium derivatives of malonic, cyanoacetic, benzoylacetic, and acetoacetic esters. In each case a *cyclo*butane ester (I) and a bromo*cyclo*propane ester (II) were formed :

(I.) $CH_2<\begin{matrix}CH{\cdot}CO_2Et(Me)\\ >CR{\cdot}CO_2Et(Me)\\ CH{\cdot}CO_2Et(Me)\end{matrix}$ (R=CO_2Et, CN, CO·Ph, CO·Me)

$CH_2<\begin{matrix}CH{\cdot}CO_2Et(Me)\\ CBr{\cdot}CO_2Et(Me)\end{matrix}$ (II.) $CH_2<\begin{matrix}C(CO_2Et){\cdot}CO\\ C(CO_2Et){\cdot}CH{\cdot}CO_2Et\end{matrix}$ (III.)

In the case of sodiomalonic ester, the compound II further condenses to the sodium derivative of ethyl keto*dicyclo*pentanetricarboxylate (III). The *cyclo*butane ester predominates (yield 70—80% in one case) when the condensation is carried out in absence of alcohol, *e.g.*, in benzene. *Ethyl bromocyclopropanedicarboxylate* on hydrolysis yields 1-*bromocyclopropane*-1 : 2-*dicarboxylic acid*, m. p. 175° (*aniline* salt, m. p. 132°). *Ethyl* cyclo*butane*-1 : 2 : 2 : 3-*tetracarboxylate* is an oil, b. p. 195—198°/12 mm. *Methyl* cyclo*butanetetracarboxylate* exists in a solid, m. p. 78°, and a liquid, b. p. 193—195°/15 mm., form. Pure *meso*- and *dl*-isomerides of methyl dibromoglutarate, separately condensed in benzene solution with methyl malonate, gave in each case a mixture of the solid and liquid forms of the *cyclo*butane ester, so that these condensations yield no evidence as to the configurations of the dibromoglutaric esters. A similar result was obtained in condensations with methyl cyanoacetate. Descriptions are given of *ethyl*-2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate*, b. p. 210—215°/20 mm.; *methyl* 2-*cyano*cyclo*butane*-1 : 2 : 3-*tricarboxylate*, solid form, m. p. 111—112°; liquid form, b. p. 185—190°/12 mm.; *ethyl* 2-*benzoyl*-cyclo*butane*-1 : 2 : 3-*tricarboxylate*, and *ethyl* 2-*acetyl*-cyclo*butane*-1 : 2 : 3-*tricarboxylate*, b. p. 195°/18 mm. Hydrolysis of *cyclo*butanetetracarboxylic esters yields a mixture of *cis*- and *trans*-*cyclo*butane-1 : 2 : 3-tricarboxylic acids (Goldsworthy and Perkin, J.C.S., 1914, **105**, 2665). The *trans*-form has been partly resolved into two optical enantiomorphs by crystallisation of the quinine salt.

A. Davidson.

Addition of cyanoacetic esters to esters of glutaconic and β-methylglutaconic acids. E. P. Kohler and G. H. Reid (J. Amer. Chem. Soc., 1925, **47**, 2803—2811).—Using carefully purified materials, methyl cyanoacetate condenses with dimethyl glutaconate in methyl alcohol in presence of just sufficient sodium methoxide to ensure alkalinity, with formation of the normal additive product (yield about 82%), which is converted, by the action of hydrochloric acid, into methanetriacetic acid (cf. Dreifuss and Ingold, J.C.S., 1923, **123**, 2967), of which the dianilic acid has m. p. 206° (cf. Ingold, *ibid.*, 1921, **119**, 352). The yield of condensation product is greatly reduced when Thorpe and Wood's procedure is followed (*ibid.*, 1913, **103**, 1597), or if the reactants are not carefully freed from water and acid. Under similar conditions, no reaction was observed between ethyl cyanoacetate and the ethyl esters of either of the isomeric β-methylglutaconic acids. Operating under the conditions of Thorpe and Wood (*loc. cit.*), a pale yellow liquid, b. p.

yields *bromomethanesulphonic acid* (*barium* salt $+H_2O$). On the other hand, when the barium or ammonium salt is heated at 160—190° with excess of base it suffers a profound decomposition. The potassium salt is quantitatively reduced in cold aqueous solution by potassium sulphite to give sulphoacetic acid.

G. M. BENNETT.

Reduction of aldehydes and ketones in the presence of platinum-black. M. FAILLEBIN (Ann. Chim., 1925, [x], **4**, 156—182).—The effect of impurities present in the catalyst on the products obtained by the catalytic reduction of aldehydes and ketones with platinum-black have been studied by the preparation of a pure platinum catalyst to which known amounts of iron, aluminium, and silica were added. The catalyst was prepared by the method of Loew (A., 1890, 453), the metallic impurity being introduced before the reduction of the chloroplatinic acid. The essential factors for the preparation of an active catalyst are that the reduction should proceed slowly, and be carried out at a low temperature by the slow addition of the alkali, and the precipitated platinum well washed and aërated. In the reduction of aliphatic ketones without a solvent, the use of a pure platinum catalyst favours the reduction of the carbonyl group to a methylene group, the hydrocarbon being the main or sole product. Thus acetone yields propane, methyl ethyl ketone yields butane and *sec.*-butyl alcohol, and methyl propyl ketone yields pentane. In aqueous solution, acetone also yields only the hydrocarbon when a platinum–silica catalyst is used. In all cases, the use of a platinum–iron catalyst (iron 5—10%) causes almost quantitative reduction to the secondary alcohol, no hydrocarbon being produced. In the reduction of ethyl acetoacetate, either without solvent or in ether or *n*-hexane solution, a pure platinum catalyst yields only ethyl butyrate, whilst with a platinum–iron catalyst quantitative reduction to ethyl β-hydroxybutyrate occurs. A platinum–aluminium catalyst gave similar results, only a trace of ethyl butyrate being obtained, but a platinum–silica catalyst yielded both reduction products, its action being intermediate between that of the pure platinum and the platinum–iron catalysts. In alcoholic solution, however, with a pure platinum catalyst comparable yields of the two reduction products were obtained, this solvent favouring the production of the hydroxymethylene rather than the methylene group. Ethyl β-hydroxybutyrate is not an intermediate in the reduction of ethyl acetoacetate to ethyl butyrate, since it is not reduced by the platinum catalyst in ether or ethyl acetate solutions.

J. W. BAKER.

Hydrogenation of aldehydes and ketones in the presence of platinum-black. Hydroxy-substituted styryl methyl ketones. M. FAILLEBIN (Ann Chim., 1925, [x], **4**, 410—496).—The use of pure platinum-black and of platinum-black containing iron, aluminium, or silica (cf. preceding abstract) has been extended to the catalytic reduction of a large number of ketones and aldehydes of the type R·CH:CH·CO·CH_3 and R·CHO, where R is a substituted phenyl group. In general, subsequent to the reduction to the corresponding saturated ketone which is the primary reaction, the use of a platinum–iron catalyst causes quantitative reduction of the carbonyl group to a secondary alcoholic group, whilst with a pure platinum catalyst it is reduced to a methylene group, followed by deep-seated reduction in the benzene nucleus. Reduction of a methoxy-group attached to the nucleus also occurs in this case, but only in accordance with the scheme R·OMe $\longrightarrow$ RH+Me·OH, the benzene nucleus being always simultaneously reduced to a *cyclo*hexane ring. The differential effect of the various catalysts is also observed in the reduction of aldehydes, but is less sharply defined, the platinum–iron catalyst giving a quantitative yield of the secondary alcohol, whilst pure platinum causes incomplete reduction to the hydrocarbon, the action of the two catalysts being more similar with aromatic aldehydes. A summary of the reductions effected, usually in acetic acid or ethyl acetate solution, is as follows: *o*-methoxystyryl methyl ketone on reduction with a fatigued catalyst (the action being very rapid) yields β-o-*methoxyphenylethyl methyl ketone*, b. p. 147°/10 mm., 81°/0·16 mm., n_D^{18} 1·5215, d^{18} 1·050, which on reduction with a platinum–iron catalyst yields δ-o-*methoxyphenylbutan*-β-*ol*, b. p. 144°/13 mm., 90—91°/0·5 mm., n_D^{18} 1·5245, d^{18} 1·044 (*benzoate*, b. p. 212°/19 mm., 163°/0·3 mm.), whilst a pure platinum catalyst yields δ-*cyclo*hexylbutan-β-ol (main product), δ-2-*methoxy*cyclo*hexylbutan*-β-*ol*, b. p. 73°/0·16 mm., $n_D^{20·5}$ 1·4625, $d^{20·5}$ 0·970 (*acetate*, b. p. 133·5—134°/9 mm., $n_D^{21·5}$ 1·4540, $d^{21·5}$ 0·972), δ-*cyclo*hexyl-*n*-butane, δ-*o*-methoxyphenylbutan-β-ol, and possibly δ-2-methoxy*cyclo*hexyl-*n*-butane; *p*-methoxystyryl methyl ketone yields β-*p*-methoxyphenylethyl methyl ketone, which with a platinum–iron catalyst yields δ-p-*methoxyphenylbutan*-β-*ol*, b. p. 107°/0·5 mm., n_D^{16} 1·5249, d^{16} 1·042 (*acetate*, b. p. 160°/14 mm., 104°/0·25 mm., n_D^{21} 1·4956, d^{21} 1·0322; *benzoate*, b. p. 172°/0·3 mm., n_D^{20} 1·5427, d^{28} 1·080), whilst with a pure platinum catalyst it yields, in addition, δ-*cyclo*hexyl-*n*-butane, δ-4-*methoxy*cyclo*hexyl*-n-*butane*, b. p. 47°/0·25 mm., n_D^{19} 1·4645, d^{19} 0·907, (?)*p*-methoxyphenyl-*n*-butane, δ-*cyclo*hexylbutan-β-ol, δ-4-*methoxy*cyclo*hexylbutan*-β-*ol*, b. p. 84°/0·25 mm., n_D^{17} 1·4635, d^{17} 0·956 (*benzoate*, b. p. 207°/9 mm., 150°/0·25 mm., n_D^{18} 1·5101, d^{18} 1·052). Reduction with a platinum–aluminium catalyst yields δ-*p*-methoxyphenylbutan-β-ol (60%) together with the products obtained when platinum is employed, and, in addition, the hydrocarbon δ-*p*-methoxyphenyl-*n*-butane. Reduction of the δ-*p*-methoxyphenylbutan-β-ol yields only the corresponding δ-*cyclo*hexyl and δ-4-methoxy*cyclo*hexyl alcohols, and this compound cannot, therefore, be an intermediate product in the reduction of the original ketone with a pure platinum catalyst. Reduction of 4-hydroxy-3-methoxystyryl methyl ketone yields β-4-hydroxy-3-methoxyphenylethyl methyl ketone (zingerone), which on reduction with a platinum–iron catalyst gives δ-4-*hydroxy*-3-*methoxyphenylbutan*-β-*ol*, b. p. 192°/15 mm., 138°/0·25 mm., n_D^{17} 1·5431, d^{17} 1·135 (*diacetate*, m. p. 46°, b. p. 143°/0·25 mm., n_D^{20} 1·5000, d^{20} 1·121; *benzoyl*-derivative, m. p. 84°; b. p. 198°/0·25 mm.); 3 : 4-dimethoxystyryl methyl ketone on reduction yields β-3 : 4-dimethoxyphenylethyl methyl ketone, which, reduced

with a platinum–iron catalyst, yields δ-3 : 4-*dimethoxyphenylbutan*-β-*ol*, b. p. 125°/0·2 mm., n_D^{18} 1·5316, d^{18} 1·095 (*acetate*, b. p. 132°/0·3 mm., n_D^{18} 1·509, d^{18} 1·086). Reduction of piperonal ketone (cf. Vavon and Faillebin, A., 1919, i, 447) with a platinum–iron catalyst yields δ-3 : 4-*methylenedioxyphenylbutan*-β-*ol*, b. p. 168°/10 mm., 120°/0·3 mm., n_D^{21} 1·5340, d^{21} 1·146 (*acetate*, b. p. 125°/0·5 mm., n_D^{20} 1·5104, d^{20} 1·134; *benzoate*, b. p. 245°/13 mm., $n_D^{21\cdot5}$ 1·5550, $d^{21\cdot5}$ 1·170), but with a pure platinum catalyst reduction is difficult, less than 1 mol. of hydrogen being taken up, and no definite products could be isolated. By comparative reduction experiments on the white and yellow forms of piperonal ketone (cf. Haber, A., 1891, 704) the author's view that the yellow form is merely piperonal ketone contaminated with dipiperonal ketone (cf. Vavon and Faillebin, *loc. cit.*) is confirmed. In exception to the general behaviour, the reduction of acetophenone with a platinum–iron catalyst yields a large amount of the hydrocarbon, ethylbenzene, whilst *p*-benzoquinone is reduced to quinol. *iso*Valeraldehyde and heptaldehyde with a platinum catalyst yield, respectively, *n*-pentane and *iso*amyl alcohol, and *n*-heptane and *n*-heptyl alcohol, but with a platinum–iron catalyst only the alcohol is obtained. Reduction of acetaldehyde is slow, ethyl alcohol being the only product. Benzaldehyde yields toluene, methyl*cyclo*hexane, and benzyl alcohol when a platinum catalyst is employed, and a quantitative yield of the alcohol when iron, aluminium, or iridium is present in the catalyst. Reduction of the enolic forms of ethyl acetoacetate, ethyl oxalacetate, and acetylacetone were studied, the products obtained being the same as those produced from the ketonic modifications. In the case of acetylacetone, reduction with a platinum–iron catalyst yields mainly the dihydroglycol, no acetylacetonate of ferrous iron being formed, but with a platinum–aluminium catalyst the same products are obtained as with a pure platinum catalyst (mainly *n*-pentane), the aluminium being removed as its acetylacetonate. Two alternative theories to explain the differential action of the catalysts are discussed. J. W. Baker.

Acetone–*iso*acetone equilibrium. W. L. Evans and W. D. Nicoll (J. Amer. Chem. Soc., 1925, **47**, 2789—2792).—When freshly precipitated mercuric oxide is treated with acetone in presence of potassium hydroxide, it is converted into the *compound* $(Me{\cdot}CO{\cdot}CH_2)_2Hg,2HgO$, the formation of which was used to investigate the enolisation of acetone to *iso*acetone in presence of alkali (cf. Evans and Looker, A., 1922, i, 102). The results obtained indicate that the enolisation of acetone is entirely analogous to that of ethyl acetoacetate and similar compounds. In presence of 0·0369*M*-alkali, 26·5% of the acetone is present as the enolic form. Further increase in alkali concentration does not increase the enolisation, for which a logarithmic relationship holds from the above concentration of alkali down to 0·0021*M*.

F. G. Willson.

Partial hydrolysis of sucrosephosphoric acid to *d*-lævulose and dextrosephosphoric acid. J. Hatano (Biochem. Z., 1925, **159**, 175—178).—Sucrosemonophosphoric acid is warmed with dilute sulphuric acid until the first traces of free phosphoric acid appear. Dextrosemonophosphoric acid is isolated as the barium salt and lævulose demonstrated in the residue. E. C. Smith.

Preparation of raffinose from cotton-seed meal. D. T. Englis, R. T. Decker, and A. B. Adams (J. Amer. Chem. Soc., 1925, **47**, 2724—2726).—See B., 1925, 1004.

Sugars. VI. H. Kiliani (Ber., 1925, **58**, [*B*], 2344—2362; cf. A., 1923, i, 1059).—Although the sodium salt of *d*-saccharolactone crystallises very readily when pure and is sparingly soluble in cold water, it is not suitable for the isolation of *d*-saccharic acid from the products obtained by the action of nitric acid on dextrose or starch, since its separation is readily inhibited by the presence of foreign matter. It is remarkable that the sodium salt readily separates when a solution of *d*-saccharolactone in water is treated with crystalline sodium acetate, but not when it is neutralised by sodium hydroxide. The sodium salt is not reduced by aluminium or sodium amalgam to glycuronic acid; the free lactone is, however, reduced in acid solution to glycuronolactone (yield 30%).

For the preparation of *d*-saccharic acid (cf. Kiliani, *loc. cit.*), rice starch is allowed to remain in contact with nitric acid (20%) in proportion of 1 g. to 3·4 c.c. for 12 hrs., after which the temperature is gradually raised in a manner depending on the weight of starch taken. The product is finally heated for several hrs. at 100°, after which the oxalic acid is removed by calcium carbonate. The residual acid solution is neutralised completely with potassium hydroxide, concentrated at 50°, and treated with so much acetic acid that potassium hydrogen *d*-saccharate is formed. The latter is crystallised if necessary from water and transformed successively into the normal potassium and calcium salt from which *d*-saccharomonolactone is obtained by the aid of oxalic acid. The lactone does not readily pass into *d*-saccharic acid in aqueous solution at 20·7°.

The following method is very suitable for the preparation of *l*-arabonic acid from cherry gum (cf. Neuberg and Hirschberg, A., 1910, i, 653). The gum is hydrolysed by 2% hydrochloric acid at 100° and the filtered solution is oxidised with bromine. After neutralisation of the acid with freshly slaked lime, the solution is immediately evaporated until a solid skin is formed. Calcium *l*-arabonate separates very slowly from the cold solution, crystallisation usually requiring several weeks for completion. The crude salt is very easily recrystallised from water, and the pure salt readily gives *l*-arabonolactone after treatment with oxalic acid. Brucine *l*-arabonate has $4H_2O$ (cf. Nef, A., 1908, i, 5).

For the preparation of *l*-mannonic and *l*-gluconic acids (cf. Kiliani, A., 1922, i, 223), a mixture of *l*-arabinose and hydrocyanic acid is added to a very concentrated barium hydroxide solution contained in a dish immersed in briskly boiling water. The product is evaporated as rapidly as possible on the water-bath to a thick syrup, and is subsequently well stirred with a spatula until ammonia almost ceases to be evolved. The barium is removed with

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the necessary amount of sulphuric acid, after which the solution is evaporated to a syrup and worked up for *l*-mannonolactone and brucine *l*-gluconate as previously described. The latter salt is more readily crystallised from a very little water than from 85% alcohol. Contrary to previous observations (*loc. cit.*), it contains an appreciable proportion of brucine *l*-mannonate. Separation of the acids is completely effected by transforming the brucine into the barium salts, since barium *l*-gluconate crystallises readily, whereas barium *l*-mannonate does not. Pure brucine *l*-gluconate has m. p. 167—168°.

The sparing solubility of normal sodium mucate in water (cf. Khotinska and Epifanova, A., 1925, i, 783) has been observed previously by the author; the statement that the anhydrous salt is insoluble in boiling water is incorrect. Calcium mucate and calcium galactonate form a crystalline double *salt*, $[CH{\cdot}OH]_4(CO_2)_2Ca(C_6H_{11}O_7)_2,8H_2O$. The probability that Kiliani's "oxygluconic acid" is identical with β-ketogluconic acid obtained by the action of barium hypobromite on dextrose and fermented to *d*-arabinose has been suggested by Hönig and Tempus (A., 1924, i, 712). The calcium salt of Kiliani's acid does not yield arabinose when fermented with pure yeast (cf. van Niel and Visser 't Hooft, A., 1925, i, 1237).

The preparation of β-glucoheptonolactone is greatly simplified if the mother-liquor from which the α-compound has separated is treated with only 2—2·5 parts of water and the solution is saturated with brucine at 35°. The brucine salt is converted into the barium salt, and thence into β-glucoheptonolactone, which crystallises readily.

Acetyl-d-galactonic acid, $C_6H_{11}O_6Ac$, m. p. 160° after softening, is obtained readily by the action of glacial acetic acid and nitric acid (55%) on *d*-galactonic acid at 21°; hydrochloric may replace nitric acid but with less advantage. *d*-Gluconolactone and α-glucoheptonolactone are not acetylated under these conditions.

The suggested applicability of semicarbazide to the removal of "uronic acids" from the products of the oxidation of sugars by nitric acid (A., 1923, i, 1059) has proved illusory. Further examination shows that the "semicarbazone of *l*-galacturonolactone" is the *semicarbazide* of unoxidised *d*-galactonic acid. Similarly, the "semicarbazone of *l*-mannuronolactone" is proved to be the *monosemicarbazide* of *l*-mannosaccharodilactone. The identity of the products derived from α-glucoheptonolactone and *iso*saccharin could not be established definitely. The above discovery sensibly diminishes the prospects of obtaining "uronic acids" by the bromine oxidation method, which, according to the results of experiments on *d*-galactonic and similar acids, does not appear very suitable for the purpose.

During examination of the possibility of using hydrazine and substituted hydrazines for the isolation of "uronic acids," the following observations have been made. Glucurolactone and *p*-nitrophenylhydrazine in cold, acetic acid solution readily yield the corresponding hydrazone, m. p. 224°. *l-Mannohepturonolactone-p-bromophenylhydrazone*, m. p. 165° (decomp.) after darkening at 145°, and the unstable *l*-mannohepturonolactone-*o*-tolylhydrazone are prepared similarly. *l*-Mannonolactone, *d*-galactonic acid, and *l*-arabonolactone readily yield crystalline hydrazides when treated with hydrazine hydrate in cold aqueous solution, but this is not the case with *d*-gluconic, α- and β-glucoheptonolactones, ketorhamnonolactone, *d*-saccharic, and pentahydroxypimelic acids. *l*-Mannosaccharodilactone gives a product, m. p. 182° (decomp.), whereas with *l*-mannohepturonolactone the course of the change has not been elucidated completely.

The reducing action of *l*-mannosaccharodilactone towards Fehling's solution and iodine and sodium hydroxide has been further examined. The suggestion is advanced that the product is not homogeneous in spite of its crystalline nature.

H. Wren.

Hexahexosan and trihexosan. P. Castan and A. Pictet (Helv. Chim. Acta, 1925, **8**, 946—948; cf. A., 1924, i, 1288).—Hexahexosan is purified by fractional precipitation of its aqueous solution by alcohol. The presence of higher polymerides causes the colour produced with iodine to be violet instead of a bright red. If the iodine is added gradually, or if the mixture and iodine are heated until colourless and then cooled, the colour appears first blue, then violet, and then red, showing that the substance of higher mol. wt. forms iodine complexes of greater stability. Hexahexosan is found cryoscopically to have the formula $(C_6H_{10}O_5)_6$; it has $[\alpha]_D$ +173·2° in water. Acetyl bromide acts on it with production of hepta-acetylmaltose and only a trace of dextrose, as with starch. It is attacked by amylase and less readily by emulsin to yield maltose. Trihexosan is hydrolysed at 100° by 5% sulphuric acid to dextrose (96·3% of the theoretical yield). Amylase acts on it slowly, producing maltose. Acetyl bromide yields hepta-acetylmaltose and dextrose.

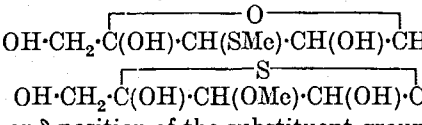
G. M. Bennett.

Dihexosan and tetrahexosan. A. Pictet and R. Salzmann (Helv. Chim. Acta, 1925, **8**, 948—949; cf. A., 1924, i, 1288).—Emulsin acts on trihexosan to give dextrose and *dihexosan*, $[\alpha]_D$ in water +135·8°. By the action of concentrated hydrochloric acid or barley amylase it is converted into maltose. Acetylation yields β-octa-acetylmaltose, m. p. 155°. Dihexosan is therefore an anhydride of maltose. From the products of the action of emulsin on trihexosan there has also been isolated a crystalline *tetrahexosan*, $(C_6H_{10}O_5)_4$, m. p. 260°, $[\alpha]_D$ +162·6° in water, which is considered to be formed by polymerisation of the dihexosan under the influence of the enzyme. Amylase slowly attacks it, producing maltose.

G. M. Bennett.

Thio-sugar from yeast. P. A. Levene and H. Sobotka (J. Biol. Chem., 1925, **65**, 551—554).—The sugar obtained on hydrolysis of the adenine nucleoside isolated from yeast by Mandel and Dunham (A., 1912, i, 320) and Levene (A., 1924, i, 802) has proved to be identical with the sugar containing sulphur recently described by Suzuki and others (A., 1925, i, 338). The substance forms a *p*-bromophenylosazone even after exposure for 96 hrs. to excess of

bromine; it cannot therefore be an aldose nor can it contain a thiol-group; a Zeisel determination indicates the presence of one methoxy- or methylthiol-group, and with acetic anhydride in pyridine it gives a *triacetyl* compound, b. p. 170°/0·1 mm. The formula indicated by these results is either



$$OH\cdot CH_2\cdot C(OH)\cdot CH(SMe)\cdot CH(OH)\cdot CH_2 \text{ or } OH\cdot CH_2\cdot C(OH)\cdot CH(OMe)\cdot CH(OH)\cdot CH_2,$$

the γ- or δ-position of the substituent group being still open to question. C. R. HARINGTON.

Distribution of lignin in wood. G. J. RITTER (Ind. Eng. Chem., 1925, **17**, 1194—1197).—See B., 1925, 985.

Synthesis of *N*-methylputrescine and of putrescine. H. W. DUDLEY and W. V. THORPE (Biochem. J., 1925, **19**, 845—849).—*Benzoyl-δ-bromo-* and *benzoyl-δ-iodo-butylamine* were prepared by benzoylating the amine halides. The iodo-compound was then converted into *monobenzoyl-N-methylputrescine*, $NHBz\cdot[CH_2]_4\cdot NHMe$, by boiling with methylamine for 2 hrs. From this compound *N-methylputrescine dihydrochloride* was obtained by heating at 130° for 8 hrs. with concentrated hydrochloric acid. *N-Methylputrescine* yields a *dipicrate*, m. p. 229—230·5° (corr.), *chloroaurate*, m. p. 192° (corr.) after softening, decomp. 215° (corr.), *chloroplatinate*, decomp. 230·5° (corr.). The *picrolonate*, decomp. 254—265°, *mercurichloride*, m. p. 149° (corr.), and the *dibenzoyl* compound, m. p. 115·5° (corr.), were also obtained. *Monobenzoylputrescine* was obtained by heating benzoyl-δ-iodobutylamine with ammonia and alcohol in a sealed tube. Putrescine dihydrochloride was obtained in a similar manner. Mono- or di-benzoylputrescine with concentrated hydrochloric acid in a sealed tube. *Di-[δ-benzamidobutyl]amine hydrochloride*, $C_{22}H_{30}O_2N_3Cl$, prisms, m. p. 233° (corr.), was obtained as a by-product in the process of preparation of monobenzoylputrescine. From this compound the monobenzoyl *base* and *di-δ-aminobutylamine hydrochloride* were obtained. The *tripicrate*,

$$C_8H_{21}N_3,3C_6H_3O_7N_3,$$

m. p. 255° (corr. decomp.), and the *chloroaurate*, m. p. 209° (corr. decomp.), were prepared from the base. S. S. ZILVA.

ββ′β″-Triaminotriethylamine and its complex metallic compounds. F. G. MANN and (SIR) W. J. POPE (Proc. Roy. Soc., 1925, **A**, **109**, 444—458; cf. A., 1924, i, 1049).—ββ′β″-Triaminotriethylamine, unlike αβγ-triaminopropane, and contrary to expectation, acts in all cases, for co-ordination purposes, as a tetrabasic amine in spite of the great diminution in the basic properties of the tertiary amino-radical, brought about by the presence of the three substituting groups. Such compounds as the following have been obtained, $[Cl_2PtN(CH_2\cdot CH_2\cdot NH_2)_3]Cl_2$, and $[PtN(CH_2\cdot CH_2\cdot NH_2)_3]I_2$. The first of these compounds (containing quadrivalent platinum) is easily represented by the Werner models of spatial configuration. The second (containing bivalent platinum) cannot be reconciled with these models so readily, for obvious steric reasons, unless the mol. wt. is doubled. This point has not yet been tested experimentally.

The following compounds are described: *triaminotriethylamine monohydrochloride dihydriodide*, $N(C_2H_4\cdot NH_2)_3,HCl,2HI$; *tricarbamidotriethylamine*, m. p. 167—168° after softening at 140°; the *chloroaurates*, $N(C_2H_4\cdot NH_2)_3,3AuCl_3,3HCl$ and $N(C_2H_4\cdot NH_2)_3,2AuCl_3,4HCl$, m. p. 187—189° (decomp.); *mercurichloride*, $N(C_2H_4\cdot NH_2)_3,5HgCl_2,3HCl$, m. p. 202—204° (decomp.); *chlororhodiates*, $2N(C_2H_4\cdot NH_2)_3,3RhCl_2,6HCl,6H_2O$, m. p. 280° after softening at 257°, and $N(C_2H_4\cdot NH_2)_3,2RhCl_2,4HCl$; *chlororutheniate*, $N(C_2H_4\cdot NH_2)_3,2RuCl_3,4HCl,2H_2O$; the *platinum* salts, $2N(C_2H_4\cdot NH_2)_3,3PtCl_2,6HCl,3H_2O$, $2N(C_2H_4\cdot NH_2)_3,3PtCl_4,6HCl,10H_2O$, m. p. (anhydrous) 231—232° (decomp.) after darkening at 225°; $N(C_2H_4\cdot NH_2)_3,2PtCl_4,4HCl,10H_2O$, m. p. (anhydrous) 271—273° (decomp.) after darkening at 260°. The following metallic, co-ordinated *derivatives* of triaminotriethylamine are described [*tren*= $N(C_2H_4\cdot NH_2)_3$]: $[Cl_2Pt\ tren]Cl_2$, m. p. 263—266° (decomp.) after darkening at 240°; $[Cl_2Pt\ tren]I_2$, decomp. 233—237° after darkening at 225°; $[Cl_2Pt\ tren]PtCl_6,2H_2O$, m. p. 287—288° (decomp.) after darkening at 275°; $[Cl_2Pt\ tren]Pt(CN)_4$, which darkens at 225° but does not melt below 300°; $[Pt\ tren]PtCl_4$, m. p. 270—275° (decomp.) after shrinking at 265°; $[Pt\ tren]I_2$, m. p. 267—269° (decomp.) after darkening at 260°. S. BARRATT.

Nitration of hexamethylenetetramine. G. C. HALE (J. Amer. Chem. Soc., 1925, **47**, 2754—2763).—*Hexamethylenetetramine dinitrate*, m. p. 165°, is precipitated when nitric acid (*d* 1·42) is added, at 0°, to a solution of hexamethylenetetramine (1 part) in water (3 parts). When added to concentrated nitric acid, the dinitrate is converted into *cyclo*trimethylenetrinitroamine (cf. Henning, U.S.P. 104280, 1899; Herz, B., 1922, 158), best yields being obtained by the use of nitric acid of 90—95%, at 30°. Direct nitration of hexamethylenetetramine to the trinitroamine (cf. Herz, *loc. cit.*) gives best results when the base (1 part) is added to 92% nitric acid (11 parts) at 30°, and the solution cooled to 0° before dilution, but yields higher than 75% are not obtainable, owing to hydrolysis of the hexamethylenetetramine to formaldehyde and ammonia, and production of the above dinitrate. F. G. WILLSON.

Steric series. VII. Configuration of aspartic acid. K. FREUDENBERG and A. NOË (Ber., 1925, **58**, [*B*], 2399—2408; cf. A., 1925, i, 1275).—The configurative relationship of *l*(+)-lactic acid to natural alanine and natural malic acid has been established, as also that of natural alanine to natural aspartic acid, so that it has been shown indirectly that the natural forms of malic and aspartic acids have the same steric arrangement. This is confirmed by direct comparison of derivatives of these acids. It is remarkable that similar behaviour is exhibited

only at a somewhat elevated temperature. With increasing temperature derivatives of malic acid have their specific rotation displaced towards the left, this behaviour being characteristic of α-hydroxy-acids of the *l*-series. With aspartic acid, the influence of temperature is irregular and frequently unusually pronounced, probably owing to association. For the same reason, the method of obtaining the specific rotation of the homogeneous substance by extrapolation from the specific rotation of its solutions of gradually increasing concentration is only partly successful with derivatives of aspartic acid. In general, the authors are of the opinion that comparisons of the specific rotations of substances can be made only with dissolved or supercooled materials if they exhibit the closest chemical similarity. Clough's observation (J.C.S., 1918, **113**, 526) that ethyl esters of α-hydroxy-acids belonging to the *d*-series are more highly dextrorotatory than the methyl esters cannot be immediately extended to α-amino-acids.

The biological significance of the doctrines of configuration is discussed at length. The direct production of *l*-malic acid by oxidation of dextrose is inconceivable, since *d*-malic acid must result if the configuration remains intact. The probable precursor of malic acid is oxalacetic acid, from which it is derived by asymmetric hydrogenation. The suggested course of the change is dextrose → saccharic acid → ketipinic acid (cf. Franzen and Schmitt, A., 1925, i, 231), and thence by benzilic acid transformation to citric acid, and by acid fission and reduction to malic acid, whereby the general simultaneous occurrence of the two acids is explained. A second argument in favour of the view that oxalacetic acid is the precursor of malic and aspartic acids is based on the configurational similarity of lactic acid formed by hydrogenation of pyruvic acid in the organism with alanine produced from the same substance in the presence of ammonia. The steric similarity of both pairs renders it probable that they are formed in a similar manner from ketonic substances.

The following new compounds are incidentally described: *ethyl cinnamoyl*-l-*malate*, b. p. 195°/2 mm.; *ethyl formyl*-l-*malate*, b. p. 120—121°/2 mm.; *ethyl* β-*phenylpropionyl*-l-*malate*, b. p. 185—186°/3 mm.; *ethyl ethanesulphonyl*-l-*malate*, b. p. 154—155°/0·5 mm.; *methyl ethanesulphonyl*-l-*malate*, b. p. 167—168°/1 mm.; *ethyl* p-*toluenesulphonyl*-l-*malate*, b. p. 197—198°/1 mm.; *acetyl*-l-*maldi-methylanilide*, m. p. 116°; *acetyl*-l-*maldianilide*, m. p. 177°; *ethyl cinnamoyl*-l-*aspartate*, m. p. 72°; *ethyl formyl*-l-*aspartate*, b. p. 145—146°/1 mm.; *ethyl* β-*phenylpropionyl*-l-*aspartate*, b. p. 203°/2 mm., m. p. 34°; *ethyl acetyl*-l-*aspartate*, b. p. 183°/20 mm., m. p. 31°; *methyl acetyl*-l-*aspartate*, b. p. 154—155°/15 mm., m. p. 65°; *ethyl* n-*heptoyl*-l-*aspartate*, m. p. 29°; *ethyl ethanesulphonyl*-l-*aspartate*, m. p. 50°; *ethyl* p-*toluenesulphonyl*-l-*aspartate*, m. p. 79°; p-*toluenesulphonyl*-l-*aspartic acid*, m. p. 139—140°; p-*toluenesulphonyl*-l-*aspartyl chloride*, m. p. 96—97°. The specific rotations of these compounds in the liquid state and in solution are recorded for the wave-lengths 637, 578, 546, and 436 at about 20° and 100°.

The paper concludes with a reply to the recent criticisms of Kuhn and Ebel (A., 1925, i, 1378).

H. WREN.

Catalytic decomposition of amides. A. MAILHE (Bull. Soc. chim., 1925, [iv], **37**, 1394—1397).—Amides undergo catalytic decomposition when passed over finely divided nickel at 400—440°, yielding carbon monoxide and an amine containing one carbon atom less than the original amide. In the case of aromatic amides, such as benzamide, the amine is stable and aniline is the principal liquid produced. Traces of benzene are also formed, whilst the gaseous products in this case consist of carbon dioxide 30%, carbon monoxide 25%, and hydrogen 35%. With the aliphatic amides, the amine primarily produced undergoes further catalytic decomposition on the nickel (cf. A., 1924, i, 623), yielding a nitrile, the next lower homologue to that produced in catalytic dehydration (Boehner and Ward, A., 1917, i, 11). Thus valeramide at 430° yields *iso*butyronitrile and a gaseous mixture containing carbon dioxide 12%, carbon monoxide 31%, hydrogen 45%, and 12% of olefines, together with some ammonia, the latter resulting from the decomposition of the amine. Propionamide at 430° similarly yields a gas containing ammonia, carbon dioxide 9%, carbon monoxide 31%, hydrogen 51%, and 9% of olefines, whilst the liquid product consists of acetonitrile. Acetamide is similarly decomposed into ammonia, hydrogen cyanide, carbon dioxide (5% at 440°), carbon monoxide (15%), and hydrogen with deposition of carbon.

R. BRIGHTMAN.

Reaction between sodium hypobromite and carbamide. M. B. DONALD (J.C.S., 1925, **127**, 2255—2259).—The reaction between carbamide and hypobromite solutions, prepared by bromination of sodium hydroxide in varying degrees up to 100%, has been studied both by measurement of the evolved gas and by titration of the excess hypobromite with thiosulphate. The nitrogen deficit becomes greater as the percentage bromination increases until the hydroxide is 75% brominated. For brominations above 75%, the nitrogen deficit still increases, but the thiosulphate figure indicates that the hypobromite is being used up in a slow side oxidation, so that for 80% hypobromite and upwards the thiosulphate required after 30 min. is about equivalent to the carbamide taken. With completely brominated sodium hydroxide, however, there is no gas evolution and no hypobromite is used up. The secondary oxidation is attributed to formation of sodium cyanate (cf. Fenton, J.C.S., 1878, **33**, 300; Lescœur, A., 1920, ii, 201; Margosches and Rose, A., 1923, ii, 590). This is increasingly formed as the ratio of hypobromite to hydroxide increases until 75% bromination is reached, when the cyanate is slowly oxidised, an action which, however, does not take place in absence of carbamide. The use of 10*N*-sodium hydroxide solutions for the determination of carbamide gasometrically leads to inaccurate results.

A. DAVIDSON.

New hydrolysis product from elastin. R. ENGELAND (Biochem. J., 1925, **19**, 850—852).—Hydrolysed elastin is precipitated with 50% phospho-

tungstic acid, and the precipitate treated with lead hydroxide and then decomposed with barium hydroxide. After removing traces of lead and barium and evaporating in a vacuum to a syrup, the preparation is boiled with copper hydroxide and filtered. The filtrate is then concentrated and methyl alcohol is added. The *copper* salt, $C_{16}H_{22}O_5N_2Cu$, separates and, when decomposed with hydrogen sulphide, yields *hyphasmine*, $C_{16}H_{24}O_5N_2$. This compound gives a pink colour with Millon's reagent. It is discoloured at 200° and softens at about 220°. S. S. ZILVA.

Double sulphates and chromates of guanidine and bi- and ter-valent metals. G. CANNERI (Gazzetta, 1925, **55**, 611—615).—Double *guanidine sulphates* of the type $(CH_5N_3)_2,H_2SO_4,XSO_4,6H_2O$ have been prepared, in which X = Mg, Zn, Cd, Fe, Ni, Co, Mn, Cu, UO_2; mixed crystals of the zinc and nickel compounds were also prepared. *Magnesium guanidine chromate*, $(CH_5N_3)_2,H_2CrO_4,MgCrO_4,6H_2O$, is isomorphous with the corresponding sulphate. *Chromium guanidine alum*,

$$(CH_5N_3)_2,H_2SO_4,Cr_2(SO_4)_3,12H_2O,$$

forms mixed crystals with the corresponding aluminium guanidine alum; *ferric guanidine alum* and *vanadium guanidine alum* are described.

T. H. POPE.

Action of nitriles on organo-magnesium compounds. Chloroacetonitrile. L. MATHUS (Bull. Soc. chim. Belg., 1925, **34**, 285—289).—α-Chlorobutyronitrile reacts with magnesium ethyl bromide, forming an imine (De Booseré, A., 1923, i, 311), but with chloroacetonitrile, the reaction is complicated by the formation of polymerides, from which definite compounds could not be isolated. Polymerisation and hydrocarbon formation are more marked in the case of magnesium alkyl halides than with magnesium phenyl bromide. From the reaction product of 1¼ mols. of the latter and 1 mol. of chloroacetonitrile, the only products isolated were diphenyl, m. p. 70—71°, and chloroacetophenone, m. p. 58°, b. p. 140—143°/15 mm. (yield 1½%), the normal product of the Blaise reaction. The latter compound, when distilled in a current of steam, yielded benzoyl carbinol, m. p. 72—73°; *semicarbazone*, m. p. 185°. The formation of diphenyl is explained on the assumption of the intermediate formation of the dinitrile of succinic acid, which could not be isolated on account of polymerisation. J. S. H. DAVIES.

Reduction of some aliphatic cyano-compounds. Reduction of cyanoacetylcarbamide. H. RUPE, A. METZGER, and H. VOGLER (Helv. Chim. Acta, 1925, **8**, 848—852).—Catalytic reduction of cyanoacetylcarbamide in aqueous solution at 60—70° yields uracil, which results from an internal condensation of the aldehyde produced by hydrolysis of the aldimine, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}NH$, the first product of the reduction. β-Keto-α-phenylbutyronitrile is reduced to benzyl methyl ketone, b. p. 98—100°/10 mm., and a little *γ-keto-β-phenylbutaldimine*, m. p. 96°. Propionitrile resists reduction and is recovered unchanged (cf. A., 1923, i, 1088). *n*-Valeronitrile gives a good yield of *di-n-amylamine*, b. p. 95—97°/12 mm. (*nitrosoamine*, *hydrochloride*, decomp. 275°, and *oxalate*, m. p. 210—211°, are described). G. M. BENNETT.

Mixed organo-aluminium compounds. Aluminium ethyl and diethyl iodide. V. GRIGNARD and R. L. JENKINS (Bull. Soc. chim., 1925, [iv], **37**, 1376—1385).—In the absence of oxygen and moisture, finely divided aluminium reacts readily with ethyl iodide. Solvents such as benzene, ether, or chloroform give less satisfactory results. Small quantities of ethane and ethylene are produced, but the main product is a mobile liquid, which decomposes below 300° under ordinary pressure, but on fractional distillation under reduced pressure yields aluminium diethyl iodide, $AlEt_2I$, b. p. 118—120°/4 mm., d_4^{27} 1·6091, and aluminium ethyl di-iodide, $AlEtI_2$, m. p. 35—37°, b. p. 158—160°/4 mm. Both compounds are spontaneously inflammable in air, and react violently with water, yielding ethane. Mol. wt. determinations indicate a double molecule. They dissolve in ether with liberation of heat, yielding the *etherates*, $AlEt_2I,0{\cdot}75Et_2O$, and $AlEtI_2,Et_2O$ (cf. Krause and Wendt, A., 1923, i, 289), which appear to be stable in dry air but react violently with water and are decomposed by alcohol. Neither compound reacts with carbon dioxide; with acetone, they yield mesityl oxide and more complex products, which were not examined. Benzaldehyde similarly gives complex condensation products of high mol. wt. Both compounds reduce mercuric chloride.

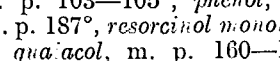
Distillation of the reaction product of aluminium and ethyl iodide at 285—300°/760 mm., yields a mixture of ethylene and ethane, the proportion of ethylene increasing as the decomposition proceeds, whilst in the final stages the saturated hydrocarbon produced differs from ethane. On similar distillation, the etherates yield a little ether, ethyl iodide, and at 90—110°, a colourless, inflammable liquid, containing iodine, which reacts vigorously with water. With ethyl bromide, aluminium similarly yields a colourless liquid, separated into two fractions, b. p. 118—120°/15—16 mm., and 121·5—124·5°/15—16 mm., the compositions of which agree only approximately with $AlEt_2Br$ and $AlEtBr_2$, respectively, possibly through the presence of $AlEt_3$. R. BRIGHTMAN.

Applications of thallium compounds in organic chemistry. II. Titrations. G. H. CHRISTIE and R. C. MENZIES (J.C.S., 1925, **127**, 2369—2373).—Thallous salts of organic acids have been prepared by titration of the acids with standard thallous hydroxide solution (cf. Menzies and Wilkins, A., 1924, i, 704). With tartaric acid, using four equivalents of thallous hydroxide, a tetrathallium tartrate is formed in which two of the thallium atoms are hydrolysable by carbon dioxide in aqueous solution. Attempts to prepare the corresponding tetrapotassium tartrate failed. β-Diketones and phenols also yield well-crystallised thallium salts, easily prepared pure by addition of a concentrated aqueous solution of thallous hydroxide to an alcoholic solution of the phenol etc. The thallium in these salts is hydrolysed by water and may be accurately determined by titration. The usefulness of both classes of thallium salts for synthetic purposes is indicated. The following salts are described: *Thallous fumarate*, m. p.

268° (decomp.); *thallous maleate*, m. p. 164—166°; *thallous succinate*, m. p. 246—248°; *thallous phthalate*, m. p. 268—270°; *thallous stearate*, m. p. 119°, *palmitate*, m. p. 115°, and *oleate*, m. p. 78—82° (these three compounds show double m. p. and appear to be anisotropic liquids between these points); thallous salts of *ethyl acetoacetate*, m. p. 91—92°, *benzoylacetone*, m. p. 103—105°, *phenol*, m. p. 231—235°, *m-cresol*, m. p. 187°, *resorcinol monomethyl ether*, m. p. 146—148°, *guaiacol*, m. p. 160—161°, α-naphthol, m. p. 180—190°, and vanillin, m. p. 193—201°.

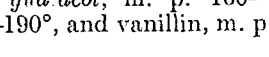
A. DAVIDSON.

Dicyclopentadienes. II. H. WIELAND and F. BERGEL [with K. SCHWARZ, R. SCHEPP, and L. FUHELMAN] (Annalen, 1925, **446**, 13—31; cf. A., 1906, i, 417).—Experimental difficulties make the direct oxidation of dicyclopentadiene very difficult to follow, but its simple derivatives behave normally. By the oxidation of the ketone,



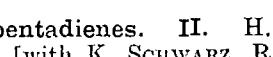
(I),

and of the glycol,



(II),

two different acids are obtained of the formula

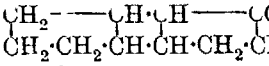


(III).

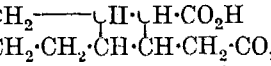
If the symmetrical formula for dicyclopentadiene is to be retained, these acids must be represented as *cis*- and *trans*-isomerides. Attempts at interconversion of the two acids or their esters met with little success, and the exact spatial representation is still in doubt.

Ketodihydrodicyclopentadiene, b. p. 102°/12 mm., exists in two forms, (*a*) m. p. 83—84°, and (*b*) a liquid, which are readily interconvertible. As no colour is obtained with ferric chloride, the possibility of keto-enolic tautomerism is rejected and two alternative explanations are given. The *semicarbazone*, m. p. 211°, *dibromide*, m. p. 142°, and *tribromo*-derivative, m. p. 186°, of this ketone are described. Reduction with palladium and hydrogen yields *ketotetrahydrodicyclopentadiene* (I), b. p. 100°/12 mm., which on oxidation with nitric acid yields the (?) trans-*acid* (III), m. p. 200°.

Dihydrodicyclopentadiene dibromide, m. p. 62·5°, yields the series: *acetate* of the *bromohydrin*, m. p. 83·5°; *glycoldiacetate*, b. p. 182—184°/20 mm.; cis-*glycol* (II), m. p. 80°; and the (?) cis-*acid* (III), m. p. 133·5° (*dimethyl* ester, b. p. 134—135°/13 mm.). *Dihydrodicyclopentadiene oxide*,



m. p. 91·5°, is hydrolysed to the trans-*glycol* (II), m. p. 118°, which yields the (?) *cis*-acid (III) on oxidation. Other substances described are: *dicyclopentadiene oxide*, m. p. 64°; *dicyclopentadiene glycol*, m. p. 120°; *dicyclopentadiene dioxide*, m. p. 165°; the *oxime of diethylaminoketodihydrodicyclopentadiene*, m. p. 96—97°; and a *substance*,



m. p. 201—202°.

R. W. WEST.

Action of sulphuryl azide on benzene. K. F. SCHMIDT (*Ber.*, 1925, **58**, [*B*], 2409—2412; cf. Curtius and Schmidt, A., 1922, i, 776).—The "pseudoaniline" formed by the action of sulphuryl azide on a large excess of benzene at 140° is identified as pyridine.

H. WREN.

Syntheses in the *p*-cymene series from *iso*propyl alcohol. I. Syntheses of *p*-cymene. L. BERT (Bull. Soc. chim., 1925, [iv], **37**, 1252—1270).—To confirm Widman's work (A., 1891, 686) on the constitution of *p*-cymene the author has attempted the synthesis using Grignard reagents. *p*-Bromotoluene was obtained in 12% yield by the action of methyl sulphate on magnesium *p*-bromophenyl bromide, and in 30% yield from *p*-toluidine by Sandmeyer's method, the Gattermann process giving a 27% yield. Magnesium *p*-tolyl bromide obtained from this, with *iso*propyl sulphate gives *p*-cymene in 10% yield. Similarly, cumene, obtained in 75% yield by the action of *iso*propyl bromide on benzene in the presence of aluminium chloride, is converted by Jacobsen's method (Ber., 1879, **12**, 430) into *p*-bromocumene (yield 83%), b. p. 111°/28 mm., 216—217°/729 mm., d_4^{21} 1·289, n_D^{21} 1·539, and the magnesium cumyl bromide obtained from this gives with methyl sulphate a 12% yield of *p*-cymene. A third synthesis was effected by treating cumene with trioxymethylene and hydrogen chloride in the presence of zinc chloride (cf. Blanc, A., 1923, i, 549), when *cuminyl chloride*, $CH_2Cl{\cdot}C_6H_4{\cdot}CHMe_2$, b. p. 228°, $d_4^{21\cdot5}$ 1·020, $n_D^{21\cdot5}$ 1·523, is obtained in 75% yield, which on treatment with magnesium in ether and decomposition of the Grignard reagent with water yields 74% of the theoretical amount of *p*-cymene, together with some dicuminyl. The *p*-cymene obtained by these last two syntheses gives identical constants in close agreement with those of *p*-cymene obtained from thymol by converting this into 3-bromo-*p*-cymene with phosphorus pentabromide, and decomposing the Grignard compound obtained from this with water. Pure *p*-cymene accordingly has b. p. 175—176°/735 mm., d_4^{20} 0·858, n_D^{20} 1·493.

R. BRIGHTMAN.

Syntheses in the *p*-cymene series starting from *iso*propyl alcohol. II. Syntheses with magnesium *p-iso*propylphenyl bromide. L. BERT (Bull. Soc. chim., 1925 [iv], **37**, 1397—1410; cf. preceding abstract).—Magnesium *p-iso*propylphenyl bromide is much more readily prepared than the corresponding compound from *p*-bromotoluene, the reaction being catalysed initially by the addition of a few drops of bromine. Decomposition with water after 1½ hrs. showed that 80% of the *p*-bromocumene had been converted into the Grignard reagent, about 15% being converted into *pp'*-di*iso*propyldiphenyl. From magnesium *p-iso*propylphenyl bromide, the following substances have been prepared by the usual Grignard reaction methods: *p*-cumenol, b. p. 119°/19 mm., 226—227°/729 mm. (yield 18%) (methyl ether, b. p. 207·5—208°/728 mm., 100°/22 mm., d_4^{7} 0·955, n_D^{7} 1·513; ethyl ether, b. p. 222°/728 mm., 113—114°/22·5 mm., $d_4^{8\cdot5}$ 0·938, $n_D^{8\cdot5}$ 1·506); *p*-cumenic acid (yield 40%), m. p. 116°, *p*-cumyl alcohol, b. p. 144—145°/31·5 mm., 244—245°/735 mm.,

d_4^{24} 0·978, n_D^{24} 1·522 (in 35% yield from trioxymethylene), and *p*-cumaldehyde, b. p. 110°/14 mm. (yield 33%, on hydrolysis of the acetal first formed from ethyl orthoformate). The *acetal* of *p*-cumaldehyde, b. p. 142—143°/18·5 mm., 263°/724 mm. (slight decomposition), d_4^{19} 0·944, n_D^{19} 1·484, is new. Glycol monochlorohydrin gives a 90—100% yield of β-p-iso*propylphenylethyl alcohol*, b. p. 155°/29 mm., d_4^{16} 0·969, n_D^{16} 1·521 (*acetate*, b. p. 143—146°/17 mm., d_4^{19} 0·986, n_D^{19} 1·499). *p*-Cumenic acid is better prepared by the action of ethyloxalyl chloride on cumene in the presence of aluminium chloride and carbon disulphide; *ethyl cumenylglyoxylate*, $C_6H_4Pr^{\beta}\cdot CO\cdot CO_2Et$, b. p. 177°/17·5 mm., 180°/20 mm., d_4^{21} 1·047, n_D^{21} 1·516, is thereby obtained in 75% yield, hydrolysed with 10% sodium hydroxide, and the p-*cumenylglyoxylic acid* on heating with concentrated sulphuric acid is converted quantitatively into *p*-cumenic acid. Since an improved procedure enables ethyloxalyl chloride to be obtained by Bouveault's process (A., 1896, i, 551) in consistent yields of 80%, this process affords a technical method of synthesising *p*-cumenic acid. The phosphorus pentachloride is prepared *in situ* from the trichloride and the mixture with ethyl oxalate heated at 135—140° until phosphoryl chloride ceases to distil, when the temperature is raised to 165—170°. The following esters of *p*-cumenic acid are described: *methyl*, b. p. 126°/14 mm., d_4^{19} 1·018, n_D^{19} 1·515; *ethyl*, b. p. 134·5°/13·5 mm., d_4^{17} 1·000, n_D^{17} 1·508; *propyl*, b. p. 148°/14 mm., d_4^{18} 0·981, n_D^{18} 1·503; iso*propyl*, b. p. 138°/14 mm., d_4^{19} 0·978, n_D^{19} 1·500; *butyl*, b. p. 161—162°/14 mm., $d_4^{19\cdot5}$ 0·970, $n_D^{19\cdot5}$ 1·501; iso*butyl*, b. p. 155°/14 mm., d_4^{19} 0·966, n_D^{19} 1·497; iso*amyl*, b. p. 173°/16·5 mm., d_4^{19} 0·961, n_D^{19} 1·497; iso*octyl*, b. p. 199°/16·5 mm., d_4^{21} 0·938, n_D^{21} 1·491; *benzyl*, b. p. 218°/16·5 mm., d_4^{22} 1·059, n_D^{22} 1·554; *cumyl*, b. p. 243°/16·5 mm., d_4^{21} 1·023, n_D^{21} 1·545. *p*-Cumenylglyoxylic acid reacts readily with boiling aniline, yielding first an acid imide, $C_6H_4Pr^{\beta}\cdot CO\cdot CO_2H + PhNH_2 \longrightarrow H_2O + C_6H_4Pr^{\beta}\cdot C(:NPh)\cdot CO_2H$, which subsequently decomposes into carbon dioxide and *p*-cumenylimide, $CHMe_2\cdot C_6H_4\cdot CH:NPh$; this on hydrolysis with 25% sulphuric acid gives *p*-cumaldehyde in nearly theoretical yield. The process affords a technical means of synthesisng the aldehydes.

R. BRIGHTMAN.

Reactions of compounds of triphenyl and triphenylsilicyl in liquid ammonia. C. A. KRAUS and R. ROSEN (J. Amer. Chem. Soc., 1925, **47**, 2739—2748).—Sodium and potassium triphenylmethyls, prepared by the action of the respective metals on triphenylmethane in liquid ammonia solution, have equivalent conductances, in 0·05 and 0·08*N*-solution in liquid ammonia, of 64 and 32, respectively. They are regarded as true salts which undergo normal ionisation in the above solvent (cf. Schlenk and Marcus, A., 1914, i, 823). In liquid ammonia solution, the salts absorb two atoms of oxygen per molecule of salt, a product being precipitated which appears to contain the metal in combination with the organic residue, but which, after warming to the ordinary temperature, consists, in the case of the sodium salt, of sodium peroxide and an ether-soluble oxide of triphenylmethyl. In the case of the potassium salt, the product initially precipitated, after being kept for some time at the ordinary temperature, absorbs a further molecule of oxygen when redissolved in liquid ammonia, with formation of potassium tetroxide. When potassamide is treated in liquid ammonia solution with triphenylmethane, immediate and practically complete formation of potassium triphenylmethyl takes place. Sodamide behaves similarly, but whilst the potassium salt is stable when isolated by evaporation of the solvent, the sodium salt changes rapidly as the temperature is raised, and the corresponding calcium salt is unstable even at low temperatures (cf. Schlenk and Ochs, A., 1916, i, 379; Kraus and Kawamura, A., 1924, i, 276). These phenomena indicate that triphenylmethane behaves, in liquid ammonia, as an acid of such strength that the salt of the strong base, potassium, is only slightly hydrolysed ("ammonolysed"), whilst salts of the weaker bases, sodium and calcium, are decomposed in this way to a considerable extent. Potassium triphenylmethyl crystallises from liquid ammonia free from solvent, whilst the sodium salt prepared similarly contains 1 mol. of ammonia of crystallisation. Triphenylmethane forms a sensitive indicator in liquid ammonia solution, giving intense red colorations in presence of metallic amides (bases), and colourless solutions in the pure solvent or in presence of ammonium salts (acids).

Triphenylmethyl chloride combines with pyridine (1 mol.) with formation of an additive *compound*, m. p. 173—174°, and with aniline (1 mol.), yielding an additive *compound*, m. p. 189—190°. When treated with liquid ammonia, or with ammonia in ethereal solution, triphenylmethyl chloride forms a complex *compound*, which decomposes when heated into triphenylmethylamine and ammonium chloride. When triphenylmethyl chloride is dissolved in liquid ammonia, it is hydrolysed to a slight extent, reversibility of the hydrolysis being indicated by the formation of triphenylmethyl when ammonium chloride is added to a solution of triphenylmethylamine in liquid ammonia. Triphenylmethylamine reacts with sodium and potassium in liquid ammonia solution, with formation of the metallic amide and salt of triphenylmethyl.

Triphenylsilicyl chloride undergoes rupture at the phenyl–silicon linking when treated with metallic sodium in liquid ammonia, in which the chloride is only slightly soluble. Definite compounds could not be isolated from the reaction product. Triphenylsilicyl chloride combines with 2 mols. of ammonia, the product decomposing into *triphenylsilicylamine*, m. p. 55—56°.

F. G. WILLSON.

"Tervalent" carbon. III. Pentaphenyl-*cyclo*pentadienyl. K. ZIEGLER and B. SCHNELL (Annalen, 1925, **445**, 266—282; cf. A., 1924, i, 850).—2 : 3 : 4 : 5-Tetraphenyl-$\Delta^{2:4}$-*cyclo*pentadiene (cf. Wislicenus and Carpenter, A., 1899, i, 60), of which an improved method of preparation is described, condenses with *p*-nitrosodimethylaniline with formation of 2 : 3 : 4 : 5-*tetraphenyl*-$\Delta^{2:4}$-cyclo*pentadienone*-p-*dimethylaminoanil*, violet-black, m. p. 224—226°. This is hydrolysed by boiling hydrochloric acid to 2 : 3 : 4 : 5 - *tetraphenyl* - $\Delta^{2:4}$ - cyclo*pentadien* - 1 - *one*,

blackish-violet, m. p. 217—218°, which is converted by the action of excess of magnesium phenyl bromide into 1 : 2 : 3 : 4 : 5-*pentaphenyl*-$\Delta^{2:4}$-cyclo*pentadien*-1-*ol*, colourless, m. p. 175—176°. This affords 1-*chloro*-1 : 2 : 3 : 4 : 5-*pentaphenyl*-$\Delta^{2:4}$-cyclo*pentadiene*, yellow, m. p. 167°, when treated with hydrogen chloride in boiling acetic acid. The corresponding *bromo*-derivative, yellow, m. p. 188—189°, is obtained similarly; it is much less readily hydrolysed than the corresponding triphenylmethyl bromide. Both the chloro- and bromo-derivatives yield *pentaphenyl*-$\Delta^{2:4}$-cyclo*pentadiene*, m. p. 244—246°, when treated with zinc dust in glacial acetic acid solution. The mixture of benzamarones produced by Knoevenagel's method (A., 1893, i, 352) is slowly reduced by zinc dust in glacial acetic acid solution to 3 : 4-dihydroxy-1 : 2 : 3 : 4 : 5-pentaphenyl*cyclo*pentane, m. p. 241° (cf. Wislicenus, *loc. cit.*). This is very resistant to dehydrating agents, but is converted by concentrated sulphuric acid, in boiling acetic acid solution, into the above pentaphenyl*cyclo*pentadiene, m. p. 250°. Treatment of the bromopentaphenyl*cyclo*pentadiene with molecular silver in benzene affords 1 : 2 : 3 : 4 : 5-*pentaphenyl*-$\Delta^{2:4}$-cyclo*pentadienyl*, reddish-violet, m. p. 260°. The free radical is only slightly less stable in air than the tetra-arylallyl radicals (cf. A., 1924, i, 308). It absorbs oxygen in nitrobenzene solution, but the resulting *peroxide* is itself further oxidised.

F. G. Willson.

Polarity theories and four-membered rings. Non-existence of 2 : 3 : 3-triphenylmethylene-1 : 2-oxaimine. G. N. Burkhardt, A. Lapworth, and J. Walkden (J.C.S., 1925, **127**, 2458—2461).—The interaction of nitrosobenzene and *as*-diphenylethylene yields a compound to which Ingold and Weaver (A., 1924, i, 1116) gave an oxaimine formula; this is in reality the *N*-phenyldiphenylnitrone, $CPh_2{:}NPh{:}O$, a methylene group having been lost in the reaction. Thus the facts are found to be in accord with the theory of alternate polarities, as in the other cases investigated (cf. A., 1925, ii, 937).

B. W. Anderson.

Influence of nitro-groups on the reactivity of substituents in the benzene nucleus. VIII. 2 : 3- and 2 : 5-Dinitro-*p*-chlorotoluenes. J. Kenner, C. W. Tod, and E. Witham (J.C.S., 1925, **127**, 2343—2349).—The action of methyl-alcoholic ammonia at 150° on 4-*chloro*-2 : 3-*dinitrotoluene*, m. p. 106·5° (prepared from 2 : 3-dinitro-*p*-toluidine), gave a 70% yield of 4-*chloro*-2-*nitro*-m-*toluidine*, m. p. 53°; *acetyl*-derivative, m. p. 210—212°. 4-Chloro-2 : 5-dinitrotoluene was similarly converted into 20% and 30%, respectively, of 4-*chloro*-6-*nitro*-m-*tolyl methyl ether*, m. p. 122°, and 4-*chloro*-6-*nitro*-m-*toluidine*, m. p. 121°; *acetyl*-derivative, m. p. 135°. To verify completely the constitution of these compounds they were synthesised from 4-chloroaceto-*m*-toluidide, and the alternative bases, 4-*chloro*-3-*nitro*-o-*toluidine* (m. p. 60—62·5°; *acetyl*-derivative, m. p. 195°) and 4-*chloro*-5-*nitro*-o-*toluidine* (m. p. 164°; *acetyl*-derivative, m. p. 182°) from 4-chloroaceto-*o*-toluidide. 4-Chloro-5-nitro-*o*-toluidine yielded on reduction 5-*chloro*-2-*methyl*-p-*phenylenediamine*, m. p. 146°. Thus in each case the influence of the methyl group on the mobility of the *m*-nitro-group is seen to be stronger than that of the chlorine atom, in contrast with the results obtained by the study of direct substitution.

B. W. Anderson.

Preparation of *iso*nuclear bromonitronaphthalenes by dehydrogenation of the corresponding derivatives of tetralin (*ar*-tetrahydronaphthalene). V. Veselý and L. K. Chudožilov (Bull. Soc. chim., 1925, [iv], **37**, 1436—1444).—*ar*-Bromonitro- and bromodinitro-tetrahydronaphthalenes are converted into the corresponding bromonitronaphthalenes by the method previously described (A., 1923, i, 550; cf. Braun, Hahn, and Seemann, A., 1922, i, 728). The reaction fails with *ar*-trinitrotetrahydronaphthalene, although an *ac*-dibromo-derivative is formed at 100°. Elimination of hydrogen bromide from this compound, however, takes place only very slowly on raising the temperature and the product remains liquid. In contrast to 1-chloro-2 : 4-dinitronaphthalene (Ullmann and Bruck, A., 1909, i, 21) the halogen atom in *ar*-1-bromo-2 : 4-dinitrotetrahydronaphthalene and *ar*-2-bromo-1 : 3-dinitrotetrahydronaphthalene does not react with ethyl sodiomalonate, and only very slow reaction occurs with 2-bromo-1 : 3-dinitronaphthalene. The following compounds are described: ar-2-*Bromo*-1-*nitrotetrahydronaphthalene*, m. p. 101—102°, b. p. 162—185°/13—15 mm., from *ar*-1-nitro-2-aminotetrahydronaphthalene (Schroeter, A., 1922, i, 123) by the Sandmeyer reaction. *ar*-2-Nitro-1-aminotetrahydronaphthalene, obtained by the action of alcoholic ammonia on the 1 : 2-dinitro-compound, similarly yields ar-1-*bromo*-2-*nitrotetrahydronaphthalene*, m. p. 50—51·5°; ar-2-*bromo*-3-*nitrotetrahydronaphthalene*, m. p. 50—51° (yielding 2-*bromo*-3-*nitronaphthalene*, m. p. 82—83° on dehydrogenation); ar-1-*bromo*-3-*nitrotetrahydronaphthalene*, m. p. 106—106·5°; ar-3-*bromo*-1-*nitrotetrahydronaphthalene*, m. p. 76—76·5° (yielding on dehydrogenation 3-*bromo*-1-*nitronaphthalene*, m. p. 97—98°, also obtained from 4-nitro-β-naphthylamine), and ar-4-*bromo*-1-*nitrotetrahydronaphthalene*, m. p. 68—69°, were similarly obtained from the corresponding nitroaminotetralins described by Schroeter (*loc. cit.*). Aceto-2 : 4-dinitro-*ar*-tetrahydro-α-naphthalide after hydrolysis to the amine, m. p. 184°, with sulphuric acid, is similarly converted (yield 60%) into 1-bromo-2 : 4-dinitro-*ar*-tetrahydronaphthalene, m. p. 94° (cf. Morgan, Micklethwait, and Winfield, J.C.S., 1905, **87**, 747), yielding on dehydrogenation 1-*bromo*-2 : 4-*dinitronaphthalene*, m. p. 151—152°. ar-2-*Bromo*-1 : 3-*dinitrotetrahydronaphthalene*, m. p. 135—136°, was similarly obtained from the acetodinitrotetrahydronaphthalide and by nitration of 2-bromo-1-nitro-*ar*-tetrahydronaphthalene. The product, m. p. 105—106°, obtained by Morgan (*loc. cit.*) from the nitration of a mixture of 1- and 2-bromo-*ar*-tetrahydronaphthalene is impure, repeated crystallisation raising its m. p. to 133—134°. 2-*Bromo*-1 : 3-*dinitronaphthalene*, m. p. 183—184°, is obtained on dehydrogenation.

R. Brightman.

Reactivity of the methyl-hydrogen atoms in 2 : 4-dinitro-1-methylnaphthalene. V. Veselý and I. Pastak (Bull. Soc. chim., 1925, [iv], **37**, 1444—1451).—Nitration of α-methylnaphthalene

yields the 4 : 5- and 4 : 8-dinitro-derivatives, 2 : 4-dinitro-1-methylnaphthalene being prepared from 1-chloro-2 : 4-dinitronaphthalene through reaction with ethyl sodiomalonate. The methyl-hydrogen atoms of 2 : 4-dinitro-1-methylnaphthalene react readily with aromatic aldehydes and with nitrosodimethylaniline, their reactivity being intermediate between that of 2 : 4-dinitrotoluene and 2 : 4 : 6-trinitrotoluene. Ethyl oxalate readily yields a condensation product, insoluble in alkali, which is probably the corresponding tetranitrodinaphthylethane.

1-Chloro-2 : 4-dinitronaphthalene, obtained by Ullmann and Bruck's method (A., 1909, i, 21), using dimethylaniline in place of diethylaniline, condenses with ethyl acetoacetate in the presence of sodium, yielding *ethyl* 2 : 4-*dinitro*-α-*naphthylacetoacetate*, m. p. 131°, which on heating with acetic and dilute sulphuric acids gives 2 : 4-*dinitro*-α-*naphthylmethyl methyl ketone*, m. p. 161°. Similarly ethyl malonate condenses with 1-chloro-2 : 4-dinitronaphthalene, yielding *ethyl* 2 : 4-*dinitro*-1-*naphthylmalonate*, m. p. 107—108°, together with a small quantity of *ethyl* 2 : 4-*dinitro*-1-*naphthylacetate*, m. p. 128°. On heating with acetic anhydride containing a little sulphuric acid, the malonate is converted into 2 : 4-*dinitro*-α-*naphthylacetic acid*, m. p. 211°, falling in 8 days to 161° and then rising in 3 months to 171°, from which 2 : 4-*dinitro*-1-*methylnaphthalene*, m. p. 161°, is obtained on treatment with cold pyridine. With *p*-nitrosodimethylaniline in a mixture of acetone and alcohol 2 : 4-dinitro-1-methylnaphthalene yields the *product*,

$$C_{10}H_5(NO_2)_2CH{:}N{\cdot}C_6H_4{\cdot}NMe_2,$$

m. p. 168°, from which on treatment with concentrated hydrochloric acid 2 : 4-*dinitro*-1-*naphthaldehyde*, m. p. 156°, is obtained. R. BRIGHTMAN.

The imino-residue. K. F. SCHMIDT (Ber., 1925, **58**, [*B*], 2413—2415; cf. A., 1924, i, 721).—A reply to Oliveri-Mandalà (A., 1925, ii, 815). H. WREN.

Preparation of acetoacetanilide. H. PFEIFFER (J. pr. Chem., 1925, [ii], **111**, 240—241; cf. Knorr, A., 1887, 159; Roos, Ber., 1888, **21**, 624; Knorr and Reuter, A., 1894, i, 371).—The best yield (50%) of acetoacetanilide is obtained by heating together aniline (1 mol.) and ethyl acetoacetate (1 mol.) for 15 min. in an open flask at 160°. The whole sets, when cooled in a freezing mixture, to a crystalline mass, which, after washing with a mixture of benzene and light petroleum, has m. p. 86°. A further small quantity, equally pure, is obtained from the mother-liquors on keeping. C. HOLLINS.

Ready method for the preparation of *o*-nitroaniline in the laboratory. E. SAKELLARIOS and D. JATRIDES (Ber., 1925, **58**, [*B*], 2286—2288).—Sulphanilic acid is converted into *potassium acetylsulphanilate* by the addition of acetic anhydride in slight excess to an aqueous solution of potassium sulphanilate in such a manner that the temperature is maintained at 65—70°. The finely divided salt is dissolved in concentrated sulphuric acid and nitrated with a mixture of nitric acid (85%) and sulphuric acid at 5°. The acetyl and sulphonyl groups are removed from the resultant *potassium o-nitroacetylsulphanilate* by boiling sulphuric acid (67%), whereby *o*-nitroaniline is obtained in 80% yield. H. WREN.

Action of cyanamide on picryl chloride. M. GIUA (Gazzetta, 1925, **55**, 662—665).—The action of excess of 12% aqueous cyanamide solution on alcoholic picryl chloride solution yields: (1) 2 : 4 : 6-trinitrophenylcarbamide (picrylcarbamide), m. p. 201—203° (decomp.); Kniphorst (A., 1925, i, 905) gave m. p. 196—199°; (2) "*dipicrylguanylcarbamide*," $C_6H_2(NO_2)_3{\cdot}N(CO{\cdot}NH_2){\cdot}C(NH_2){:}N{\cdot}C_6H_2(NO_2)_3$, or "*dipicryldicyanodiamidine*,"

$C_6H_2(NO_2)_3{\cdot}N(CO{\cdot}NH_2){\cdot}C(:NH){\cdot}NH{\cdot}C_6H_2(NO_2)_3$,

m. p. 254—255° (decomp.), which can be regarded as formed by the combination of 1 mol. of picrylcyanamide with 1 mol. of picrylcarbamide. T. H. POPE.

Indanyl bases. C. COURTOT and A. DONDELINGER (Ann. Chim., 1925, [x], **4**, 222—292).—A detailed account of the preparation of substituted indanylamines previously described (A., 1923, i, 1090; 1924, i, 279). The following, however, do not seem to have been previously described: *di-indanylmethylamine*, m. p. 92—93°; *diphenylindanylamine*, m. p. 85—86°; m-*nitrophenylindanylamine*, m. p. 127—128° and 137—138° (the two m. p. are probably those of two crystalline forms); p-*nitrophenylindanylamine*, m. p. 126—127°; α-*naphthylindanylamine* (which could not be obtained in a pure condition); β-*naphthylindanylamine*, m. p. 169—170°. The *hydrochlorides* of all these bases were prepared. J. W. BAKER.

Indanyl bases. C. COURTOT and A. DONDELINGER (Ann. Chim., 1925, [x], **4**, 293—369).—A detailed account of the optical data, absorption spectra, measurements of the affinity constants and degree of dissociation of the hydrochlorides of the indanyl bases (cf. preceding abstract) previously described (cf. A., 1925, ii, 274; Bourgeaud and Dondelinger, *ibid.*, 117) is given. The hydrogen oxalates of the bases were also prepared and examined. The action of the hydrogen halides on indene has been investigated. The addition of hydrogen chloride has been investigated previously (cf. Weissgerber, A., 1911, i, 623); hydrogen bromide and iodide give a quantitative yield of 1-*bromo*- and 1-*iodo-hydrindene*, respectively, which cannot be purified, since they readily lose hydrogen halide and yield a polymeride of indene, but they may be used immediately after preparation as synthetic agents, condensing with *o*-toluidine to yield *o*-tolylindanylamine in 74% yield. Hydrofluoric acid behaves like sulphuric acid, causing only polymerisation of the indene. J. W. BAKER.

Formation of *cyclo*hexyl ether. V. N. IPATIEV and J. ORLOV (Compt. rend., 1925, **181**, 793—795; cf. A., 1908, i, 342; 1912, i, 544; 1924, i, 725).—The material of high b. p. obtained from the hydrogenation products of phenol and diphenyl ether appears to be cyclo*hexyl*cyclo*hexanol*, since when heated with aluminium oxide and copper oxide in the presence of hydrogen a mixture of *cyclo*hexene and *dicyclohexyl*, b. p. 237—238·5°, d_4^{20} 0·8835, separated by treatment with sulphuric and nitric acids, is obtained. *Dicyclohexyl* of slightly different properties, possibly a stereo-

isomeride, b. p. 236—237·5°, d_4^{20} 0·8919, is obtained by treatment of diphenylene oxide with hydrogen in the presence of nickel oxide and *cyclo*hexane.
L. F. HEWITT.

Reduction of organic compounds containing oxygen by active carbon. G. STADNIKOV, N. GAVRILOV, and A. WINOGRADOV (Ber., 1925, **58**, [*B*], 2428—2429).—Reduction of cresols to toluene, carbon monoxide, and carbon dioxide is effected by carbon deposited on finely divided iron at 430°. The catalyst is prepared by soaking asbestos in ferric nitrate solution free from chloride and treating the drained product with 10% ammonia. It is reduced by hydrogen at 460—470° and subsequently treated with cresol at 480—490°, whereby the latter substance decomposes into hydrogen, carbon monoxide, and carbon which is deposited on the iron. H. WREN.

Influence of substituents on the formation and the stability of some cyclic compounds. M. GIUA (Atti R. Accad. Lincei, 1925, [vi], **2**, 343—346).—Although condensation of β-naphthol with oxalyl chloride yields the lactone of hydroxynaphthylglyoxylic acid (A., 1917, i, 204), malonyl chloride and β-naphthol yield, under identical conditions, β-*dinaphthyl malonate*, m. p. 146—147°.
F. G. TRYHORN.

Condensation products of dextrose and *p*-phenetidine. M. AMADORI (Atti R. Accad. Lincei, 1925, [vi], **2**, 337—342).—Two different products have been obtained by the interaction of equimolecular quantities of anhydrous dextrose and *p*-phenetidine. When the reaction occurs in the cold, or with brief boiling, a compound (m. p. 118°) is obtained, similar to that described by Irvine (J.C.S., 1909, **95**, 1545), but without water of crystallisation. When the reactants are heated together in the dry state at 50—80°, subsequent brief extraction with boiling alcohol results in the isolation of a product of m. p. 155°, which is probably that described by Claus and Ree (Chem.-Ztg., 1898, **22**, 545). The physical and chemical properties of these products are described. Both have the same empirical formula, $C_{14}H_{21}O_6N$.
F. G. TRYHORN.

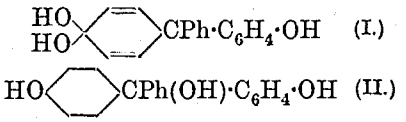
Oxidation-reduction. VII. Dichloro-substitution products of phenol-indophenol. H. D. GIBBS, B. COHEN, and R. K. CANNAN (U.S. Pub. Health Repts., 1925, **40**, 649—663; cf. A., 1925, ii, 1164).—An investigation (including preparation and analysis) of the indo-2 : 6-dichlorophenols of phenol, *o*-cresol, *m*-cresol, *o*-chlorophenol, and Schäffer's salt, and the leuco-derivatives of phenol- and *m*-cresol-indo-2 : 6-dichlorophenols. The oxidation-reduction potentials in buffer solutions from p_H 3 to p_H 13 are in agreement with the formula already developed. The following compounds are selected for indicators of oxidation-reduction in biological systems at p_H 7 and 0·001*M* concentration: *m*-bromophenol-indophenol, *o*-chlorophenol-indophenol, phenol-indo-2 : 6-dichlorophenol, *o*-cresol-indo-2 : 6-dichlorophenol, and "α-naphthol-2-sulphonate-dichlorophenol."
CHEMICAL ABSTRACTS.

Guaiacol derivatives. L. WINKELBLECK (J. Amer. Pharm. Assoc., 1924, **13**, 619—622).—The *phenylurethane*, m. p. 146°, and *α-naphthylurethane*, m. p. 116—117°, of guaiacol are described; *guaiacyl-acetophenone* [*o-anisyl acetate*?] has m. p. 104° (*phenylhydrazone*, m. p. 106—108°; *semicarbazone*, m. p. 142—147°).
CHEMICAL ABSTRACTS.

Relation between chemical constitution and pungency in acid amides. E. C. S. JONES and F. L. PYMAN (J.C.S., 1925, **127**, 2588—2598).—By varying both the acyl- and the amido-residues the following acid amides have been prepared and their pungencies compared with that of *n*-nonovanillylamide=100; α-iso*propyl*-n-*hexovanillylamide*, m. p. 125° (pungency about 5); *phenylacetovanillylamide*, m. p. 112° (non-pungent); β-*phenylpropiovanillylamide*, m. p. 83° (pungency 40); γ-*phenyl*-n-*butyro*- and δ-*phenyl*-n-*valero-vanillylamides*, m. p. 93—95° and 67°, respectively (both slightly >40). The pungencies of chloroacetovanillylamide, m. p. 119—122°, *dichloroacetovanillylamide*, m. p. 139—143°, *trichloroacetovanillylamide*, m. p. 76—79°, *bromoacetovanillylamide*, m. p. 95°, and *iodoacetovanillylamide*, m. p. 114°, are all about 3; thus the shape rather than the weight of the side chain is the important factor. Where no phenolic hydroxyl group is present in the molecule, as in n-*nono*-3 : 4-*methylenedioxybenzylamide*, m. p. 92°, and n-*nono*-4-*methoxybenzylamide*, m. p. 103°, no pungency was observed, whilst n-*nono*-4-*hydroxybenzylamide*, m. p. 92°, n-*nono*-3 : 4-*dihydroxybenzylamide*, m. p. 78°, and Δ$^{\omega}$-*undeceno*-3 : 4-*dihydroxybenzylamide*, m. p. 70—74°, had pungencies of 10, 25, and 50, respectively.
B. W. ANDERSON.

Absorption spectra of benzaurin. W. R. ORNDORFF, R. C. GIBBS, and S. A. MCNULTY (J. Amer. Chem. Soc., 1925, **47**, 2767—2777).—Absorption spectra of solutions of benzaurin in neutral alcohol, alcoholic hydrochloric acid, 93% sulphuric acid, alcoholic alkali, and 33% aqueous alkali, and of *pp'*-dihydroxytriphenylmethane in neutral alcohol, are recorded. The continuous spectrum obtained by the discharge from a Tesla coil between electrodes immersed in water, which extends from the green of the visible spectrum to well into the ultra-violet, was used as the source of illumination, calibration being obtained by the use of line spectra from a spark in air between electrodes of suitable metals. Pure benzaurin, orange-red crystals, forms a yellowish-orange solution in absolute ethyl alcohol, the colour of which fades on keeping to a light yellow, due to a weakening of an absorption band at frequency 2300 to about 1/18 of its original strength in 10 days. When the faded solution is heated, the orange tint is temporarily restored. The presence of bands at 2033 and 2714 could not be confirmed (cf. Formánek and Grandmougin, "Unters. Nachweis Farbstoffe," 1908, I, 126), whilst the results of Meyer and Fischer (A., 1913, ii, 167) are considerably extended. The absorption of *pp'*-dihydroxytriphenylmethane in alcohol is similar to that of the faded benzaurin solution; no band corresponding with that exhibited by benzaurin at 2300 is observed. It is concluded that the benzaurin first absorbs water with formation

of the quinoid hydrate (I), to which the orange tint is ascribed, and which then passes reversibly into the colourless carbinol (II), the residual colour of the



faded solution being due to the small proportion of quinoid hydrate present at equilibrium. The addition of hydrochloric acid to the alcoholic benzaurin solution causes development of an orange colour, two new absorption bands being produced at 1985 and 2490. Further addition of acid intensifies these and also brings out bands at 3760 and 3450. These are due to the formation of the quinoid hydrochloride (cf. Baeyer, A., 1903, i, 811). When kept, the acid solution becomes colourless, owing to the reducing action of the alcohol (cf. Kauffmann and Pannwitz, A., 1912, i, 351). The absorption in 93% sulphuric acid is similar, and the same type of absorption spectrum is also given by solutions of benzaurin in alcoholic potassium hydroxide, indicating that the colour of the alkaline solution is due to the quinoid structure of the monopotassium salt, and that this group is alone responsible for the colour of benzaurin and of the analogous Döbner's violet. In 33% aqueous alkali, benzaurin gives a colourless solution, indicating the formation of the dipotassium salt of the carbinol.

F. G. WILLSON.

Photochemical transformations in the triphenylmethane series. III. A. LIFSCHITZ (Ber., 1925, **58**, [*B*], 2434—2440; cf. A., 1921, ii, 365).—The transformation of derivatives of di- and triaminotriphenylmethane by exposure to light of short wave-length into the isomeric salts of the dye has been described previously (*loc. cit.*). Similar observations are recorded with *pp'*-dihydroxytriphenylmethanes and with derivatives of triphenylmethane. Thus benzaurin which has been decolorised by addition of an excess of alkali hydroxide or cyanide regains its characteristic colour on exposure to light, and this is also the case with phenolphthalein. Triphenylacetonitrile, triphenylmethanesulphonic acid, and triphenylmethyl thiocyanate are changed in such a manner as to produce a salt-like isomeride or triphenylcarbinol and the respective acid; in these cases, coloration of the solution is never directly caused by light. It is emphasised that triphenylacetonitrile and triphenylmethyl thiocyanate are non-electrolytes when pure. The former does not give a trace of colour with concentrated sulphuric acid or sulphuric and acetic acids, whereas the latter gives the reaction for the thiocyanogen ion only after its solution has been heated, illuminated, or preserved. Consequently, the triphenylmethyl derivatives must exist in a non-dissociated, homopolar form and an electrically dissociable form containing a heteropolar *C*-linking, thus affording independent evidence in favour of the views advanced by Hantzsch (A., 1922, i, 24) on the constitution of carbonium salts. The complete course of the action of light on triphenylmethane derivatives is therefore $(NR_2\cdot C_6H_4)_3CX \rightarrow [(NR_2\cdot C_6H_4)_3C]^+ + X' \rightarrow [(NR_2\cdot C_6H_4)_2C{:}C_6H_4{:}NR_2]'$, and the primary photochemical effect consists in the transference of a valency electron from the carbon atom to the group X.

The bearing of the discovery of colourless solutions of triphenylmethyl-derivatives which are good electrolytes on the theories of halochromism advanced by Hantzsch (*loc. cit.*) and Pfeiffer ("Organische Molekülverbindungen," 1922) is discussed.

H. WREN.

Azoxybenzenes and aromatic nitro-derivatives. VII. Organic molecular compounds. M. GIUA and G. GUASTALLA (Gazzetta, 1925, **55**, 646—652).—Investigation of the m. p. curves indicates the formation of a compound, m. p. about 64°, containing 3 mols. of 2 : 4 : 6-trinitrotoluene and 2 mols. of azoxybenzene. The equilibrium curve exhibits two maxima, but one of these results from an abnormal reaction owing to the slowness with which the above compound is formed. The eutectic between the compound and azoxybenzene or 2 : 4 : 6-trinitrotoluene has m. p. 26·7° or 53·7°, respectively (cf. Meisenheimer and Smolnikov, A., 1920, i, 334). The system 2 : 3 : 4-trinitrotoluene–azoxybenzene forms a simple eutectic, which solidifies at 25° and contains about 25% of the trinitrotoluene. The system 3 : 4 : 6-trinitrotoluene–azoxybenzene forms a eutectic, solidifying at 22°, at about 35% of the trinitrotoluene. The system 2 : 4-dinitrotoluene–azoxybenzene forms a eutectic solidifying at about 16° and containing 31·3% of dinitrotoluene, and 1-bromo-2 : 4-dinitrobenzene–azoxybenzene a eutectic solidifying at 16° and containing about 42% of the nitro-compound.

T. H. POPE.

Azo-compounds and aromatic nitro-derivatives. VIII. Organic molecular compounds. M. GIUA and G. REGGIANI (Gazzetta, 1925, **55**, 652—661; cf. preceding abstract).—The following systems form eutectics containing the given proportions of the former component and solidifying at the temperatures stated: azobenzene–2 : 4-dinitrotoluene, 49·15%, 39·6°; azobenzene–*p*-nitrotoluene, 46%, 28·6°; azobenzene–*m*-dinitrobenzene, 56·21%, 46·5°; *p*-aminoazobenzene–*p*-nitrotoluene, about 30%, 34·4°; *p*-aminoazobenzene–*p*-nitrochlorobenzene, 41·5%, 53·8°; dimethyl-*p*-aminoazobenzene–2 : 4-dinitrotoluene, about 34%, 52·7°; dimethyl-*p*-aminoazobenzene–*p*-nitrotoluene, 30%, 40·8°; dimethyl-*p*-aminoazobenzene–*m*-dinitrobenzene, 45·3%, 63°. Azobenzene (1 mol.) forms an additive compound with 2 : 4 : 6-trinitrotoluene (2 mols.), m. p. about 65°. *p*-Aminoazobenzene (1 mol.) and *m*-dinitrobenzene (1 mol.) form an additive compound, m. p. about 86°. Dimethyl-*p*-aminoazobenzene (1 mol.) and 2 : 4 : 6-trinitrotoluene (2 mols.) form an additive compound, m. p. 82°, which gives a eutectic solidifying at 73° (77·2°) with the latter (former) component.

T. H. POPE.

Effect of sulphonic acid groupings in certain positions in lightening the colour of azo dyes. J. OBERMILLER (Z. angew. Chem., 1925, **38**, 1044).—See B., 1925, 982.

Occurrence of free radicals in chemical reactions. III. H. WIELAND, H. VOM HOVE, and K. BÖRNER (Annalen, 1925, **446**, 31—48).—During

the decomposition of an arylazotriphenylmethane, free aryl and triphenylmethyl radicals are formed (A., 1922, i, 772). It is now found that when a compound of the acylazotriphenylmethane series, *e.g.*, $COPh{\cdot}N{:}N{\cdot}CPh_3$, is heated in xylene solution, nitrogen is evolved and a deep carmine-coloured solution is generally obtained. This colour, said to be due to the free R·CO′ radicals, gradually fades and a β-benzpinacolin is formed: $R{\cdot}CO' + Ph_3C' \longrightarrow R{\cdot}CO{\cdot}CPh_3$. If this theory is correct, the passing of oxygen through the solution during the decomposition of the azo-compound should lead to the formation of the peroxides of the free radicals. Whilst triphenylmethyl peroxide was isolated in most instances, only one acyl radical, carbethoxyl, formed a peroxide, $CO_2Et{\cdot}O{\cdot}O{\cdot}CO_2Et$, the presence of which could be detected by the liberation of iodine from hydriodic acid. When the thermal decomposition is carried out in carbon tetrachloride solution, the free aryl radical removes chlorine from the solvent with formation of the acid chloride. By heating triphenylmethyl chloride or tri-*p*-tolylmethyl chloride with a substituted hydrazine in benzene or pyridine solution, hydrazo-compounds are obtained. These yield the corresponding azo-compounds when a chloroform solution of the substance is oxidised by shaking it with an ice-cold aqueous solution of potassium ferricyanide. The thermal decomposition of the azo-compounds was carried out in xylene or petroleum solution in an atmosphere of nitrogen or carbon dioxide. By these reactions the following substances were obtained: *benzoyltriphenylmethylhydrazine*, m. p. 148°; *benzoylazotriphenylmethane*, m. p. 80—81° (decomp.); p-*bromobenzoyltriphenylmethylhydrazine*, m. p. 177°; p-*bromobenzoylazotriphenylmethane*, m. p. 67—68° (decomp.); p-*toluoyltriphenylmethylhydrazine*, m. p. 136—139°; p-*toluoylazotriphenylmethane*, m. p. 60° (decomp.); p-*dimethylaminobenzoyltriphenylmethylhydrazine*, m. p. 192—195°; p-*dimethylaminobenzoylazotriphenylmethane*, m. p. 77° (decomp.); p-*dimethylamino*-β-*benzpinacolin*, m. p. 224—226°; *benzoyltri*-p-*tolylmethylhydrazine*, m. p. 206—208° (decomp.); *benzoylazotri*-p-*tolylmethane*, m. p. 70—72° (decomp.); *tri*-p-*methyl*-β-*benzpinacolin*, m. p. 148—149°; p-*toluoyltri*-p-*tolylmethylhydrazine*, m. p. 176—178°; p-*toluoylazotri*-p-*tolylmethane*, m. p. 60—65° (decomp.); *tetra*-p-*methyl*-β-*benzpinacolin*, m. p. 145—146°; p-*dimethylaminobenzoyltri*-p-*tolylmethylhydrazine*, m. p. 180°; p-*dimethylaminobenzoylazotri*-p-*tolylmethane*, m. p. 69—70° (decomp.); *ethyl triphenylmethylhydrazinecarboxylate*, m. p. 145°; *ethyl triphenylmethylazocarboxylate*, $CPh_3{\cdot}N{:}N{\cdot}CO_2Et$, m. p. 98° (decomp.); *ethyl tri*-p-*tolylmethylhydrazinecarboxylate*, m. p. 134—135°; *ethyl tri*-p-*tolylmethylazocarboxylate*, m. p. 96° (decomp.). *Dicarbethoxyperoxide* was prepared by the interaction of ethyl chloroformate and sodium peroxide in chloroform solution. It is an oil which explodes violently at 45°.

R. W. West.

Action of thiosemicarbazide on certain aromatic nitro-compounds. M. Giua and R. Petronio (Gazzetta, 1925, **55**, 665—673; cf. A., 1923, i, 790; 1924, i, 338).—With aromatic halogenated nitro-derivatives containing a labile halogen atom, thiosemicarbazide reacts by means of a hydrogen atom of the hydrazine residue, yielding nitro-derivatives of β-phenylthiosemicarbazide, *e.g.*,

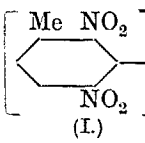
$$C_6H_2(NO_2)_3{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2.$$

With nitro-derivatives containing a labile nitro-group the reaction is somewhat complex. Thus, 3 : 4 : 6-trinitrotoluene (1 mol.) and thiosemicarbazide (1 mol.) yield 4 : 6-dinitro-*m*-tolyl-β-thiosemicarbazide and 4 : 6 : 4′ : 6′-dinitrodi-*m*-tolyl disulphide and probably also the compound, $C_6H_2Me(NO_2)_2{\cdot}N{:}N{\cdot}CS{\cdot}NH_2$, resulting from the oxidation of the former by the nitrous acid liberated; when 2 mols. of thiosemicarbazide are used per 1 mol. of 3 : 4 : 6-trinitrotoluene, 4 : 6-dinitro-*m*-tolyl-β-thiosemicarbazide is formed in almost pure condition. With 2 : 3 : 4-trinitrotoluene, a similar reaction takes place.

2 : 4-*Dinitrophenyl*-β-*thiosemicarbazide*, $C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}NH_2$ or $C_6H_3(NO_2)_2{\cdot}NH{\cdot}NH{\cdot}C(SH){:}NH$, from 1-chloro-2 : 4-dinitrobenzene, has m. p. 210° (decomp.). In presence of sodium acetate, the reaction yields 2 : 4 : 2′ : 4′-tetranitrodiphenyl sulphide.

2 : 4 : 6-*Trinitrophenyl*-β-*thiosemicarbazide* (*picryl*-β-*thiosemicarbazide*), obtained from picryl chloride, has m. p. 183—184° (decomp.), and yields *picrylazothiocarbamide*(?), $C_6H_2(NO_2)_3{\cdot}N{:}N{\cdot}CS{\cdot}NH_2$, m. p. 166° (decomp.), when treated with ferric chloride.

2 : 4-*Dinitro*-m-*tolyl*-β-*thiosemicarbazide*, prepared from 2 : 3 : 4-trinitrotoluene, has m. p. 203—204°. 2 : 6 : 2′ : 6′-*Tetranitrodi*-m-*tolyl sulphide* (I), m. p. 222°, is the principal product of the interaction of 2 : 3 : 4-trinitrotoluene (1 mol.) and thiosemicarbazide. 4 : 6-*Dinitro*-m-*tolyl*-β-*thiosemicarbazide* has m. p. 188° (decomp.).



(I.)

T. H. Pope.

4-*m*-Nitrophenylsemicarbazide and certain derivatives. A. S. Wheeler and T. T. Walker (J. Amer. Chem. Soc., 1925, **47**, 2792—2796).—4-m-*Nitrophenylsemicarbazide*, pale yellow, m. p. 138—139° (*hydrochloride*), is obtained by the action of hydrazine hydrate on *m*-nitrophenylcarbamide. 4-m-*Nitrophenylsemicarbazones* of the following ketones are described: *acetone*, yellow, m. p. 210—211°; *chloroacetone*, pale yellow, m. p. 238° to a dark brown liquid, after sintering at 223°; *methyl ethyl ketone*, similar, m. p. 205°; *acetophenone*, m. p. 211—212°; *benzophenone*, light yellow, m. p. 133—136°; *camphor*, m. p. 240—242°; and cyclo*hexanone*, m. p. 219—220°. The corresponding derivative of benzoquinone could not be purified.

F. G. Willson.

Diazotisation of picramide. L. Blangey (Helv. Chim. Acta, 1925, **8**, 780—783; cf. A., 1920, i, 887).—Picramide is diazotised in sulphuric acid solution by nitrosylsulphuric acid in 24 hrs., the solution then giving an 80% yield of azo-compound when coupled with β-naphthol in glacial acetic acid or ethyl alcohol, the temperature being kept at 2—3° during addition. An orange *dye* resulted from coupling with β-naphthol-6-sulphonic acid and a bluish-violet *dye* with β-naphthylamine-6-sulphonic acid. Both are very sensitive to alkalis.

G. M. Bennett.

Reaction between organic peroxides and organo-magnesium halides. H. GILMAN and C. E. ADAMS (J. Amer. Chem. Soc., 1925, **47**, 2816—2821).—Benzoyl peroxide (1 mol.) reacts with magnesium phenyl bromide (1 mol.) in benzene at 0° to −5°, with formation of phenyl benzoate and benzoic acid. If 2 mols. of the Grignard reagent are applied, the excess reacts with the ester with formation of triphenylcarbinol. Magnesium ethyl bromide yields similarly ethyl benzoate, whilst excess of magnesium *n*-butyl bromide affords phenyldi-*n*-butylcarbinol, and magnesium benzyl chloride yields, analogously, phenyldibenzylcarbinol. Succinic peroxide is inert towards magnesium phenyl bromide at low temperatures. At higher temperatures, violent reaction sets in after a period of quiescence, resulting in complex mixtures. Triacetone peroxide reacts with magnesium phenyl bromide in anisole, with production of phenyldimethylcarbinol and phenol, whilst ethyl peroxide in ether affords similarly phenetole and diphenyl. Triphenylmethyl peroxide is practically inert towards magnesium phenyl bromide in a boiling mixture of ether and benzene, whilst in boiling toluene *s*.-diphenoxytetraphenylethane is produced. The general reaction between organic peroxides and the Grignard reagent may thus be formulated: R·O·O·R + R′MgX → R·O·R′ + R·OMgX. The large proportion of diphenyl obtained from ethyl peroxide in this reaction suggests analogy between this peroxide and azobenzene (cf. Gilman and Pickens, A., 1925, i, 1336), and indicates the formula Et·O:O·Et for ethyl peroxide. F. G. WILLSON.

Organic peroxides. VIII. Further reactions which appear to proceed according to the *R·H* scheme. H. GELISSEN and P. H. HERMANS (Ber., 1925, **58**, [*B*], 2396—2399; cf. A., 1925, i, 663).—The action of benzoyl peroxide on Δ^{β}-pentene leads, according to Lippmann (A., 1910, i, 149), to the production of "amylene hydride" and a benzoic ester which is hydrolysed to benzoic acid and "diamylene oxide." It is shown that the course of the change probably follows the authors' *R·H* scheme. Lippmann's "amylene hydride" is probably benzene and the ester is the *benzoate* of γ-hydroxy-Δ^{β}-pentene, CHMe:CEt·OBz. The latter substance, when hydrolysed, gives γ-hydroxy-Δ^{β}-pentene, which immediately becomes isomerised to diethyl ketone and thence converted into the substance, CEt_2:CMe·CO·Et, which constitutes the "diamylene oxide."

Benzenesulphonic peroxide (cf. Weinland and Lewkowitz, A., 1903, i, 808; Fichter and Stocker, A., 1925, i, 239) is decomposed by water at 61° in accordance with the *R·H* scheme, yielding benzenesulphonic acid, phenol, and sulphur trioxide. H. WREN.

Derivatives (esters and sulphonic acids) of anthranilic and methylanthranilic acids. O. KELLER and G. SCHULZE (Arch. Pharm., 1925, **263**, 481—502).—Since it is still doubtful whether Ewins (J.C.S., 1912, **101**, 544) was correct in stating that damascenine (from *Nigella damascena*) is identical, and not isomeric, with the methyl ester of damasceninic acid, a number of esters of anthranilic and methylanthranilic acid have been investigated, and other experiments made. Keller's own results (A., 1908, i, 283) tend to confirm Ewins' statement, in that his so-called methyldamascenine (from *Nigella aristata*), which is admitted to be the above methyl damasceninate, is in part converted into damasceninic acid when its hydrochloride is crystallised from water. The following esters of anthranilic and *N*-methylanthranilic acid, on the other hand, are stable towards cold or hot water, or even hot dilute hydrochloric acid, but their hydrochlorides are hydrolytically dissociated in aqueous solution, and in this they again differ from damascenine.

The esters in question were prepared by the usual methods from the parent acid and the b. p. of each was determined by Siwoloboff's method. Methyl anthranilate has m. p. 24°, b. p. 256°; its hydrochloride crystallises with $1H_2O$ and has m. p. 178°. Ethyl anthranilate has b. p. 264°; *hydrochloride*, m. p. 168°. n-*Propyl anthranilate* has b. p. 270°; *hydrochloride*, m. p. 160°. Esters with alcohols of higher mol. wt. were not obtainable by the ordinary procedure. Methyl *N*-methylanthranilate (m. p. 22°, b. p. 255°) yields a *hydrochloride*, m. p. 137°, and the corresponding ethyl ester (b. p. 266°) yields a *hydrochloride*, m. p. 127°. Methylanthranilic acid forms no sodium salt in sodium carbonate solution; from such solution the acid is readily extracted by ether.

The opinion of Willstätter and Kahn (A., 1904, i, 235) that when sodium anthranilate is treated with an excess of methyl iodide in alkaline solution the sole product is methylanthranilic acid, and not the dimethyl-derivative, is confirmed.

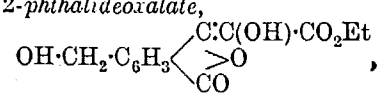
As a preliminary to an attempt to synthesise damasceninic acid by another method, various sulphoanthranilic acids have been prepared. When anthranilic acid is sulphonated by weakly fuming sulphuric acid at 180°, it yields primarily 2-amino-5-sulphobenzoic acid, but this is partly converted during the reaction, and also gradually when boiled with water, into sulphanilic acid. Attempts to prepare 2-amino-4-sulphobenzoic acid from 2-nitrotoluene-4-sulphonic acid (Hart, A., 1881, 1144) and 2-amino-3-sulphobenzoic acid from *o*-bromobenzoic acid gave unsatisfactory results. W. A. SILVESTER.

Reduction of aromatic nitro-cyano-compounds. H. RUPE and H. VOGLER (Helv. Chim. Acta, 1925, **8**, 832—838).—A number of nitro-cyano-compounds have been reduced by means of hydrogen and a nickel catalyst, the substance being dissolved in a mixture of ethyl acetate, ethyl alcohol, and water. *p*-Nitrophenylacetonitrile, *o*-nitroaniline, and *o*-nitrobenzylideneaniline are completely reduced to β-*p*-aminophenylethylamine, *o*-phenylenediamine, and *o*-aminobenzylaniline, respectively. In the reduction of *m*- and *p*-nitrobenzonitriles the aminobenzaldimine is produced and hydrolysed so that a good yield of the aminobenzaldehyde results. The following derivatives of *m*-aminobenzaldehyde are described: *acetyl*-derivative, m. p. 122°, *semicarbazone*, decomp. above 280°, *oxime*, m. p. 195°. In the case of *o*-nitrophenylacetonitrile and *o*-nitrobenzonitrile, the amino-group appears to protect the cyano-group from reduction, the products isolated being *o*-aminophenyl-

acetonitrile and *anthranilamide*, m. p. 110°. *Ammonium anthranilate hydrochloride* is monoclinic with $a : b : c = 0{\cdot}4566 : 1 : 1{\cdot}4362$, $\beta = 75°\ 34'$ and d 1·1744.

G. M. BENNETT.

Action of halogens on 2 : 4-dimethylbenzoyl chloride. W. H. PERKIN, jun., and J. F. S. STONE (J.C.S., 1925, **127**, 2275—2297; cf. Davies and Perkin, J., 1922, **121**, 2203).—In ultra-violet light bromine reacts at 160° with 2 : 4-dimethylbenzoyl chloride to form mainly 2-*bromomethyl*-p-*toluoyl bromide*, b. p. 169—171°/15 mm., together with some 4-*bromomethyl*-o-*toluoyl bromide* (not isolated). Decomposition of the mixture with formic acid yields 2-*bromomethyl*-p-*toluic acid*, m. p. 143—145°, which forms 4-*methyl*-1 : 2-*phthalide*, m. p. 118°, at the m. p. With methyl alcohol, the mixed acid bromides yield *methyl* 2-*bromomethyl*-p-*toluate*, which when boiled gives 4-methyl-1 : 2-phthalide. This phthalide on hydrolysis yields 2-*hydroxymethyl*-p-*toluic acid*, m. p. 133°, with regeneration of the phthalide. The more stable ester, *methyl* 4-*bromomethyl*-o-*toluate*, m. p. 56°, forms on hydrolysis 4-*hydroxymethyl*-o-*toluic acid*, m. p. 142°. In this hydrolysis 4 : 4′-*dicarboxy*-3 : 3′-*dimethyldibenzyl ether*, m. p. 222°, is also formed. At 150—190°, the bromination of 2 : 4-dimethylbenzoyl chloride yields mainly an acid bromide, b. p. 223—228°/15 mm., from which 2 : 4-*di*(*bromomethyl*)-*benzoic acid*, m. p. 158°, is obtained. The *methyl* ester, m. p. 84°, forms on boiling 4-*bromomethyl*-1 : 2-*phthalide*, m. p. 159°, and this, on hydrolysis, yields 4-*hydroxymethyl*-1 : 2-*phthalide*, m. p. 125°, which is further hydrolysed to 2 : 4-*di*(*hydroxymethyl*)*benzoic acid*, m. p. 146°. 4-Hydroxymethyl-1 : 2-phthalide condenses with ethyl oxalate yielding *ethyl* 4-*hydroxymethyl*-1 : 2-*phthalideoxalate*,



m. p. 170°. Potassium cyanide reacts with 2 : 4-di(bromomethyl)benzoic acid to form 4-*cyanomethyl*-1 : 2-*phthalide*, m. p. 124°, from which the *amide*, m. p. 219° (decomp.), and thence 1 : 2-*phthalide*-4-*acetic acid*, m. p. 162°, is obtained. Higher brominated derivatives of 2 : 4-dimethylbenzoic acid proved too unstable for isolation. When 2 : 4-dimethylbenzoyl chloride is treated with chlorine at 180—210° in ultra-violet light, a mixture of the di-, tetra-, and some tri-chlorinated dimethylbenzoyl chloride is obtained. Distillation of the methyl esters prepared from these yields 4-*chloromethyl*-1 : 2-*phthalide*, m. p. 144°. The mixture of acid chlorides digested with chalk forms 2 : 4-*dialdehydobenzoic acid*, m. p. 141° (*dianilino*-derivative, m. p. 208°, *disemicarbazone*, decomp. 335°, *anhydrophenylhydrazone*, m. p. 266°), and some 4-*aldehydo*-1 : 2-*phthalide*, m. p. 160°, *phenylhydrazone*, m. p. 172°, which undergoes the Cannizzaro reaction, yielding a mixture of 2 : 4-di(hydroxymethyl)benzoic acid, m. p. 146°, and 2-*hydroxymethylterephthalic acid*; this last at 110°, forms 1 : 2-*phthalide*-4-*carboxylic acid*, m. p. 280°. Suitable chlorination of 2 : 4-dimethylbenzoyl chloride yields 2 : 4-*di*(*dichloromethyl*)*benzoyl chloride*, b. p. 192—193°/10 mm., from which 2 : 4-*di*(*dichloromethyl*)-*benzoic acid*, m. p. 160°, is obtained. The *methyl* ester of this acid, b. p. 186—188°/12 mm., decomposes at higher temperatures into 4-*dichloromethyl*-1 : 2-*chlorophthalide*, b. p. 297°/763 mm. More thorough chlorination of 2 : 4-dimethylbenzoyl chloride gives an acid chloride fraction, b. p. 188—192°/14 mm., which after hydrolysis contains 4-*aldehydophthalic acid* (not isolated), and 2-*aldehydoterephthalic acid*, m. p. 242°, *anhydrophenylhydrazone*, m. p. 327°; the *oxime*, m. p. 136° (decomp.), changes into the *imide* of *trimellitic acid*, m. p. 242°. The 2-aldehydo-acid, when boiled with 25% sodium hydroxide, forms 1 : 2-phthalide-4-carboxylic acid, m. p. 280°. Impure 4-aldehydophthalic acid (above) forms a *phenylhydrazone hydrate*, m. p. 118°; anhydrous *phenylhydrazone*, m. p. 174°; and *phenylhydrazone anhydride*, m. p. 217°. Chlorination of 2 : 4-dimethylbenzoyl chloride until six chlorine atoms have been absorbed yields 70—80% of 2 : 4-*di*(*trichloromethyl*)*benzoyl chloride*, b. p. 192—196°/15 mm., which with formic acid gradually forms 2 : 4-*di*(*trichloromethyl*)*benzoic acid*, m. p. 171°. The *methyl* ester decomposes on heating into 4-*trichloromethylphthalyl chloride*, b. p. 186—187°/12 mm., *dianilide*, m. p. 220°. Other derivatives are the *amide*, m. p. 176° (decomp.), and *anilide*, m. p. 203° (decomp.). B. W. ANDERSON.

Polymerisation and depolymerisation by light of different wave-lengths. II. α- and β-*trans*-Cinnamic acid, *allo*cinnamic acid, and their dimerides. H. STOBBE and A. LEHFELDT (Ber., 1925, 58, [*B*], 2415—2427; cf. A., 1924, ii, 11).—According to Stoermer (A., 1910, i, 114; 1911, i, 295) and Stobbe and Steinberger (A., 1922, i, 1018) α-*trans*-cinnamic acid, m. p. 133°, and *allo*cinnamic acid become isomerised to an equilibrium mixture when exposed to light in solution or in the molten condition, the radiations of wave-length 320—270 μμ being most active. The reaction is greatly accelerated by addition of hydrochloric acid. When the solid acids are exposed to sunlight, isomerisation is accompanied by polymerisation, whereby α-*trans*-cinnamic acid yields mainly α-truxillic acid with a little β-truxinic acid, and *allo*cinnamic acid affords chiefly β-truxinic acid in addition to *trans*-cinnamic acid and a little α-truxillic acid. Similar reactions proceed in aqueous suspension and are then accelerated by the presence of hydrochloric acid or sodium chloride singly, whereas the latter causes no acceleration if hydrochloric acid is already present. Rays of long wave-length favour polymerisation, which is hindered by those of shorter wave-length. Exposure of α-truxillic and β-truxinic acids to light of short wave-length causes their depolymerisation to *trans*- and *cis*-cinnamic acids, respectively, each dimeride giving the monomeride from which it is formed by exposure to longer rays. Extension of similar observations to suspensions of the acids in benzene and aqueous solutions of their sodium salts proves that an equilibrium is set up according to the scheme : α-truxillic acid $\underset{\text{short radiations}}{\overset{\text{long radiations}}{\rightleftarrows}}$ *trans*-cinnamic acid $\rightleftarrows$ *cis*-cinnamic acid $\underset{\text{short radiations}}{\overset{\text{long radiations}}{\rightleftarrows}}$ β-truxinic acid.

Experiments on the behaviour of β-*trans*-cinnamic

acid when exposed to sunlight and re-examination according to the methods of de Jong (A., 1922, i, 339) show that the metastable β-*trans*-cinnamic acid is much more readily isomerised than the stable α-*trans*-cinnamic acid, whereby *cis*-cinnamic acid is produced; the latter acid is directly polymerised by light of longer wave-length to β-truxinic acid. The β-*trans*-acid therefore readily affords good yields of β-truxinic acid, whereas the difficultly isomerised α-*trans*-acid affords little β-truxinic but much α-truxillic acid.

It cannot yet be decided whether the *trans*-cinnamic acids are chemical isomerides or represent two forms of a dimorphous *trans*-cinnamic acid. H. WREN.

p-Dimethylaminodiphenylacetic acid. DALIP SINGH (J.C.S., 1925, **127**, 2445—2449).—By the action of magnesium phenyl bromide on ethyl *p*-dimethylaminophenylglyoxylate, *ethyl* p-*dimethylaminobenzilate*, m. p. 97°, and the corresponding *acid*, m. p. 50—55°, were obtained, p-*dimethylaminotetraphenylethylene glycol*, m. p. 144°, being a by-product in this reaction. The above acid on reduction yielded p-*dimethylaminodiphenylacetic acid*, m. p. 105°. The *barium* salt of this acid gave on dry distillation *di*-p-*dimethylaminobenzhydryl ketone*, m. p. 190°, amongst other products, but none of the desired allene derivative. *Ethyl phenyl-4-pyridylpyruvate*, m. p. 124°, and the corresponding *acid*, m. p. about 110° (*oxime hydrochloride*, m. p. 53°, *sodium* salt), were synthesised. The ester condensed with *o*-phenylenediamine to form 2-α-4-*pyridylbenzyl*-3-*quinoxalone*, $C_6H_4<\begin{matrix}N{=}C\cdot CHPh\cdot C_5H_4N\\ NH\cdot CO\end{matrix}$, m. p. 295°.

B. W. ANDERSON.

Additive product of mandelic acid and benzene. C. W. ZAHN (Rec. trav. chim., 1925, **44**, 1048—1050).—Mandelic acid forms a molecular *compound* with benzene of the composition $CHPh(OH)\cdot CO_2H,C_6H_6$, biaxial crystals, stable only in contact with benzene or its vapour, and decomposed on heating, the transition temperature as determined in a dilatometer being 32·6—32·7°. G. M. BENNETT.

Catalytic reduction of some cyano-compounds of naphthalene. H. RUPE and A. METZGER (Helv. Chim. Acta, 1925, **8**, 838—848).—Nitro-nitriles of the naphthalene series are reduced by hydrogen in presence of nickel (cf. Rupe and Vogler, p. 63) to amino-nitriles, the cyano-group being protected by the amino-group. On the other hand, nitriles substituted by other atoms or groups such as Br, OH, SO_3H are reduced under similar conditions, the products being primary and secondary amines with the aldehyde as an occasional by-product. The action of the amino-group is not due to its basic properties, since the product of benzoylation, 5-*benzamido-α-naphthonitrile* (m. p. 211—212°), is also not reducible.

5-Nitro-α- and -β-naphthonitriles and 1-nitro-β-naphthonitrile yield the corresponding aminonitriles. Reduction of sodium α-naphthonitrile-4-sulphonate in aqueous solution gives a good yield of 1-*aminomethylnaphthalene*-4-*sulphonic acid* (*sodium* and *barium* salts described). From 5-bromo-α-naphthonitrile the products of reduction are: 5-*bromo-α-naphthaldehyde*, m. p. 102—103°, volatile in steam (*semicarbazone*, decomp. 257—259°, *oxime*, m. p. 133—134°), 5-*bromo*-1-*aminomethylnaphthalene*, m. p. 138—139° (decomp. 141°) (*hydrochloride*, *nitrate*, and *oxalate* described), and *di*-(5-*bromo*-1-*naphthylmethyl*)*amine*, m. p. 142° (*hydrochloride* and *nitrate* described). Reduction of 5-*bromo*-β-*naphthonitrile* furnishes: 5-*bromo*-β-*naphthaldehyde*, m. p. 78°, volatile in steam (*oxime*, m. p. 178°, *semicarbazone*, m. p. 270°, *phenylhydrazone*, m. p. 151°), 5-*bromo*-2-*aminomethylnaphthalene*, m. p. 111—112° (*hydrochloride*, *nitrate*, and *hydrogen oxalate* described), and a trace of *di*-(5-*bromo*-β-*naphthylmethyl*)*amine hydrochloride*. *o*-Hydroxybenzonitrile is reduced to *di*(*o-hydroxybenzyl*)*amine*, m. p. 162°.

G. M. BENNETT.

Phenylalanine series. VI. Decarboxylation of tyrosine and leucine. E. WASER (Helv. Chim. Acta, 1925, **8**, 758—773; cf. A., 1925, i, 540).—Dry distillation of tyrosine gives tyramine in 70—75% yield. Quantities of 500 g. of tyrosine are converted into tyramine (yield 90—95%) by solution in 3—4 parts of fluorene at 280—290°. The base is separated as the hydrochloride (m. p. 271—272°, corr.), crystallised from saturated brine, converted into the *sulphite*, m. p. 297—298°, and finally liberated, or, better, the crude material is distilled under reduced pressure, b. p. 205—207°/25 mm., 195°/13 mm., 165—167°/2 mm., m. p. 164—164·5°. Dry distillation of leucine yields *iso*amylamine (67%) together with leucineimide (m. p. 268°) and *iso*butyl cyanide, whereas when the decomposition is carried out in fluorene at 235° the yield of the first is 97% of the theoretical. G. M. BENNETT.

Conversion of r-phenyl-α-naphthylglycollic acid into ketones. A. MCKENZIE and H. J. TATTERSALL (J.C.S., 1925, **127**, 2522—2530).—Phenyl-α-naphthylglycollic acid was prepared from ethyl benzoylformate and magnesium α-naphthyl bromide and the acid converted into phenyl-α-naphthylchloroacetyl chloride. The chloride reacts with excess of magnesium phenyl bromide to form α-naphthyldeoxybenzoin, phenyl-α-naphthylketen probably being first formed. α-Naphthyldeoxybenzoin treated with methyl iodide yields αβ-*diphenyl*-α-(α-*naphthyl*)*propan*-β-*ol*, m. p. 124—125°. Phenyl-α-naphthylglycollic acid on reduction with red phosphorus and hydriodic acid gives phenyl-α-naphthylacetic acid, the chloride of which, heated with aluminium chloride and benzene, yields, not α-naphthyldeoxybenzoin, but a *compound*, $C_{18}H_{12}O$, m. p. 115·5—116·5°. By the action of different Grignard reagents on phenyl-α-naphthylchloroacetyl chloride, *phenyl-α-naphthylacetone*, $C_{10}H_7\cdot CHPh\cdot COMe$, m. p. 85°, *phenyl-α-naphthylacetonaphthone* (*phenyl-α-naphthylmethyl α-naphthyl ketone*), m. p. 126°, and *phenyl-α-naphthylmethyl* p-*tolyl ketone*, m. p. 142°, were obtained. B. W. ANDERSON.

Odour and molecular asymmetry. II. J. VON BRAUN and W. TEUFFERT (Ber., 1925, **58**, [*B*], 2210—2215).—It is shown in the case of the active and inactive *m*-methyl*cyclo*hexylethylene oxides that isomerides of this type may differ from one another in odour (cf. von Braun and Kaiser, A., 1924, i, 3).

d-*m*-Methyl*cyclo*hexanone, prepared from pulegone,

is converted by zinc and ethyl bromoacctate into ethyl *d*-1-hydroxy-3-methyl*cyclo*hexyl-1-acetate, b. p. 126—128°/15 mm., d_4^{15} 1·004, $[\alpha]_D$ +1·44°, and thence by potassium hydrogen sulphate at 160° into ethyl 3-methyl-Δ^1-*cyclo*hexenyl-1-acetatc, b. p. 107—109°/15 mm., d_4^{14} 0·9644, and 3-methyl-Δ^1-*cyclo*hexenyl-1-acetic acid, b. p. 146°/15 mm., d_4^{14} 1·0253. The unsaturated ester is hydrogenated in methyl-alcoholic solution in the presence of palladium to *ethyl* d-3-*methyl*cyclo*hexylacetate*, b. p. 107—110°/18 mm., d_4^{15} 0·9322, n_D^{15} 1·4442, $[\alpha]_D$ −7° 25′, which is hydrolysed to d-3-*methyl*cyclo*hexylacetic acid*, b. p. 148°/18 mm., d_4^{20} 0·9847, n_D^{20} 1·4595, $[\alpha]_D$ −9° 26′. The latter compound is converted by successive treatment with bromine and phosphorus and ethyl alcohol into *ethyl* d-3-*methyl*cyclo*hexylbromoacetate*, b. p. 139—140°/18 mm., d_4^{18} 1·2528, n_D^{18} 1·4775, $[\alpha]_D$ −6° 3′, and thence by dimethylamine in dry benzene into *ethyl* 3-*methyl*-cyclo*hexyldimethylaminoacetate*,

$$C_6H_{10}Me\cdot CH(NMe_2)\cdot CO_2Et,$$

b. p. 127°/16 mm., d_4^{20} 0·9398, n_D^{20} 1·4553, $[\alpha]_D$ −5° 13′ (*hydrochloride*, m. p. 187°; *methiodide*, m. p. 161°; *picrate*). Reduction of ethyl 3-methyl*cyclo*hexyl-dimethylaminoacetate by sodium and alcohol leads to the formation of β-*dimethylamino*-β-3-*methyl*-cyclo*hexylethyl alcohol*, $C_6H_{10}Me\cdot CH(NMe_2)\cdot CH_2\cdot OH$, b. p. 128°/16 mm., d_4^{18} 0·9351, n_D^{18} 1·4742, $[\alpha]_D$ −6° 10′ (*picrate*; *hydrochloride*; *methiodide*, m. p. 160—161°). The alcohol is transformed into the quaternary iodide which, when treated with silver oxide and subsequently distilled, affords d-3-*methyl*cyclo*hexyl-ethylene oxide*, $C_6H_{10}Me\cdot CH<\begin{matrix}O\\|\\CH_2\end{matrix}$, b. p. 72—73°/ vacuum), d_4^{18} 0·9165, n_D^{18} 1·4527, $[\alpha]_D$ −10° 54′. *d*-3-Methyl*cyclo*hexylethylene glycol, b. p. 138—140°/16 mm., is prepared by the action of water at 160—170° on the oxide, which with dilute sulphuric acid appears to yield 3-methyl*cyclo*hexylacetaldehyde.

The following constants are recorded for the analogous series of optically inactive compounds: ethyl 1-hydroxy-3-methyl*cyclo*hexyl-1-acetatc, b. p. 126—128°/15 mm., d_4^{15} 1·004; *ethyl* 3-*methyl*-Δ^1-cyclo*hexenylacetate*, b. p. 107—110°/15 mm., d_4^{16} 0·9626; 3-*methyl*-Δ^1-cyclo*hexenylacetic acid*, b. p. 146°/15 mm., d_4^{16} 1·023; *ethyl* 3-*methyl*cyclo*hexylacetate*, b. p. 107—110°/18 mm., d_4^{14} 0·9338, n_D^{14} 1·4434; 3-*methyl*cyclo*hexylacetic acid*, b. p. 148°/18 mm., d_4^{15} 0·9911, n_D^{15} 1·4607; *ethyl* 3-*methyl*cyclo*hexylbromoacetate*, b. p. 139—140°/18 mm., d_4^{15} 1·255, n_D^{15} 1·4771; *ethyl* 3-*methyl*-cyclo*hexyldimethylaminoacetate*, b. p. 127°/18 mm., d_4^{16} 0·943, n_D^{16} 1·4544 (*hydrochloride*, m. p. 189°; *methiodide*, m. p. 177°; *picrate*); β-*dimethylamino*-β-3-*methyl*cyclo*hexylethyl alcohol*, b. p. 128°/16 mm., d_4^{18} 0·9351, n_D 1·4740 (*picrate*; *hydrochloride*; *methiodide*, m. p. 173—174°); 3-*methyl*cyclo*hexylethylene oxide*, b. p. 72—73°/vacuum, d_4^{18} 0·9165, n_D^{18} 1·4527; 3-*methyl*cyclo*hexylethylene glycol*, b. p. 138—140°/16 mm.; 3-methyl*cyclo*hexylacetaldehyde. H. WREN.

Ethyl 1-ketohydrindyl-2-glyoxylate. H. LEUCHS and G. KOWALSKI (Ber., 1925, **58**, [*B*], 2288—2293).—*Ethyl* 1-*ketohydrindyl*-2-*glyoxylate*, $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>CH\cdot CO\cdot CO_2Et$, m. p. 71—72°, is readily prepared by the action of alcoholic sodium ethoxide on a mixture of 1-hydrindone and ethyl oxalate. Unlike the analogous compound prepared from 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (Hückel and Goth, A., 1924, i, 1196), it does not readily lose carbon monoxide with production of ethyl 1-hydrindone-2-carboxylate. It is converted by aniline at 100° into the corresponding *anilide*, m. p. 229—231°, and by gentle hydrolysis into 1-*ketohydrindyl*-2-*glyoxylic acid*, m. p. 215° (decomp.) after softening at 205°, which loses carbon monoxide and carbon dioxide at 220—230°, giving thereby 1-hydrindone in small amount. The ester is converted by cold phenylhydrazine into the additive *compound*, $C_{19}H_{20}O_4N_2$, m. p. 95—96° after softening at 90°, whereas in boiling alcoholic solution two apparently stereoisomeric *phenylhydrazones*, $C_{19}H_{18}O_3N_2$, m. p. 156—158° and 173—174°, are produced. The form of higher m. p. is rapidly transformed by aqueous 5*N*-hydrochloric acid into the anhydride $\begin{matrix}CH_2-C\cdot C(CO_2Et)\\C_6H_4\cdot C=\!=\!=N\end{matrix}>NPh$, m. p. 126—127°, whereas that of lower m. p. remains unchanged. Either form yields the anhydride when treated with alcoholic hydrochloric acid owing to the transformation of the variety of higher into that of lower m. p. which occurs also when the former is melted; the reverse change could not be accomplished. Ethyl 1-ketohydrindyl-2-glyoxylate is converted by semicarbazide into the corresponding *semicarbazone*, $C_{14}H_{15}O_4N_2$, m. p. 161—163°, which is transformed by alcoholic hydrogen chloride into the *compound*, $C_{13}H_{12}O_2N_2$, m. p. 173—174°. The *oxime* of the ester, m. p. 155—157° after softening at 145°, is similarly not simply converted into an anhydride by alcoholic hydrogen chloride, but yields a *compound*, $C_{15}H_{17}O_4N$, m. p. 61°, containing two ethoxy-groups. Attempts to alkylate ethyl 1-ketohydrindyl-2-glyoxylate were unsuccessful. H. WREN.

Formation and stability of associated alicyclic systems. II. Formation and disruption of dicyclic dihydroresorcinols. E. H. FARMER and J. Ross (J.C.S., 1925, **127**, 2358—2369).—The action of ethyl sodiomalonate on 1-methyl-Δ^1-*cyclo*hexan-3-one (I) at 100° in presence of alcohol yielded mainly *ethyl* β-*methylpimelate*-β-*acetate* (II), b. p. 200°/18 mm. The formation of this ester must have been preceded by a Michael addition followed by internal condensation and two stages of ring fission. With sodium the ester yielded β-*methylpimelic*-β-*acetic acid*, m. p. 125° (*imide*, m. p. 139°; *anhydro-acid*, m. p.

(I.) $CMe<\begin{matrix}CH-CO\\CH_2\cdot CH_2\end{matrix}>CH_2$ $CMe<\begin{matrix}CH_2\cdot CO_2Et\\[CH_2]_3\cdot CO_2Et\\CH_2\cdot CO_2Et\end{matrix}$ (II.)

$CMe<\begin{matrix}CH_2\cdot CH_2\\CH_2-CO\end{matrix}>CH\cdot CO_2Et$
$CH_2\cdot CO_2Et$ (III.)

$CMe<\begin{matrix}CH_2\cdot C(OH)\\CH_2-CH_2\\CH_2-CO\end{matrix}>C$ (IV.)

83°), and also *ethyl* 1-*methyl*cyclo*hexan*-3-*one*-4-*carboxylate*-1-*acetate* (III), b. p. 182°/15 mm., which on hydrolysis gave 1-*methyl*cyclo*hexan*-3-*one*-1-*acetic acid*, m. p. 37° (*silver* salt; *semicarbazone*, m. p. 184°), and from this *ethyl* 1-*methyl*cyclo*hexan*-3-*one*-1-*acetate* (b. p. 147°/15 mm.; *semicarbazone*, m. p. 159°) was obtained. The last-mentioned ester gave with sodium

methoxide a product which was probably the dicyclic dihydroresorcinol (IV). In determining the constitution of these products, *β-methyladipic-β-acetic acid*, m. p. 149°, *ethyl ethane-*$^{1:2}$*II*$^{1:4}$*-1-methylcyclohexane-3 : 5-dione-2-carboxylate*, m. p. 111°, *ethyl hydrogen 1-methylcyclohexan-3-one-4-carboxylate-3-acetate*, m. p. 91°, and other compounds were obtained.

B. W. ANDERSON.

Action of various diamines on naphthalic anhydride. A. BISTRZYCKI and J. RISI (Helv. Chim. Acta, 1925, **8**, 810—820; cf. A., 1923, i, 848).—The action of hydrazine hydrate in boiling alcoholic solution on naphthalic anhydride yielded 1 : 8-*naphthalylhydrazide*, $C_{10}H_6<^{CO\cdot NH}_{CO\cdot NH}$, m. p. 254—255° (*diacetyl*-derivative, m. p. 214—215°), which is indifferent to benzaldehyde, whilst in other experiments under similar conditions the product was the isomeric *N*-aminonaphthalimide, $C_{10}H_6<^{CO}_{CO}>N\cdot NH_2$ (m. p. 262°), of Ostrogovich and Mihailescu (A., 1912, i, 311), which readily forms a benzylidene derivative, m. p. 206°, and a *monoacetyl*-derivative, m. p. 260—261°.

Ethylenediamine and naphthalic anhydride in alcoholic solution combine to give N-β-*aminoethylnaphthalamic acid*,

$$C_{10}H_6(CO_2H)\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot NH_2,$$

decomp. 196—197°, soluble in alkalis or acids (*lead* salt described) and converted on heating at 230—240° into 1′ : 8′-*naphthoylene-4 : 5-dihydro-1 : 2-iminazole*, $C_{10}H_6<^{CO\cdot N\cdot CH_2}_{C=N\cdot CH_2}$, m. p. 179—180°.

With *o*-phenylenediamine, naphthalic anhydride yields N-o-*aminophenylnaphthalamic acid*,

$$C_{10}H_6(CO_2H)\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2,$$

m. p. 236—238° (decomp.) (*silver* salt described), converted at 150° into 1 : 2(1′ : 8′)-naphthoylenebenziminazole (m. p. 189°, whereas Chakravarti, A., 1925, i, 162, gives m. p. 198°). In the same way, 1 : 2-naphthylenediamine gives N-1-*amino-2-naphthylnaphthalamic acid*,

$$C_{10}H_6(CO_2H)\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH_2,$$

m. p. 143—144° (bath preheated) (*silver* salt described), converted on heating into 1 : 2(1′ : 8′)-naphthoylene-1 : 3-naphthiminazole (m. p. 238—239°, decomp., whereas Chakravarti gives m. p. 256°). Phthalic anhydride and 1 : 2-naphthylenediamine yield N-(1-*amino-2-naphthyl*)*phthalamic acid*,

$$C_6H_4(CO_2H)\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH_2,$$

m. p. 205° (decomp.) (*silver* salt described), the constitution of which follows from its conversion, by elimination of the amino-group, into N-2-naphthylphthalamic acid (m. p. 198—200° decomp.). The aminonaphthylphthalamic acid is converted, on heating, into 1 : 2(1′ : 2′)-benzoylene-α-naphthiminazole (m. p. 208°; Lieb gives 213°, A., 1919, i, 175).

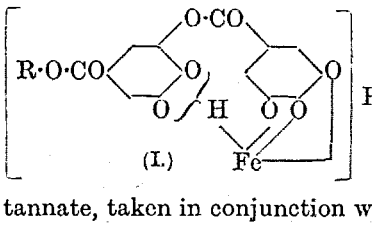
G. M. BENNETT.

Phenylalanine series. VII. Synthesis of *l*-3 : 4 : 5-trihydroxyphenylalanine. E. WASER, A. LABOUCHÈRE, and H. SOMMER (Helv. Chim. Acta, 1925, **8**, 773—779; cf. A., 1921, i, 788; 1924, i, 514).—Dinitrotyrosine (A., 1915, i, 1060) is best reduced by means of hydrogen and a platinum catalyst in acid solution, the diaminotyrosine being separated as the hydrochloride or sulphate. The latter is converted into the corresponding *l*-3 : 4 : 5-trihydroxyphenylalanine by adding barium nitrite to the solution of the sulphate and running the resultant solution into a boiling saturated solution of copper sulphate. The crude product decomposes at 225—230°. Its colour reactions under a variety of conditions are described in detail and compared with those of pyrogallol.

G. M. BENNETT.

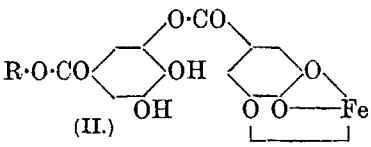
Formation and ageing of written characters. II. F. ZETSCHE and A. LOOSLI (Annalen, 1925, **445**, 283—296; cf. A., 1924, i, 401).—*Ferric salts* have been prepared of the following hydroxy-compounds by methods similar to those previously described (*loc. cit.*): *trihydroxybenzophenone*, $C_{13}H_7O_4Fe,2{\cdot}5H_2O$, black, insoluble, no m. p., soluble in alkali with reddish-brown coloration and deposition of ferric hydroxide; *gallacetophenone*, $C_8H_5O_4Fe,1{\cdot}5H_2O$, dark olive-green, soluble to a greenish-black, colloidal solution; *maclurin*, $C_{13}H_7O_6Fe,2H_2O$, similar; *luteolin*, $[(C_{15}H_8O_6)_2Fe]H,3H_2O$, olive-green, insoluble; *quercetin*, $C_{15}H_7O_7Fe,1{\cdot}5H_2O$, greenish-black, insoluble, soluble in alkali with yellow coloration and deposition of ferric hydroxide; *rhamnetin*, $C_{16}H_9O_7Fe,2{\cdot}5H_2O$, similar; *morin*, (1 : 1), $C_{15}H_7O_7Fe,2H_2O$, olive-brown, soluble in ethyl acetate, becoming insoluble on exposure to light; *morin* (2 : 1), $C_{30}H_{17}O_{14}Fe,3H_2O$, similar. The following *aluminium* salts are also described: *aluminium gallate*, $C_7H_2O_5Al,H_2O$, colourless, darkening in the atmosphere owing to oxidation; *maclurin*, $C_{13}H_7O_6Al,2H_2O$, yellow, readily hydrolysed, darkening on exposure; *morin*, $C_{15}H_7O_7Al,2H_2O$, similar; and O-*benzoylpyrogallol*, $C_{26}H_{17}O_8Al,2H_2O$, colourless, insoluble. Maclurin and morin are obtained from yellow-wood extract by dissolving the latter in 5% alkali, adding aluminium sulphate solution until the mixture is faintly acid, shaking thoroughly, and filtering. Soxhlet extraction of the residue with water yields the maclurin, which mostly crystallises out, whilst the morin is obtained by extracting the water-freed residue with alcohol, and pouring the evaporated alcoholic extract into dilute hydrochloric acid.

Whilst the addition of 1 mol. of alkali to the ferric derivatives (Fe : phenol = 1 : 1) of di- and tetrahydric phenols (group 1) produces no colour change, those of similar composition derived from trihydric phenols (group 2) change from bluish-violet to wine-red, the addition of a second mol. of alkali producing a change towards red in both groups. The maximal ferric salts of digalloylglycol, trigalloylglycerol, hexagalloylmannitol, and pentagalloylglucose behave analogously, the wine-red tint being attained when 1 mol. of alkali has been added for each galloyl group. The similar behaviour of triferritannate, taken in conjunction with the non-formation



(I.)

of dextrose when its aqueous solution is boiled for long periods, gives support to the formula (II) for this salt, rather than (I), the decomposition of the molecule on further oxidation being probably a fission of the depside linking, the ferric gallate then losing carbon dioxide, and the resulting pyrogallol being then further oxidised to purpurogallein and phenolic humic acids.



(II.)

Oxidation of ferric gallate and tannate by hydrogen peroxide in aqueous solution, or by atmospheric oxygen at the b. p., affords ferrous oxalate, which must therefore be regarded as the end-product of the oxidative change of written characters. In this respect, the tannate is more resistant than the gallate.

The intensity of the red coloration obtained by the addition of salicylic acid to solutions of iron salts "aged" by oxidation gives a measure of the proportion of iron liberated as hydroxide during the ageing process; this liberation must occur if the process is accompanied by the formation of products of high mol. wt., such as purpurogallein, which are still only capable of holding one atom of iron. Considerable proportions of iron were in this way found to have been liberated from iron salts of pyrocatechol, pyrogallol, and gallic acid. Derivatives of digallic acid, however, such as Chinese tannin, yield, by the decomposition process as above formulated, a second galloyl derivative which is itself capable of combining with liberated iron, and this may explain the greater permanency of inks made with this material.

The autoxidative decomposition of iron compounds of hæmatoxylin, hæmin, and brasilin proceeds similarly to that of the corresponding gallic acid derivatives, but resembles that of pyrocatechol and pyrogallol in the large proportion of oxygen absorbed. Carbon dioxide is liberated only towards the end of the oxidation. F. G. Willson.

Constitution of Grignard's magnesium compounds. III. J. Meisenheimer (Annalen, 1925, **446**, 76—86; cf. A., 1925, i, 527).—When benzaldehyde and magnesium ethyl bromide react in ice-cold ether solution for 30 min., a crystalline precipitate is obtained which, after washing with ether and quickly drying between filter-papers, gives a considerable quantity of ethane on decomposition with ammonium chloride solution. If the drying is continued for 10 min., no ethane is obtained on decomposition. It is probable that the precipitate consists of a mixture of (I) Ph·CHO—MgEtBr and (II) CHPhEt·O·MgBr, and that (I) changes rapidly into (II). When the aldehyde and magnesium ethyl bromide were allowed to react for 24 hrs., no ethylene could be detected, although 10% of the aldehyde was reduced to benzyl alcohol. It is evident that the benzyl alcohol is not formed by the changing of (I) into $CH_2Ph·O·MgBr+C_2H_4$, but by a secondary reaction between phenylethylcarbinol and benzaldehyde: $CHPhEt·O·MgBr+Ph·CHO \longrightarrow Ph·CO·Et+CH_2Ph·O·MgBr$. The magnesium bromide compound of phenylethylcarbinol on boiling in benzene solution with benzaldehyde for 3 hrs. gave 65% of the theoretical yield of benzyl alcohol and 47% of propiophenone, no residual benzaldehyde being detected (cf. the reduction of aldehydes by magnesium ethoxychloride, Meerwein and Schmidt, A., 1925, i, 1239). When magnesium *iso*butyl bromide was used, 12% out of a total of 25% of the benzyl alcohol formed was due to the decomposition of the compound (I) with formation of *iso*butylene.

The method for the determination of benzyl alcohol in presence of phenylethylcarbinol by conversion into its *p*-nitrobenzoate has been improved and may be applied to mixtures containing as little as 5% of the alcohol. By a better method, depending on the refractive indices of mixtures of phenylethylcarbinol and benzyl alcohol, it is shown that the interaction of molecular proportions of magnesium ethyl bromide or iodide and benzaldehyde in ice-cold ether solution leads to the formation of the following amounts of benzyl alcohol in the stated times: very short time, 2—3%; 3 hrs., 5—6%; 24 hrs., 12%; after removal of the ether and boiling the residue in benzene solution for 3 hrs., 17—20%. A method for the determination of propiophenone is based on its conversion into its 2:4-*dinitrophenylhydrazone*, m. p. 190—191°. R. W. West.

2-Amino-3-methoxybenzaldehyde and some derivatives. J. Tröger and E. Dunker (J. pr. Chem., 1925, [ii], **111**, 207—216; cf. following abstract).—2-Nitro-3-methoxybenzaldehyde, m. p. 102° (Rieche, A., 1889, 1169), dissolved in a solution of sodium hydrogen sulphite is added to boiling ferrous sulphate solution, the mixture made alkaline with sodium carbonate, and shaken well at the boil for some time. From the filtered solution, after cooling, 2-*amino*-3-*methoxybenzaldehyde* (*oxime*, m. p. 142°; *semicarbazone*, m. p. 223°; *phenylhydrazone*, m. p. 139°) separates as an oil in 84% yield. The new aldehyde condenses readily with ethyl acetoacetate at 100° to form *ethyl* 8-*methoxy*-2-*methylquinoline*-3-*carboxylate*, m. p. 76—79° ($+1H_2O$) or 102·5° (anhydrous; *chloroplatinate* described), which is hydrolysed by hydrochloric acid at 120° to the free *acid*,

$$C_{12}H_{11}O_3N,3H_2O,$$

m. p. 126° [decomp.; *hydrochloride*, *chloroplatinate*, *nitrate* (m. p. 146°, decomp.), and *silver* salt described]. By condensation of the new aldehyde with ethyl acetoacetate at 160°, 8-*methoxy*-3-*acetylcarbostyril*, m. p. 183° (*phenylhydrazone*, m. p. 119°), is formed. C. Hollins.

Influence of position of nitro- and amino-groups on the reactivity of the aldehydo-group in nitro- and amino-derivatives of *m*-hydroxy- and *m*-methoxy-benzaldehydes. J. Tröger and H. Fromm (J. pr. Chem., 1925, [ii], **111**, 217—239).—The orientation of the isomeric nitro-*m*-hydroxybenzaldehydes and their methyl ethers, concerning which much confusion exists in the literature, is cleared up. Nitration of *m*-hydroxybenzaldehyde, m. p. 104°, by the method of Tiemann and Ludwig (A., 1883, 188) gives 4-nitro-3-hydroxybenzaldehyde, m. p. 128°, volatile in steam, and a mixture of the 6-nitro- (m. p. 166°) and 2-nitro- (m. p. 152°) isomerides,

separable by crystallisation from chloroform. The corresponding methyl ethers melt at 107° (4-nitro-), 83° (6-nitro-; phenylhydrazone, m. p. 154°), and 102° (2-nitro-), respectively. From the nitration product of *m*-methoxybenzaldehyde (prepared from 50 g. of hydroxybenzaldehyde, 60 c.c. of 25% sodium hydroxide, 200 c.c. of water, and 55 g. of methyl sulphate) only the 2-nitro-compound can be isolated in pure condition.

4-Nitro-3-hydroxybenzaldehyde condenses with arylsulphonylacetonitriles to give α-arylsulphonyl-β-4-nitro-3-hydroxyphenylacrylonitriles,

$$(NO_2)(OH)C_6H_3\cdot CH{:}C(CN)\cdot SO_2Ar,$$

where Ar is *phenyl* (m. p. 155—156°), p-*tolyl* (m. p. 184°), p-*chlorophenyl* (m. p. 170°), p-*bromophenyl* (m. p. 182—183°), o-*anisyl* (m. p. 187°; *acetate*, m. p. 156—157°), p-*phenetyl* (m. p. 188°), or β-*naphthyl* (m. p. 174°). 6-Nitro-3-hydroxybenzaldehyde condenses less easily, giving α-p-*toluenesulphonyl*-β-(6-*nitro*-3-*hydroxyphenyl*)*acrylonitrile*, m. p. 115—116°, and the corresponding p-*chlorobenzenesulphonyl* (oily; *acetate*, m. p. 130—131°) and o-*anisolesulphonyl* (oily; *acetate*, m. p. 142—143°) derivatives. Similarly, the 4-nitro-3-methoxybenzaldehyde reacts readily, whilst the 6-nitro ether gives much difficulty. α-p-*Toluenesulphonyl*-β-(4-*nitro*-3-*methoxyphenyl*)*acrylonitrile*, m. p. 188°, and the corresponding p-*chlorobenzenesulphonyl* (m. p. 206°) and p-*bromobenzenesulphonyl* derivatives are described. From the 6-nitro-ether and *p*-chlorobenzenesulphonylacetonitrile a small amount of a *substance*, m. p. 117—118°, was obtained.

Reduction of the sodium hydrogen sulphite compound of 6-nitro-3-methoxybenzaldehyde with hot ferrous sulphate and sodium carbonate solution gives 6-*amino*-3-*methoxybenzaldehyde* (*phenylhydrazone*, m. p. 179—180°), isolated as *hydrochloride* from an ethereal solution. The amino-aldehyde condenses with *p*-chlorobenzenesulphonylacetonitrile to form 2-*amino*-6-*methoxy*-3-p-*chlorobenzenesulphonylquinoline*, m. p. 181—182° (described in error as a 2-methylquinoline derivative in the original), and with *p*-toluenesulphonylacetonitrile to give a *base*, m. p. 164°.

2-Nitro-3-methoxybenzaldehyde reacts with arylsulphonylacetonitriles, forming α-arylsulphonyl-β-(2-nitro-3-hydroxyphenyl)acrylonitriles; the p-*toluenesulphonyl* (m. p. 209°), p-*chlorobenzenesulphonyl* (m. p. 202°), p-*bromobenzenesulphonyl* (m. p. 215°), and o-*anisolesulphonyl* (m. p. 193°) compounds are obtained much more easily than their 6-nitro-isomerides. Similarly, 2-amino-3-methoxybenzaldehyde (see preceding abstract) reacts more readily than the 6-amino-aldehyde, forming 2-amino-8-methoxy-3-arylsulphonylquinolines,

$$MeO\cdot C_6H_3\begin{cases}CH{:}C\cdot SO_2Ar\\ N{=}C\cdot NH_2\end{cases},$$

where Ar is *phenyl* (m. p. 243—244°), p-*chlorophenyl* (m. p. 266°), p-*bromophenyl* (m. p. 281°), p-*tolyl* (m. p. 256—257°), o-*anisyl* (m. p. 260°), or p-*phenetyl* (m. p. 272—273°). C. HOLLINS.

Isomerism of the oximes. XXIII. Acyl derivatives. O. L. BRADY and G. P. MCHUGH (J.C.S., 1925, **127**, 2414—2427; cf. A., 1925, i, 674).—The action of benzoyl chloride, not only on α-aldoximes, but also on β-aldoximes, invariably yields the α-benzoyl derivatives. In this way, *benzoyl*-o-*nitro*-α-*benzaldoxime*, m. p. 112°, *benzoyl*-p-*nitro*-α-*benzaldoxime*, m. p. 196°, *benzoyl*-3 : 4-*methylenedioxy*-α-*benzaldoxime*, m. p. 168°, *benzoyl*-o-*methoxy*-α-*benzaldoxime*, m. p. 96°, and *benzoyl*-p-*dimethylamino*-α-*benzaldoxime*, m. p. 138°, were prepared. The action of keten on α-aldoximes yields the acetyl-α-aldoxime (*e.g.*, *acetyl*-3 : 4-*methylenedioxy*-α-*benzaldoxime*, m. p. 105°), and on the β-aldoximes the acetyl-β-aldoxime. By Hantzsch's method, *acetyl*-o-*nitro*-β-*benzaldoxime*, m. p. 73°, was prepared, but in other cases the derivatives were contaminated with unchanged oxime. Phenylcarbimide reacts with 3 : 4-methylenedioxy-α-benzaldoxime to give a mixture of *carbanilino*-3 : 4-*methylenedioxy*-α-*benzaldoxime*, m. p. 104° (decomp.), and the β-*isomeride*, m. p. 84° (decomp.), the β-compound being more readily prepared from the β-aldoxime. In a similar manner, *carbanilino*-o-*methoxy*-α-*benzaldoxime*, m. p. 107° (decomp.), was obtained. Diphenylcarbamyl chloride with *o*-methoxybenzaldoxime causes inversion to *diphenylcarbamyl*-o-*methoxy*-β-*benzaldoxime*, m. p. 124° (decomp.), and ethyl chloroformate forms with α-cinnamaldoxime *carbethoxy*-α-*cinnamaldoxime*, m. p. 64°; with the β-oxime, the nitrile is formed. α-Naphthylcarbimide with α-cinnamaldoxime yields α-*naphthylcarbamyl*-α-*cinnamaldoxime*, m. p. 152°, and with β-cinnamaldoxime yields α-*naphthylcarbamyl*-β-*cinnamaldoxime*, which exists in yellow amorphous and colourless crystalline modifications, both m. p. 125° (decomp.). B. W. ANDERSON.

Isomerism of the oximes. XXIV. 4-Methoxy-3-methyl-, 3-nitro-4-methyl-, and some *o*-substituted benzaldoximes. O. L. BRADY, A. N. COSSON, and A. J. ROPER (J.C.S., 1925, **127**, 2427—2432).—Through the hydrochloride of *o*-chloro-α-benzaldoxime the β-isomeride was prepared. Similarly, o-*bromo*-β-*benzaldoxime*, m. p. 126°, was obtained from *o*-bromo-α-benzaldoxime (*acetyl* derivative, m. p. 66°; *hydrochloride*, m. p. 115°, decomp.). No β-compound could be obtained from *o*-iodo- or *o*-ethoxy-α-benzaldoximes. Thus *o*-substitution exerts a hindering but not an inhibiting effect on the formation of the β-isomeride. From 4-methoxy-3-methyl-α-benzaldoxime (*acetyl* derivative, m. p. 70°), 4-*methoxy*-3-*methylbenzonitrile*, m. p. 52°, 4-*methoxy*-3-*methylbenzoic acid*, m. p. 192°, and 4-*methoxy*-3-*methyl*-β-*benzaldoxime*, m. p. 121°, were prepared. 3-*Nitro*-4-*methyl*-α-*benzaldoxime*, m. p. 118—120° (*acetyl* derivative, m. p. 104°), gave through the *hydrochloride*, m. p. 140° (decomp.), 3-*nitro*-4-*methyl*-β-*benzaldoxime*, m. p. 135°. The action of alkali on *o*-iodo-α-benzaldoxime yielded potassium iodide and salicylic acid.

B. W. ANDERSON.

Isomerism of styryl alkyl ketones. II. Isomerism of homologues of 2-hydroxystyryl and of 3-methoxy-4-hydroxystyryl methyl ketones. A. MCGOOKIN and D. J. SINCLAIR (J.C.S., 1925, **127**, 2539—2544).—2-Hydroxystyryl ethyl ketone, m. p. 116°, 2-hydroxystyryl *n*-propyl ketone, m. p. 113°, and 2-hydroxystyryl *n*-hexyl ketone, m. p. 103°, exist in both yellow and colourless

stereoisomerides (having identical m. p.), of which the yellow form is the less stable. The stability of the yellow form decreases, and the resistance of the molecule to fission by alkaline reagents increases, with increasing mol. wt. Similar properties are observed in the isomerides of the ethyl and *n*-propyl homologues of 3-methoxy-4-hydroxystyryl methyl ketone. The existence of two distinct isomerides of 3 : 4-methylenedioxystyryl methyl ketone and of 3-methoxy-4-hydroxystyryl methyl ketone has been established by solubility measurements.

B. W. ANDERSON.

Isomerisation of αγ-diphenylallyl alcohol to phenyl β-phenylethyl ketone. H. NOMURA (Bull. Soc. chim., 1925, [iv], **37**, 1245—1247).—*αγ-Diphenylallyl alcohol*, m. p. 56·5—57° (*acetate*, b. p. 211°/9 mm.), obtained by the action of magnesium phenyl bromide on cinnamaldehyde (cf. Kohler, A., 1904, i, 595), is converted by sodium ethoxide or alcoholic potassium hydroxide almost quantitatively into phenyl β-phenylethyl ketone, m. p. 72° (oxime, m. p. 84·5—85°; cf. Schneidewind, A., 1888, 704; Perkin, J.C.S., 1891, **59**, 1007).

R. BRIGHTMAN.

Phenyl α-acenaphthyl ketone [3-benzoylacenaphthene] and phenyl-α-acenaphthylmethane [3-benzylacenaphthene]. K. DZIEWOŃSKI and M. RYCHLIK (Ber., 1925, **58**, [*B*], 2239—2249).—3-Benzoylacenaphthene (annexed formula), m. p. 100—101° (cf. Perrier, A., 1904, i, 804; Graebe and Haas, A., 1903, i, 409), is conveniently prepared in 60—70% yield by the action of aluminium chloride on a solution of benzoyl chloride and acenaphthene in carbon disulphide at 15—20° and separation of the benzoyl compound from unchanged material by fractional distillation with superheated steam. It is reduced by zinc dust and potassium hydroxide or by sodium amalgam to *phenyl-α-acenaphthylcarbinol*, m. p. 113—114°, which is transformed by sodium and boiling ethyl alcohol into 3-benzylacenaphthene, m. p. 110—111°, identical with the product obtained previously (Dziewoński and Dotta, A., 1904, i, 390) from benzyl chloride and acenaphthene in the presence of molten zinc chloride and considered erroneously to be 2-benzylacenaphthene. The incorrectness of the previous conclusion is further established by the oxidation of the benzyl or benzoyl compound to the same 4-benzoylnaphthalic anhydride, m. p. 200—201°. The 3-benzoyl- and 3-benzyl-naphthalic acids (Dziewoński and Wechsler, A., 1904, i, 803) and the tribenzyldecacyclene and dibenzyldinaphthylenethiophen (Dziewoński and Dotta, A., 1904, i, 803) are therefore all to be regarded as 4- instead of 3-derivatives. 4-Benzoylnaphthalic anhydride is converted by hydroxylamine in hot dilute aqueous alkaline solution into the *d*-oxime, m. p. 254—255° (decomp.) [cf. Dziewoński and Dotta, *loc. cit.*), which is transformed by a boiling mixture of glacial acetic acid and acetic anhydride into the β-oxime, m. p. 199—200° (cf. Graebe and Haas, *loc. cit.*); the reverse transformation is effected in more dilute acetic acid solution. The oximes appear to be stereoisomeric. 4-Benzylnaphthalic anhydride may be prepared by reduction of 4-benzoylnaphthalic anhydride with activated zinc dust and sodium hydroxide solution. 4-Benzoylnaphthalic acid is converted by potassium hydroxide at 180° into naphthalic and benzoic acids. *3-Benzoylacenaphthenequinone*, m. p. 199—200°, obtained by oxidation of 3-benzoylacenaphthene in boiling glacial acetic acid solution with sodium dichromate, yields an amorphous *trioxime*, decomp. 94—96°.

3-Benzoylacenaphthene is converted by sulphur at 200—210° into a mixture of *dibenzoyldinaphthylenethiophen* (I), m. p. 213—215°, and *tribenzoyldecacyclene* [*tribenzoyltrinaphthylenebenzene*], m. p. 335—336°. Nitration of 3-benzoylacenaphthene leads to the formation of (?) *4-nitro-3-benzoylacenaphthene*, m. p. 169—171°, in which the nitro-group is certainly present in the α-position of the naphthalene nucleus. *5-Nitro-4-benzoylnaphthalic anhydride*, m. p. 273°, and the corresponding *imide*, m. p. 302—304° (decomp.), are also described.

H. WREN.

Ketens in the Friedel-Crafts reaction. C. DE W. HURD (J. Amer. Chem. Soc., 1925, **47**, 2777—2780).—Keten reacts with anisole, in presence of one equivalent of aluminium chloride, in carbon disulphide solution, with formation of *o*- and *p*-methoxyacetophenones, together with higher ketones. Benzene yields similarly acetophenone and products of higher b. p. Keten is practically inert towards acetophenone in presence of one or two equivalents of aluminium chloride. Naphthalene reacts similarly with keten at 0°, affording α- and β-naphthyl methyl ketones, and a dark, resinous *solid*, m. p. 110—160°. α- and β-Dinaphthyls are also produced when the reaction is carried out at the b. p. of the solvent. Keten forms an additive *product* with aluminium chloride when passed into a suspension of the latter in carbon disulphide. The additive product forms a white powder at −10°, and reacts readily with benzene and anisole, with evolution of hydrogen chloride.

F. G. WILLSON.

Affinity of the group, ·C(OH)·C(:N·OH)·, for copper. Relationship between atomic grouping and specific affinity. F. FEIGL, G. SICHER, and O. SINGER (Ber., 1925, **58**, [*B*], 2294—2303).—The ability of α-benzoinoxime to yield an insoluble copper salt (I) and its permanence towards ammonia have been reported previously (Feigl, A., 1923, ii, 880). Further investigation has shown that the ability to yield green copper salts insoluble in water but decomposed by acids is a general property of acyloins. Variation of the radicals R and R′, in the compounds CHR(OH)·CR′(:N·OH), has no influence in this respect, but affects the behaviour of the copper salts towards ammonia. Insolubility in ammonia or inability to add ammonia is observed only with those compounds in which the groups R and R′ co-ordinatively saturate the copper atom. This ability is possessed by all aryl groups and it is a matter of indifference whether the acyloins are symmetrical or

unsymmetrical. Substituents in the benzene nucleus are without influence; a phenyl group may be replaced by the co-ordinatively unsaturated amino-group. Only those aliphatic acyloins in which the carbon chain contains more than three atoms have a similar influence. This must be ascribed to the existence of an affinity field in aliphatic residues, and not merely to the effect of the size of the groups, since the copper compounds of phenylbenzoinoxime, $CPh_2(OH)\cdot CPh(:N\cdot OH)$, and benzylbenzoinoxime, in which heavy groups are present, are soluble in ammonia, owing, probably, to the mutual saturation of the residual affinities of the two aromatic residues attached to the same carbon atom.

The copper salts are prepared by treating an alcoholic solution of the oxime with aqueous or alcoholic copper acetate solution. The amorphous precipitates are purified from co-precipitated, basic copper salts by digestion with dilute acetic acid, whilst excess of the oxime can be removed by alcohol. The *copper* salts of the following compounds are described: lævuloseoxime, acetoloxime, acetoinoxime, propioinoxime, *n*-butyroinoxime, *n*-valeroinoxime, *n*-hexoinoxime, *n*-heptoinoxime, diphenylacetoin-oxime, benzoinoxime, furoinoxime, anisoinoxime, cuminoinoxime, piperonyloinoxime, α-hydroxyphenyl-acetamideoxime, benzfuroinoxime, benzanisoinoxime, cuminanisoinoxime, *p*-dimethylaminobenzoinoxime, *p*-chloro-*p*-dimethylaminobenzoinoxime, phenyl-benzoinoxime, benzylbenzoinoxime. H. WREN.

Reactions between solutions of benzoin and of aromatic aldehydes in pyridine and metallic copper. H. MOHLER (Helv. Chim. Acta, 1925, **8**, 740—757).—The dissolution of copper in pyridine solutions of benzoin has been traced to a reaction of benzoic acid with copper. The deep blue compound which results consists of copper benzoate with pyridine of crystallisation. The mean rate of dissolution of the metal has been determined at constant temperature. Parallel experiments were carried out by passing in a current of air or nitrogen and by using benzil, benzoic acid, and benzilic acid. The dissolution of copper in pyridine solutions of benzoin is a heterogeneous double reaction with at least two induction phenomena. The oxidation of benzoin to benzoic acid by oxygen is bound up with the presence of copper, and pyridine plays a definite part in the whole reaction. The benzoic acid will react with copper only in the presence of oxygen or a reducible substance. The combination of copper, pyridine, and oxygen is therefore a very strong oxidising system.

The rate of dissolution of copper in dilute pyridine solutions of the following aldehydes has been measured: benzaldehyde, anisaldehyde, *p*-tolualde-hyde, *p*-dimethylaminobenzaldehyde, *p*-nitrobenzalde-hyde, cinnamaldehyde. Not only the rates of oxid-ation of the aldehyde, but also the rates of dissolution of copper depend on the chemical constitution of the respective aldehydes. R. A. MORTON.

Ketone-alcohols of the general formula, CHPh(OH)·CO·R. M. TIFFENEAU and (MLLE.) J. LEVY (Bull. Soc. chim., 1925, [iv], **37**, 1247—1251).—Ketone-alcohols have been obtained by the action of magnesium alkyl halides on phenylglycollamide or on phenylglycollonitrile, obtained by the action of sodium cyanide on the sodium hydrogen sulphite compound of benzaldehyde; with the nitrile secondary alcohols of the type CHPhR·OH are always formed as by-products and lower yields result. Phenyl-acetylcarbinol is obtained in not more than 15% yield (cf. A., 1923, i, 789); *phenylpropionylcarbinol* (*α-hydroxyphenylmethyl ethyl ketone*), m. p. 32—33°, b. p. 124—128°/11 mm., 40% yield from the amide (*semicarbazone*, m. p. 89—90°; *oxime*, m. p. 97°); *phenylbutyrylcarbinol* (*α-hydroxyphenylmethyl propyl ketone*), b. p. 159—162°/28 mm., *d* 1·064 (*semi-carbazone*, m. p. 157—158°; *oxime*, oil); *phenyliso-butyrylcarbinol* (*α-hydroxyphenylmethyl* iso*propyl ketone*), m. p. 44—45°, distils at 160—170°/35 mm., 28—30% yield, from the amide (*semicarbazone*, m. p. 158—159°; *oxime*, liquid); *α-hydroxyphenylmethyl* n-*butyl ketone*, a yellow oil, *d* 1·045, distilling at 145—160°/13 mm., 20% yield, from the amide (*semi-carbazone*, m. p. 152—153°; *oxime*, m. p. 95—96°); *α-hydroxyphenylmethyl* iso*butyl ketone*, orange-yellow, b. p. 155—157°/38 mm., *d* 1·048, 17% yield (*semi-carbazone*, m. p. 123°; *oxime*, m. p. 99—100°), and *α-hydroxyphenylmethyl benzyl ketone*, m. p. 115—116°, 30% yield (*semicarbazone*, m. p. 189—190°). The last-named differs from the remaining ketols in being non-volatile in steam. R. BRIGHTMAN.

Co-ordinated compounds of the alkali metals. II. N. V. SIDGWICK and F. M. BREWER (J.C.S., 1925, **127**, 2379—2387; cf. Sidgwick and Plant, A., 1925, i, 298).—The sodium or potassium derivatives of ethyl acetoacetate and some similar compounds exist in a non-polar form, in which the metal exhibits 2-covalency, forming part of a chelate ring; these are soluble in benzene and have a definite m. p. Many metallic derivatives which are insoluble in benzene alone dissolve readily in presence of the parent substance or some similar compound, the metal being here 4-covalent and forming a bichelate compound. The sodium derivative of benzoylacetone behaves as a salt, but readily takes up 2 mols. of water from 96% alcohol, the hydrate containing 4-covalent sodium, and being soluble in hydrocarbons. Several similar compounds, and some containing lithium and potass-ium, have been prepared. Sodium and potassium derivatives of salicylaldehyde combine with excess of the aldehyde, forming bichelate additive compounds, and the same aldehyde forms similar compounds with sodium and potassium *o*-nitrophenoxides. Whereas lithium atoms are limited to a covalency of four, 6-covalent metallic atoms are found in additive com-pounds of the disodium and dipotassium salts of quinizarin with 4 mols. of salicylaldehyde.

B. W. ANDERSON.

Perylene and its derivatives. XI. A. ZINKE, R. SPRINGER, and A. SCHMID (Ber., 1925, **58**, [*B*], 2386—2391; cf. A., 1925, i, 1436, and previous abstracts).—4 : 10-Dichloro- or 4 : 10-dibromo-peryl-ene is converted by concentrated sulphuric acid at 165—170° into hydrogen halide and 4 : 10-*perylene-quinone*, which could be isolated only as the additive compound $(C_{20}H_{10}O_2)_2,H_2O$. It is transformed by

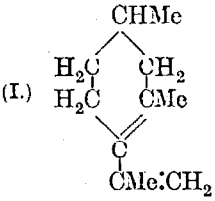
distillation with zinc dust and zinc chloride into perylene. Reduction with sodium hyposulphite in alkaline solution followed by treatment with the appropriate aroyl chloride affords the *dibenzoyl*, m. p. 324°, and *di*-p-*bromobenzoyl*, m. p. 359—361°, derivatives of 4 : 10-perylenequinol; the mol. wts. of these compounds are established by Rast's method, using perylene as solvent. H. WREN.

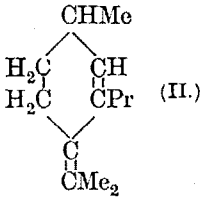
Olefinic terpene ketones from the volatile oil of flowering *Tagetes glandulifera*. I. T. G. H. JONES and F. B. SMITH (J.C.S., 1925, **127**, 2530—2539).—The volatile oil of *T. glandulifera* contains, in addition to ocimene (30%) and *d*-limonene (3%), 5—10% and 50—60%, respectively, of two new terpenes. These are *γη-dimethyl-*Δ^{α}*-octen-ε-one*, b. p. 185°, $d^{15\cdot5}$ 0·8354, n_D^{20} 1·4295, $[\alpha]_D$ +1·5° (*semicarbazone*, m. p. 92·5°; *oxime*, b. p. 222°), and *η-methyl-γ-methylene-*Δ^{α}*-octen-ε-one*, "*tagetone*," b. p. 210°, $d^{15\cdot5}$ 0·8803, n_D^{20} 1·4895 (*oxime*, b. p. 126°/25 mm.). *γη*-Dimethyl-Δ^{α}-octen-ε-one on reduction yields *γη-dimethyloctan-ε-one*, b. p. 188° (*semicarbazone*, m. p. 91·5°; *oxime*, b. p. 225°), and on oxidation gives β-iso*valeryl-α-methylpropionic acid*, m. p. 25° (*semicarbazone*, m. p. 165°), with some *iso*valeric and formic acids. Reduction of tagetone in ether by sodium gives a *substance*, $C_{10}H_{18}O$, b. p. 197°, $d^{15\cdot5}$ 0·8524, n_D^{20} 1·4490, and a *pinacol*, $C_{20}H_{34}O_2$, b. p. 183°/4 mm., $d^{15\cdot5}$ 0·9258, n_D^{20} 1·4820, containing four double linkings. Oxidation of tagetone yields *iso*valeric and oxalic acids. B. W. ANDERSON.

Occurrence of sylvestrene. B. S. RAO and J. L. SIMONSEN (J.C.S., 1925, **127**, 2494—2499).—The oils from *Pinus sylvestris* and *P. pumilio* contain no sylvestrene; treatment of the oil with hydrogen chloride yields sylvestrene dihydrochloride, but this is formed from the Δ^3-carene present. It is improbable that sylvestrene occurs in nature.
B. W. ANDERSON.

Action of metals on dipentene dihydrohalide. Preparation of a synthetic diterpene. K. C. ROBERTS (J.C.S., 1925, **127**, 2451).—When alcoholic solutions of *cis*- and *trans*-dipentene dihydrobromide and of *trans*-dipentene dihydrochloride were shaken with finely divided silver or copper, loss of hydrogen halide took place, with production of dipentene, which polymerised to a diterpene, $C_{20}H_{32}$, b. p. 173—183°/13 mm., n_D^{20} 1·5170, d^{20} 0·9361, iodine value, 103.
B. W. ANDERSON.

Constitution of pulegone, tertiary alkylpulegols, and pulegenes. V. GRIGNARD and J. SAVARD (Compt. rend., 1925, **181**, 589—592; cf. Grignard, A., 1901, i, 681; Rupe, A., 1908, i, 556; Auwers and Eisenlohr, A., 1910, ii, 368).—Treatment with ozone demonstrates the presence in pulegone of two isomerides, β-pulegone, *i.e.*, 1-*methyl*-4-$\Delta^{4(8)}$-iso*propylidene*cyclo*hexan*-3-*one*, and 15—18% of α-pulegone, *i.e.*, 1-*methyl*-4-Δ^3-iso*propylidene*cyclo*hexan*-3-*one*. Treatment with organo-magnesium compounds yields the isomeric tertiary alkylpulegols present in the same relative proportions. When these alcohols are treated with dehydrating agents (*e.g.*, acetic anhydride, phosphorus trichloride), however, different proportions of the isomeric unsaturated hydrocarbons are obtained, the reaction products containing the following proportions of α-isomeride : methylpulegene, 68%; *n*-propylpulegene, 24%; *n*-butylpulegene, 50%; *iso*propylpulegene, 43%. α-Methylpulegene on treatment with ozone yields γ-methyl-ε-ketoheptoic acid (Rupe, *loc. cit.*), and must therefore have the structure, 1 : 3-*dimethyl*-4-Δ^8-iso*propylidene*-Δ^3-cyclo*hexene* (I). β-*n*-Propylpulegene when treated with ozone gives α-methylglutaric acid and is therefore 1-*methyl*-3-n-*propyl*-

(I.) 



(II.)

4-$\Delta^{4(8)}$-iso*propylidene*-Δ^2-cyclo*hexene* (II). It is suggested that the homologous compounds have analogous formulæ, but the absence of the exaltation of molecular refraction to be anticipated from the system of conjugated unsaturated linkings is remarkable.
L. F. HEWITT.

Borneol in spruce turpentine. A. S. WHEELER and C. R. HARRIS (J. Amer. Chem. Soc., 1925, **47**, 2836—2838).—See B., 1925, 1012.

Camphor oils. III. Action of oxalic acid on terpin hydrate. K. ONO (Mem. Coll. Sci. Kyōtō, 1925, **9**, [A], 75—79; cf. Aschan, A., 1919, i, 336).—Terpin hydrate, heated on an oil-bath for 5 hrs. with twice its volume of 0·5% oxalic acid solution, gave good yields of α-terpineol and some β-terpineol. B. W. ANDERSON.

Camphor oils. IV. Reaction of Japanese acid clay to terpin hydrate and terpineol. K. ONO (Mem. Coll. Sci. Kyōtō, 1925, **9**, [A], 153—159).—Both terpineol and terpin hydrate when treated with Japanese acid clay yield principally *p*-cymene and *p*-menthane, probably undergoing dehydration before decomposing into these products.
B. W. ANDERSON.

Esters of camphylcarbinol. H. RUPE and M. SCHAERER (Helv. Chim. Acta, 1925, **8**, 853—865).—Since the reduction of hydroxymethylenecamphor to camphylcarbinol introduces a new asymmetric carbon atom, this substance should occur in two stereoisomeric forms. No evidence of the existence of these stereoisomerides is found with camphylcarbinol or with the majority of its esters, but the *iso*butyrate has been isolated in two forms. Camphylcarbinol has $[\alpha]_D^{20}$ +62·22°, and its *formate* $[\alpha]_D^{20}$ +18·13°. A series of esters has been prepared by the action of the respective acid chlorides on the carbinol in presence of pyridine, and distilled in a high vacuum : *propionate*, b. p. 63°, m. p. 28—36° indef., d_4^{20} 1·042, $[\alpha]_D^{20}$ +55·37°, and in 10% benzene solution +16·15°; iso*butyrate*, b. p. 61°, d_4^{20} 1·0217, $[\alpha]_D^{20}$ +56·16°, which deposited crystals, m. p. 31·5—33°, having $[\alpha]_D^{20}$ in 10% benzene solution +23·48°, whilst the liquid portion had the corresponding value +36·85°; n-*butyrate*, b. p. 73°, d_4^{20} 1·0254, $[\alpha]_D^{20}$ +53·45°

(+33·35° in benzene); n-*valerate*, b. p. 82°, d_4^{20} 1·0140, $[\alpha]_D^{20}$ +49·18° (+29·57° in benzene); *hexahydrobenzoate*, b. p. 95°, d_4^{20} 1·0507, $[\alpha]_D^{20}$ +49·49° (+32·16° in benzene); *phenylacetate*, b. p. 120°, d_4^{20} 1·0902, $[\alpha]_D^{20}$ +40·94° (+26·59° in benzene); β-*phenylpropionate*, b. p. 141°, d_4^{20} 1·0791, $[\alpha]_D^{20}$ +38·56° (+27·43° in benzene); *cinnamate*, b. p. 145°, d_4^{20} 1·1004, $[\alpha]_D^{20}$ +46·06° (+21·82° in benzene); *crotonate*, b. p. 79°, d_4^{20} 1·0506, $[\alpha]_D^{20}$ +56·52° (+34·30° in benzene); *sorbate*, b. p. 99°, d_4^{20} 1·0433, $[\alpha]_D^{20}$ +54·55° (+33·86° in benzene). Optical rotatory powers are tabulated in all cases for four different wave-lengths: the value $[\alpha]_F/[\alpha]_C$ is remarkably constant throughout=2·36 with λ_a 591·5, λ_0^2 0·09271, these figures being almost identical with those for the hydroxymethylenecamphor derivatives. The curves relating $1/[\alpha]$ to λ^2 for the propionate and *iso*butyrate are not quite straight lines, a fact which is taken to confirm the indications of the presence of the expected stereoisomerides.

G. M. BENNETT.

Cymarin and strophanthin. A. WINDAUS, G. REVEREY, and A. SCHWIEGER (Ber., 1925, **58**, [*B*], 1509—1514; cf. Windaus and Hermanns, A., 1915, i, 703, 704; Jacobs and co-workers, A., 1923, i, 123; 1924, i, 65, 867, 1331).—Strophanthidin resembles cholesterol in that it contains a tetracyclic system. It is an unsaturated hydroxylactone similar to the genins of the *Digitalis* glucosides, from which it differs by the presence of the ketonic group in addition to three hydroxy-groups. Further, it has one carbon atom less than the *Digitalis* genins, so that the fundamental substance of strophanthidin, $C_{23}H_{36}O_3$, appears to be the next lower homologue of hexahydrodigitaligenin.

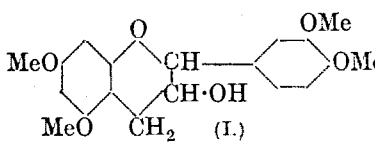
The methylsemiacetal of dianhydrostrophanthidin (cf. A., 1924, i, 867) is hydrogenated in glacial acetic acid suspension in the presence of platinum, pretreated with hydrogen, to *hexahydrodianhydrostrophanthidin*, $C_{23}H_{34}O_4$, m. p. 208°, whereas, if the metal has been treated previously with oxygen, *octahydrodianhydrostrophanthidin*, $C_{23}H_{36}O_4$, m. p. 265—266° (*monoacetyl* derivative, m. p. 185°), is obtained. The octahydro-compound is converted by cautious oxidation with chromic acid into the hexahydro-derivative. The latter compound is transformed by amalgamated zinc and hydrochloric acid into *deoxyoctahydrodianhydrostrophanthidin*, $C_{23}H_{36}O_3$, m. p. 224°.

H. WREN.

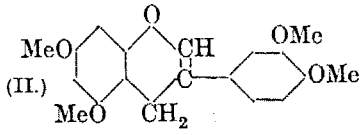
Strophanthin. VIII. Carbonyl group of strophanthin. W. A. JACOBS and A. M. COLLINS (J. Biol. Chem., 1925, **65**, 491—505; cf. A., 1925, i, 566, 1082, and earlier abstracts).—Oxidation with chromic acid in acetic acid solution of dianhydrostrophanthidin yielded a *dilactone*, $C_{23}H_{26}O_4$, m. p. 253—254°, $[\alpha]_D^{28}$ −178° in chloroform, together with a small amount of a *lactonic acid*, $C_{23}H_{28}O_5$, m. p. 268°, $[\alpha]_D^{25}$ −100° in 95% alcohol. This acid was also obtained by the oxidation of dianhydrostrophanthidin with potassium permanganate in acetone solution, in which case none of the dilactone was formed. This result is taken to show that dianhydrostrophanthidin exists as an equilibrated mixture of an oxidic and an aldehydic form, the former of which is oxidised specifically by chromic acid and the latter by potassium permanganate. The above dilactone, on hydrolysis, gave a *dibasic acid*, $C_{23}H_{30}O_6$, m. p. 249—251°. The lactone, with hydrogen and palladium, gave a *tetrahydro*-derivative, $C_{23}H_{30}O_4$, m. p. 275—277°, $[\alpha]_D^{24}$ +3·0° in chloroform; hydrolysis of this compound by boiling for 2 hrs. with 0·05*N*-sodium hydroxide opened one lactone ring, giving a lactonic acid, m. p. 225—230°; for complete hydrolysis, boiling for 5 hrs. with 2*N*/3-sodium hydroxide was required. The tetrahydrodilactone still contained a double linking. With some difficulty two more hydrogen atoms were introduced to form a *hexahydrodilactone*, $C_{23}H_{32}O_4$, m. p. 265—267°, $[\alpha]_D^{25}$ +14° in chloroform; this substance did not reduce Tollens' reagent; its second lactone group showed a resistance to hydrolysis similar to that observed with the tetrahydro-derivative. The lactonic acid obtained previously (A., 1923, i, 65) by the oxidation of strophanthidin with potassium permanganate in acetone solution is now given the formula $C_{23}H_{32}O_7$, it being assumed to be formed by the oxidation of the aldehydic form of strophanthidin as indicated above; on treatment with concentrated hydrochloric acid, it gave a *dilactone*, $C_{23}H_{30}O_6$, m. p. 235—236°, $[\alpha]_D^{27}$ +100° in methyl alcohol; dihydrostrophanthidin under similar conditions yielded an analogous *lactonic acid*, $C_{23}H_{34}O_7$, platelets with $2H_2O$, effervescing at 132—133°, $[\alpha]_D^{28}$ +47° in methyl alcohol, and this in turn a *dilactone*, $C_{23}H_{32}O_6$, m. p. 232—234°, $[\alpha]_D^{28}$ +84° in methyl alcohol; the latter substance did not reduce Tollens' reagent; both these dilactones showed a resistance to the hydrolysis of the second lactone group similar to that observed with the anhydro-derivatives described above. Oxidation with chromic acid of the dilactone, $C_{23}H_{30}O_6$, yielded a *ketodilactone*, $C_{23}H_{28}O_6$, m. p. 285°, $[\alpha]_D^{28}$ +93° in pyridine, which in turn gave an *oxime*, m. p. above 285°. The same ketodilactone was obtained by a similar oxidation of pseudostrophanthidin (A., 1925, i, 566), which is not oxidised by potassium permanganate in acetone; pseudostrophanthidin is therefore to be regarded as a stable oxidic form of the hydroxyaldehyde, strophanthidin.

C. R. HARINGTON.

Tannins and related substances. XXI. Molecular rearrangement of catechin derivatives. K. FREUDENBERG, G. CARRARA, and E. COHN (Annalen, 1925, **446**, 87—95; cf. A., 1925, i, 1165).—*trans*-Epicatechin tetramethyl ether (I) on dehydration yields an anhydroepicatechin tetramethyl ether (II). The wandering of the dimethoxyphenyl group during the dehydration has been proved by the synthesis of the hydrogenation product of (II).



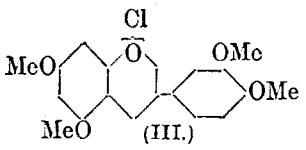
(I.)



(II.)

By the condensation of 3 : 4-dimethoxyphenylacetonitrile with phloroglucinol trimethyl ether is

obtained 2 : 4 : 6-*trimethoxyphenyl* 3 : 4-*dimethoxybenzyl ketone*, m. p. 110°. This is converted by magnesium methyl iodide into α-(3 : 4-*dimethoxyphenyl*)-β-(2′ : 4′ : 6′-*trimethoxyphenyl*)-α-*propylene*, m. p. 87·5—88·5°, which on reduction with platinum-black gives α-(3 : 4-*dimethoxyphenyl*)-β-(2′ : 4′ : 6′-*trimethoxyphenyl*)*propane*, m. p. 65—66°. The fact that this product is not identical with the reduction and methylation product of (II) is used as evidence that formula (II) is correct. Hydrogen chloride in ether solution brings about the condensation of 3 : 4-dimethoxyphenylacetaldehyde with acetophloroglucinaldehyde dimethyl ether, the oxonium chloride (III) being formed



(III.)

(cf. Drumm, A., 1923, i, 1221), which on reduction with platinum-black yields 3-(3′ : 4′-*dimethoxyphenyl*)-5 : 7-*dimethoxychroman*, m. p. 134° (*bromo*-derivative, m. p. 162—163°). The chroman is identical with the hydrogenation product of anhydroepicatechin. From the condensation of 3 : 4-*dimethoxybenzyl bromide*, m. p. 59°, with phloracetophenone dimethyl ether, two isomeric *substances*, $C_{19}H_{22}O_6$, m. p. 118° and 148°, were obtained. R. W. West.

4 : 6-Diphenylcoumalin [4 : 6-diphenyl-2-pyrone]. F. Arndt and B. Eistert (Ber., 1925, **58**, [*B*], 2318—2320).—The product, m. p. 138—138·5°, obtained by the interaction of equal quantities of ethyl benzoylacetate and concentrated sulphuric acid at the atmospheric temperature (cf. following abstract), is identified as 4 : 6-*diphenyl*-2-*pyrone* instead of the expected 2 : 6-diphenyl-4-pyrone, m. p. 139—140°, with which it gives a very marked depression of m. p. It is converted into 4 : 6-*diphenyl*-2-*thiopyrone*, m. p. 121—122°, which, unlike the 4-thiopyrone compound, remains unchanged at 180° and does not react with hydroxylamine. Bromine causes simultaneous addition and substitution, whereby ultimately 3-*bromo*-4 : 6-*diphenyl*-2-*pyrone*, m. p. 130°, is produced; the latter substance is transformed by sodium hydroxide into 2 : 4-diphenylfuran, m. p. 110°. H. Wren.

Transformation of ethyl benzoylacetate by concentrated and fuming sulphuric acid. F. Feist [with H. Pauschardt and H. Dibbern] (Ber., 1925, **58**, [*B*], 2311—2317).—Ethyl benzoylacetate is converted by concentrated sulphuric acid at the atmospheric temperature into ethyl benzoate, acetophenol, and 4 : 6-diphenyl-2-pyrone, (cf. Arndt and Eistert, preceding abstract). Fuming sulphuric acid (70% SO_3), on the other hand, transforms ethyl benzoylacetate into a *compound*, m. p. 136° (see later), and *ethyl anhydrosulphobenzoylacetate*, $SO_2<\overset{C_6H_4}{O}>C{:}CH\cdot CO_2Et$ or $C_6H_4<\overset{CO}{SO_2}>CH\cdot CO_2Et$, m. p. 140°, which behaves as a monobasic acid towards alkali hydroxide and yields *sodium*, *lead*, *stannous*, *mercurous*, *mercuric*, *copper*, *ferrous*, *ferric*, and *cobalt* salts. It is hydrolysed by boiling alkali hydroxide to *o-sulphobenzoylacetic acid*, m. p. 158—160° (in addition to *o*-sulphobenzoic acid), the *methyl ethyl* ester, $SO_3Me\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2Et$, m. p. 104°, being obtained directly from the anhydride and methyl sulphate in alkaline solution. With bromine in the presence of chloroform, it gives the *compound*, $C_{11}H_9O_5BrS$, m. p. 98·5°. When treated with ozone, it affords *o*-sulphobenzoic and oxalic acids; the production of glyoxylic acid could not be detected. These observations appear to favour the first without excluding the second constitution. On the other hand, a substance of the first constitution would be expected to be converted by ammonia into an imide yielding saccharin when treated with ozone, whereas the compound is merely transformed into an ammonium salt which regenerates the original substance on treatment with acid. The red coloration with ferric chloride indicates the enolic form of the second constitution, but derivatives could not be obtained with benzoyl chloride, phenylcarbimide, or *p*-nitrophenylhydrazine. If the anhydro-compound is treated successively with phosphorus pentachloride and ammonia, the *compounds*,

$$C_6H_4<\overset{C(NH_2)}{SO_2}>C\cdot CO\cdot NH_2,$$

m. p. 315°, and $C_6H_4<\overset{C(NH_2)}{SO_2}>C\cdot CO_2Et$, m. p. 232—234°, are formed according to experimental conditions. The latter compound behaves as a primary amine and is reconverted by nitrous acid into the nitrogen-free anhydride. When oxidised by permanganate, it yields ammonia, and oxalic and *o*-sulphobenzoic acids.

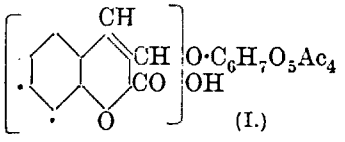
The by-product, m. p. 136° (see above), obtained during the preparation and ozonisation of the anhydro-compound and during its conversion into the amino-derivative appears to be the sulphone corresponding to acetophenone-*o*-sulphonic acid, $C_6H_4<\overset{CO}{SO_2}>CH_2$. H. Wren.

Formation of chromones. A criticism. W. Baker (J.C.S., 1925, **127**, 2349—2358; cf. Baker and Robinson, A., 1925, i, 1299).—That the so-called "chromones" of Jacobson and Ghosh (J.C.S., 1915, **107**, 424, 959, 1051; Ghosh, *ibid.*, 1916, **109**, 106) are in fact coumarins, as suggested by Baker and Robinson (*loc. cit.*), is confirmed by the preparation of thirteen of the true chromones, which are in all cases different from the products described by Jacobson and Ghosh. The condensation of substituted acetoacetic esters with phenols in the presence of sulphuric acid, or acetic acid and zinc chloride, or hydrochloric–acetic acid, yields coumarins; in the presence of phosphoric oxide, chromones are formed (cf. Simonis and co-workers, A., 1913, i, 890; 1914, i, 424, 980; Heilbron, Barnes, and Morton, J.C.S., 1923, **123**, 2569). The nitriles corresponding with these esters likewise give with phenols only coumarins. The corrected names for Jacobson and Ghosh's compounds, together with m. p. of these and the corresponding authentic chromone derivatives, are given.

Benzylresacetophenone, m. p. 88°, prepared from β-phenylpropionitrile and resorcinol by the Hoesch reaction, condenses with benzoic anhydride and sodium benzoate at 170—180° to give 7-*hydroxy*-3-

benzyl-2-phenylbenzo-γ-pyrone, m. p. 272—274°. *Benzylphloracetophenone*, m. p. 139—140°, from β-phenylpropionitrile and phloroglucinol, condenses with acetic anhydride and sodium acetate to form 5 : 7-*dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone*, m. p. 200—201° (*diacetate*, m. p. 112°), or with benzoic anhydride and sodium benzoate to form 5 : 7-*dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone*, m. p. 202—203° (*diacetate*, m. p. 126°). *Benzylorcacetophenone*, m. p. 118·5°, from β-phenylpropionitrile and orcinol, similarly yields 7-*hydroxy-3-benzyl-2* : 5-*dimethylbenzo-γ-pyrone*, m. p. 294—295° (*acetate*, m. p. 138—139°; *methyl ether*, m. p. 109°). 7 : 8-*Dihydroxy-3-phenyl-2-methylbenzo-γ-pyrone*, m. p. 219—220° (*diacetate*, m. p. 111·5°), and 7 : 8-*dihydroxy-2* : 3-*diphenylbenzo-γ-pyrone*, m. p. 297° (*diacetate*, m. p. 177—178°), are obtained from 2 : 3 : 4-trihydroxyphenyl benzyl ketone; 7 : 8-*dihydroxy-3-benzyl-2-methylbenzo-γ-pyrone*, m. p. 203—205° (*diacetate*, m. p. 126°), and 7 : 8-*dihydroxy-3-benzyl-2-phenylbenzo-γ-pyrone*, m. p. 275—276° (*diacetate*, m. p. 175—176°), from benzylgallacetophenone. C. HOLLINS.

Constitution and synthesis of daphnin. P. LEONE (Gazzetta, 1925, **55**, 673—678).—The action of β-acetobromoglucose on daphnetin in sodium hydroxide solution yields *tetra-acetylgluco-daphnetin* (I), m. p. 220°, $[\alpha]_D^{17}$ −52·52° (in methyl alcohol), which, on hydrolysis, yields a compound identical with natural daphnin. The latter is thus (II) or (III).



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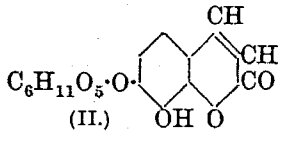

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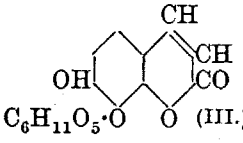


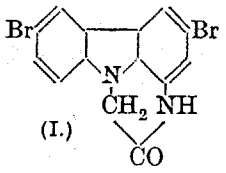
(III.)

T. H. POPE.

Mercury and arsenic compounds of pyrroles. H. FISCHER and R. MÜLLER (Z. physiol. Chem., 1925, **148**, 155—179).—By mixing solutions of mercuric chloride and of a series of pyrroles (R), the following additive *compounds* [$R_2Hg(HgCl_2)_4$] are prepared: with 2 : 3 : 5-trimethylpyrrole, m. p. 120—125° (decomp.); with 2 : 4-dimethylpyrrole, m. p. 136° (decomp.); with pyrrole, m. p. 143° (decomp.); with *N*-methylpyrrole, m. p. 120—130°; with ethyl 2 : 5-dimethylpyrrole-3-carboxylate, m. p. 230—232°; with ethyl 2 : 4-dimethylpyrrole-3-carboxylate, m. p. 218° (decomp.); with cryptopyrrole and with ethyl 2 : 4-dimethyl-3-acetylpyrrole-5-carboxylate. In all cases the original pyrrole can be recovered by treatment of an aqueous suspension of the additive compound with hydrogen sulphide. This precipitation–recovery method is applied to the isolation and quantitative separation of the acid and basic products of reduction of hæmin and ætioporphyrin by means of acetic acid and hydrogen iodide. Treatment with iodine and potassium iodide of ethyl 2 : 5-dimethylpyrrole-3-carboxylate gives ethyl 4-iodo-2 : 5-dimethylpyrrole-3-carboxylate, m. p. 136—137°, and of ethyl 2 : 4-dimethylpyrrole-3-carboxylate gives ethyl 5-iodo-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 146°. Treatment of tetraphenylethylene with ozone gives benzophenone and of dibiphenylene-ethylene, a substance m. p. 250—252°, together with diphenylene ketone, m. p. 82°. By treatment of the corresponding pyrroles with arsenic acid are obtained: 2 : 5-*dimethyl-3-carbethoxypyrryl-5-arsinic acid*, m. p. 245—247°, and 2 : 3 : 5-*trimethylpyrryl-4-arsinic acid*, m. p. 230—235° (decomp.). Pyrrole gives a similar *compound*, m. p. 120—130°. P. W. CLUTTERBUCK.

Derivatives of 1-aminocarbazole. H. LINDEMANN and F. MÜHLHAUS (Ber., 1925, **58**, [*B*], 2371—2377; cf. Lindemann, A., 1924, i, 550, 1234; 1925, i, 1098; Seka, A., 1924, i, 1234).—Previous attempts to obtain cyclic compounds from *N*-derivatives of carbazole by ring closure in the 1 : 9-position have been unsuccessful, but such compounds are derived from suitable 1-substituted carbazoles.

Carbazole dissolved in boiling carbon disulphide is transformed by bromine into 3 : 6-dibromocarbazole, m. p. 213°, which yields 3 : 6-*dibromo-9-acetylcarbazole*, m. p. 189°, 3 : 6-*dibromo-9-nitrosocarbazole*, m. p. 192° (decomp.) after darkening at 180°, and 3 : 6-*dibromo-9-methylcarbazole*, m. p. 158—160°, by customary methods. It is converted by nitric acid (*d* 1·4) in boiling glacial acetic acid solution into 3 : 6-*dibromo-1-nitrocarbazole*, m. p. 260°, the constitution of which is established by its production from bromine and 1-nitrocarbazole. 3 : 6-*Dibromo-1-nitro-9-methylcarbazole* has m. p. 221°. Reduction of 3 : 6-dibromo-1-nitrocarbazole by sodium disulphide and alcohol or stannous chloride and glacial acetic acid affords 3 : 6-*dibromo-1-aminocarbazole*, m. p. 192°, which gives amorphous, non-homogeneous products with nitrous acid and does not couple with phenanthraquinone; the *benzoyl* derivative, m. p. 273° (decomp.), and the *acetyl* compound are described. 3 : 6-*Dibromo-1-chloroacetamidocarbazole*, m. p. 265—267°, prepared from dibromoaminocarbazole and chloroacetyl chloride in boiling benzene, is converted by boiling, concentrated, aqueous-alcoholic potassium hydroxide into 3 : 6-*dibromo-1* : 9-*carbazole-3'-keto-piperazine* (I), m. p. 333°, the constitution of which is established by its conversion by sodium nitrite and boiling glacial acetic acid into 3 : 6-*dibromo-1* : 9-*carbazole-2'* : 3'-*diketopiperazine*, m. p. 435°, which is transformed by potassium hydroxide solution (50%) into 3 : 6-dibromo-1-aminocarbazole.



(I.)

Carbazole and bromine (3 mols.) in boiling carbon disulphide yield 3 : 6 : 8-*tribromocarbazole*, m. p. 184°, which is further brominated in hot glacial acetic acid solution to 1 : 3 : 6 : 8-tetrabromocarbazole, m. p. 220°. Nitration of the tribromo-compound affords 3 : 6 : 8-*tribromo-1-nitrocarbazole*, m. p. 264°, which is also obtained from 1-nitrocarbazole and an excess of bromine in carbon disulphide or glacial acetic acid. 3 : 6 : 8-*Tribromo-1-aminocarbazole*, m. p. 239°, and its *acetyl* derivative, m. p. 305°, are described. 3 : 6 : 8-*Tribromo-1-chloroacetamidocarbazole*, m. p. 285°, is

transformed by potassium hydroxide into 3 : 6 : 8-*tribromo*-1 : 9-*carbazole*-3'-*ketopiperazine*, m. p. 375°.

H. WREN.

Synthesis of 4-keto-1 : 2 : 3 : 4-tetrahydroquinolines and attempted synthesis of 4-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline. G. R. CLEMO and W. H. PERKIN, jun. (J.C.S., 1925, **127**, 2297—2307; cf. A., 1924, i, 1103).—The synthesis of 4-keto-tetrahydroquinolines from toluene-*p*-sulphonyl-β-anilinopropionic acid is extended to the *o*-, *m*-, and *p*-toluidine, *p*-anisidine, and *p*-phenetidine derivatives.

Toluene-p-*sulphonyl*-β-o-*toluidinopropionic acid*, m. p. 127—128°, prepared from toluene-*p*-sulphon-*o*-toluidide, β-chloropropionic acid, and sodium hydroxide, is converted by phosphoryl chloride into 1-p-*toluenesulphonyl*-4-*keto*-8-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 147—148°, and the corresponding *ketomethyltetrahydroquinoline*, m. p. 92°. The former, by treatment with cold sulphuric acid, yields β-o-*toluidinopropion*-o-*toluidide*, m. p. 126°, which is synthesised from toluenesulphonyl-β-o-toluidinopropionyl chloride and *o*-toluidine with subsequent hydrolysis in cold sulphuric acid.

Toluene-o-*sulphonyl*-β-m-*toluidinopropionic acid*, m. p. 103°, with phosphoryl chloride yields *toluene*-p-*sulphonyl*-3-*chloro*-4-*keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 138°, and a little of the 5-*methyl isomeride*, m. p. 98—100°. As in the case of the product from anilinopropionic acid (*loc. cit.*), these are hydrolysed by hydrochloric–acetic acid with loss of chlorine, forming 4-*keto*-7- and -5-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinolines*, m. p. 109° and 104—105°, respectively (*toluenesulphonyl* derivatives, m. p. 98° and 136°, respectively).

From *toluene*-p-*sulphonyl*-β-p-*toluidinopropionic acid*, m. p. 116—117°, and phosphoric oxide, *toluene*-p-*sulphonyl*-4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 136—137°, results, whilst with phosphoryl chloride the 3-*chloro*-derivative of this, m. p. 176—177°, is produced. Both are hydrolysed by hydrochloric–acetic acid to 4-*keto*-6-*methyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 85—86° (*benzylidene* derivative, m. p. 224—225°; *monobrominated benzylidene* derivative, m. p. 194—195°). When the 3-chloro-compound is refluxed with methyl-alcoholic potassium hydroxide it is converted into 4-*methoxy*-6-*methylquinoline*, m. p. 51°.

Toluene-p-*sulphonyl*-β-p-*anisidinopropionic acid*, m. p. 81—82°, gives *toluene*-p-*sulphonyl*-4-*keto*-6-*methoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 124—125°, or a mixture (m. p. 115—120°) of this and its 3-*chloro*-derivative according as phosphoric oxide or phosphoryl chloride is used. On hydrolysis with hydrochloric–acetic acid these are converted into 6-*methoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 112°. In the phosphoryl chloride condensation, there is formed a small amount of a *compound*, $C_{17}H_{16}O_3NClS$, m. p. 235°, which may be toluene-*p*-sulphonyl-3-chloro-6-methoxydihydroquinoline. Similar reactions are observed with *toluene*-p-*sulphonyl*-β-p-*phenetidinopropionic acid*, m. p. 97°, leading to *toluene*-p-*sulphonyl*-6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 114—115°, its 3-*chloro*-derivative, 6-*ethoxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 60°, and a *by-product*, m. p. 232°. 6-*Hydroxy*-4-*keto*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 163—164°, is obtained by heating the corresponding methoxy-compound with concentrated hydrochloric acid at 160—170°.

Toluene-p-*sulphonylbenzylaminoacetic acid*, m. p. 137—138° (*ethyl* ester, m. p. 51°), prepared from toluenesulphonbenzylamide (J.C.S., 1905, **87**, 159) and sodium chloroacetate, could not be converted into an *iso*quinoline derivative by the action of phosphoric oxide or phosphoryl chloride, nor of aluminium chloride on the acid chloride.

C. HOLLINS.

Dihydroquinolines. J. MEISENHEIMER and E. STOTZ (Ber., 1925, **58**, [*B*], 2330—2333).—Three groups of dihydroquinolines have been described which exhibit great differences in their properties. The substances prepared by Freund (A., 1905, i, 156) are, beyond doubt, 1-methyl-2-alkyl-1 : 2-dihydroquinolines; their most important properties are their slow decomposition at the b. p. with evolution of methane, fairly ready reducibility to tetrahydro-compounds, weakly basic nature, ability to add methyl iodide and to give yellow, very unstable picrates; with the exception of the 2-phenyl derivative, they have no marked tendency to polymerise.

The constitution, $\left[C_6H_4<\begin{matrix}CH{:}CH\\ NR{\cdot}CHR\end{matrix}\right]_2$, assigned by Heller (A., 1915, i, 300) to the bimolecular dihydroquinolines rests mainly on the transformation of Freund's 1 : 2-dimethyl-1 : 2-dihydroquinoline into the bimolecular product by treatment with zinc dust and hydrochloric acid, whereby catalytic action is ascribed to the nascent hydrogen. It is considered more probable that reduction of quinolines leads primarily to unstable 1 : 4-dihydro-compounds which immediately polymerise with formation of a tetramethylene ring, $\left[C_6H_4<\begin{matrix}CH_2{\cdot}CH-\\ NH-CMe-\end{matrix}\right]_2$; the production of such compounds by Heller's method is ascribed to a preliminary oxidation of 1 : 2-dihydroquinolines by zinc oxide present in zinc dust to quinolines which are subsequently reduced.

Räth (A., 1924, i, 555, 667) has described the synthesis of a series of 1 : 2-dihydroquinolines from toluidines and halogenoacetals and has based the proof of the constitution on the assumed identity of the product of the action of α-bromopropionacetal on *N*-methyl-*o*-toluidine with Freund's 1 : 2-dimethyl-1 : 2-dihydroquinoline. Re-examination of Räth's product proves it to be a complex mixture of bases which has not been examined fully, but is certainly not identical with 1 : 2-dimethyl-1 : 2-dihydroquinoline.

H. WREN.

Action of magnesium *iso*butyl and phenyl halides on quinoline methiodide. J. MEISENHEIMER, E. STOTZ, and K. BAUER (Ber., 1925, **58**, [*B*], 2320—2330; cf. Meisenheimer and Schütze, A., 1923, i, 839).—Quinoline methiodide is converted by magnesium *iso*butyl bromide into 1-*methyl*-2-*isobutyl*-1 : 2-*dihydroquinoline*, b. p. 143—144°/12 mm., (*picrate*, m. p. 92—94°). When heated at its b. p. under atmospheric pressure, the base loses methane and becomes transformed into 2-*iso*butylquinoline,

b. p. 157°/23 mm. (*picrate*, m. p. 161°; *methiodide*, m. p. 186°). Reduction with tin and hydrochloric acid transforms 2-*iso*butylquinoline into 2-*iso*butyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 159—160°/20 mm. (hydrochloride, m. p. 217°; methiodide, m. p. 158—159°; *picrate*, m. p. 130—131°). Reduction of 1-methyl-2-*iso*butyl-1 : 2-dihydroquinoline, preferably by sodium and alcohol, affords 1-methyl-2-*iso*butyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 157°/18 mm. (*picrate*, m. p. 150°; methiodide, m. p. 151°). 2-*iso*Butyl-1 : 2 : 3 : 4-tetrahydroquinoline and 1-methyl-2-*iso*butyl-1 : 2 : 3 : 4-tetrahydroquinoline are identical respectively with the base *A* and base *B* considered by Freund and Kessler (A., 1919, i, 283) to be stereoisomeric forms of 1-methyl-2-*iso*butyl-1 : 2 : 3 : 4-tetrahydroquinoline; the 1-methyl-2-*iso*butyl-1 : 2-dihydroquinoline prepared by these authors was distilled under atmospheric pressure and the partial loss of methane occasioned thereby was not observed.

1-Methyl-2-*iso*butyl-1 : 2-dihydroquinoline resembles the corresponding propyl derivative (Meisenheimer and Schütze, *loc. cit.*) in giving a very unstable, yellow picrate. In the investigation of these picrates, 2-phenyl-1-methyl-1 : 2-dihydroquinoline has also been examined. The base, prepared from quinoline methiodide and magnesium phenyl bromide, resembles the other 1 : 2-dihydroquinolines in most respects, but becomes polymerised with unusual readiness. When heated at 250°, it loses methane and yields 2-phenylquinoline, m. p. 82° (*2-phenyl-1-methylquinolinium picrate*, prepared from 2-phenylquinoline methiodide and picric acid, has m. p. 135—136°). 2-Phenyl-1 : 2 : 3 : 4-tetrahydroquinoline (*picrate*, m. p. 129—130°) is obtained in 70% yield by the reduction of 2-phenylquinoline with tin and hydrochloric acid. *1-Benzoyl-2-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline* has m. p. 124—125°. Bromination of 2-phenyl-1-methyl-1 : 2-dihydroquinoline gives a compound, $C_{16}H_{15}NBr_2$ (cf. Freund, A., 1905, i, 156), which yields a stable *picrate*, m. p. 168—169°. If cold alcoholic or ethereal solutions of 2-phenyl-1-methyl-1 : 2-dihydroquinoline are treated with picric acid, a slight darkening in colour is observed, but crystals do not separate until some hours have elapsed. The product, m. p. 130°, has the analytical composition of 2-phenyl-1-methyl-1 : 2-dihydroquinoline picrate, but is insoluble in ether and must therefore separate immediately from ethereal solution in the presence of seeding material if derived directly from the base; when crystallised from alcohol, it becomes resolved into 2-phenyl-1-methylquinolinium picrate and a red picrate, m. p. 140°, which is regarded as *2-phenyl-1-methyl-1 : 4-dihydroquinoline picrate*. The latter compound resembles that obtained previously by Meisenheimer and Schütze (*loc. cit.*) from the 2-propyl compound and considered to be an indole picrate (this supposition is now withdrawn). The red picrate is obtained in considerably better yield by dissolving the crude picrate in cold acetone and precipitation with light petroleum. It is completely stable towards boiling alcohol, from which it can be crystallised. The crude picrate cannot therefore consist entirely of the salt of the 1 : 4-dihydro-base, but must also contain a component which passes into the 1 : 4-dihydroquinoline picrate in acetone and yields the quaternary picrate in addition to that of the 1 : 4-dihydro-base in boiling alcohol; this can scarcely be other than the picrate of the 1 : 2-dihydro-base. The main reason for the assumption that the red picrates are derived from 1 : 4-dihydroquinolines is that the change from the yellow picrates which regenerate 1 : 2-dihydroquinolines when treated with alkali to the red compounds which have not this ability does not occur if the 2-hydrogen atom necessary for the displacement of the 1 : 2- to the 1 : 4-dihydro-base is replaced by a non-migratory group; thus 1 : 2 : 2-trimethyl-1 : 2-dihydroquinoline picrate is a yellow substance which undergoes no change when recrystallised.

It is somewhat surprising that the picrates of the 1 : 4-dihydro-bases are more darkly coloured than those of the 1 : 2-dihydro-bases. The former compounds are very feeble bases similar to indoles, in which the same arrangement of double linkings is present. Like the latter, therefore, they do not give normal picrates, but deeply-coloured, molecular compounds with picric acid. The 1 : 2-dihydro-bases are somewhat stronger and yield normal picrates. The ability of 2-phenyl-1-methyl-1 : 4-dihydroquinoline to give an additive *product*,

$$C_{16}H_{15}N,C_6H_2O_7N_3Na,$$

m. p. 170°, with sodium picrate is in harmony with this conception; bases, like aniline, which give true picrates, have not this ability. H. WREN.

2-Methylquinoline oxide. J. MEISENHEIMER and E. STOTZ (Ber., 1925, **58**, [*B*], 2334—2335).—Oxidation of 2-methylquinoline with perbenzoic acid affords *2-methylquinoline-N-oxide*, $(+2H_2O)$; the compound is identical with "4-keto-2-methyl-1 : 4-dihydroquinoline" obtained by Heller and Sourlis (A., 1908, i, 913) by reduction of *o*-nitrophenylhydroxyethyl methyl ketone with zinc dust and cold 33% acetic acid. The ready reduction of the compound to 2-methylquinoline, its non-transformability into 4-hydroxy-2-methylquinoline, its weakly basic character, and the complete absence of acidic character are satisfactorily explained by the new conception. Energetic oxidation converts it into *quinoline-N-oxide-2-carboxylic acid* (Heller and Sourlis' "4-keto-1 : 4-dihydroquinoline-2-carboxylic acid"). H. WREN.

Dibenzyl-2-methylquinoline. W. H. MILLS and A. T. AKERS (J.C.S., 1925, **127**, 2475—2478).—The amide of dibenzylacetic acid reacts with excess of magnesium methyl iodide to form *as.-dibenzylacetone*, b. p. 120—122°/16 mm., and this ketone condenses readily with *o*-aminobenzaldehyde, yielding *dibenzyl-2-methylquinoline*, m. p. 74°; *methiodide*, m. p. 204° (cf. following abstract). Dibenzylacetyl chloride, used for preparing the corresponding amide, passes on heating into 2-benzyl-1-hydrindone, *semicarbazone*, m. p. 198—199°. B. W. ANDERSON.

Cyanine dyes. IX. Mechanism of the condensation of 2-methylquinoline alkyliodides in presence of bases. W. H. MILLS and R. RAPER (J.C.S., 1925, **127**, 2466—2475).—The active agents in the condensation of 2-methylquinolinium salts

with aldehydes and with nitroso-compounds are methylene bases formed by removal of the elements of the acid from the quaternary salt. These are formed as impure oils by the action of alkalis on 2-methylquinoline alkyliodides, and crystals of the corresponding 1-*methyl*-2-*methylene*-1 : 2-*dihydro*-β-*naphthaquinoline* (decomp. 80°) are similarly obtained. The methylene base formed from 2-methylquinoline ethiodide yielded with benzyl iodide *dibenzyl*-2-*methylquinoline ethiodide*, m. p. 214—216°, indicating the presence of the –N·C:C– grouping (cf. Robinson, J.C.S., 1916, **109**, 1038). In proving the constitution of the dibenzyl compound, *benzyl*-2-*methylquinoline ethiodide*, m. p. 172—173°, was prepared. These methylene bases condense readily with dimethylaminobenzaldehyde, forming unstable allene derivatives, those from β-naphtha-2-methylquinoline alkyl iodides being scarlet powders which form purple dyes with hydriodic acid or piperidine hydriodide. The methylene base obtained from 2-methylquinoline ethiodide reacts with formaldehyde and *p*-tolu-2-methylquinoline ethiodide to give the unsymmetrical pinacyanole 6-*methyl*-1 : 1′-*diethyl*-2 : 2′-*carbocyanine iodide*; similarly, the base gives with β-naphtha-2-methylquinoline ethobromide and formaldehyde 5 : 6-*benzo*-1 : 1′-*diethylcarbocyanine bromide*.

B. W. ANDERSON.

2-Phenyl-3-anisolesulphonylquinolines and 2-phenyl-3-phenetolesulphonylquinolines. J. TRÖGER and D. DIMITROFF (J. pr. Chem., 1925, [ii], **111**, 193—206; cf. Tröger and Seelen, A., 1923, i, 1127; Tröger and Brohm, A., 1925, i, 1452).—The stability of certain 2-phenyl-3-arylsulphonylquinolines towards oxidation, reduction, and Hofmann degradation is examined.

2-*Phenyl*-3-o-*anisolesulphonylquinoline*, m. p. 219° (*hydrochloride*, *nitrate*, and *hydrogen sulphate* described), prepared from *o*-aminobenzaldehyde and *o*-anisolesulphonylacetophenone, gives no definite products with acid permanganate, but is reduced by tin and hydrochloric acid to *o*-methoxythiophenol (thioguaiacol) and 2-phenyl-1 : 2 : 3 : 4-tetrahydroquinoline. The methiodide, m. p. 206—208°, treated with silver oxide in alcohol at 100°, regenerates phenyl-*o*-anisolesulphonylquinoline.

p-*Anisolesulphonylacetophenone*, m. p. 110° (*oxime*, m. p. 134°; *phenylhydrazone*, m. p. 138°), obtained from phenacyl bromide and sodium anisole-*p*-sulphinate, condenses with *o*-aminobenzaldehyde to give 2-*phenyl*-3-p-*anisolesulphonylquinoline*, m. p. 187° (*hydrochloride*, *nitrate*, and *hydrogen sulphate* described). Here also oxidation with acid permanganate leads to no definite results, but reduction gives *p*-methoxythiophenol and 2-phenyltetrahydroquinoline. The *methiodide*, m. p. 133—135°, does not undergo the Hofmann degradation.

From o-*phenetolesulphonylacetophenone*, m. p. 99° (*oxime*, m. p. 129°; *phenylhydrazone*, m. p. 177°), and *o*-aminobenzaldehyde is obtained 2-*phenyl*-3-o-*phenetolesulphonylquinoline*, m. p. 174—175° (*hydrochloride*, *nitrate*, and *hydrogen sulphate* described; *methiodide*, m. p. 122°), which is reduced by tin and hydrochloric acid to *o*-ethoxythiophenol and 2-phenyltetrahydroquinoline. 2-*Phenyl*-3-p-*phenetolesulphonylquinoline*, m. p. 153—154° (*hydrochloride*, *nitrate*, and *hydrogen sulphate* described; *methiodide*, m. p. 169—170°), is similarly reduced to *p*-ethoxythiophenol and 2-phenyltetrahydroquinoline.

C. HOLLINS.

Veranol–pyramidone and "veramone." H. RHEINBOLDT and M. KIRCHEISEN (Arch. Pharm., 1925, **263**, 513—518).—See B., 1925, 1011.

Anhydrides of amino-acid derivatives. C. GRÄNACHER, V. SCHELLING, and E. SCHLATTER (Helv. Chim. Acta, 1925, **8**, 873—883; cf. A., 1924, i, 1118).—5-Hydroxy-2-phenylglyoxaline is methylated by methyl iodide and sodium methoxide to give 5-*methoxy*-2-*phenylglyoxaline*, m. p. 56—58°, the constitution of which is proved by hydrolysis with aqueous hydrochloric acid on the water-bath, when no methylamine is produced, but ammonia, benzoic acid, and methyl aminoacetate hydrochloride. Reduction of 5-chloro-1 : 2-diphenylglyoxaline with sodium and alcohol furnishes 2 : 3-*diphenyl*-1-*benzyltetrahydroglyoxaline*, m. p. 123°, decomposed at once when dissolved in dilute hydrochloric acid into benzaldehyde and *phenylbenzylethylenediamine*, b. p. 214—216°/15 mm. (*dipicrate*, m. p. 158—160°, *dipicrolonate*, m. p. 215—217°). This base condenses readily with benzaldehyde to give the cyclic base once more, and the production of the latter in the reduction is due to the formation of phenylbenzylethylenediamine and of benzaldehyde by different modes of decomposition of the chlorodiphenylglyoxaline and their condensation together.

The action of phosphorus pentachloride on benzoylglycylglycine ester produces *ethyl* 5-*chloro*-2-*phenylglyoxaline*-1-*acetate*, a yellow oil (*picrate*, m. p. 140—142°). The *amide* of this acid sinters at 248°, m. p. 253°, and subjected to the Hofmann reaction yields only the *bromoamide*, m. p. 264° (after sintering at 260°). *Acetylglycine-ethylamide*, $NHAc\cdot CH_2CO\cdot NHEt$, m. p. 144°, from acetylglycine ester and ethylamine, is converted by phosphorus pentachloride into 5-*chloro*-2-*methyl*-1-*ethylglyoxaline*, b. p. 101°/12 mm., (*picrate*, m. p. 154°). *Acetylglycineanilide*, m. p. 191°, from glycine ester and boiling aniline, in the same way gives 5-*chloro*-1-*phenyl*-2-*methylglyoxaline* (*picrate*, m. p. 176°). *Benzoylglycyl-leucine ethyl ester* is obtained as a viscous liquid by interaction of leucine ester and hippuryl chloride in ethyl-alcoholic solution (*ethylamide*, m. p. 209°).

G. M. BENNETT.

Heterocyclic aldehydes. III. Triazolealdehydes. C. A. ROJAHN and H. TRIELOFF (Annalen, 1925, **445**, 296—306; cf. A., 1924, i, 875).—An extension of the aldehyde syntheses previously described to triazole derivatives. 1-*Phenyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*carboxyl chloride*, m. p. 133°, b. p. 105°/15 mm., is obtained by boiling the corresponding acid (cf. Dimroth, 1902, i, 403) with excess of thionyl chloride. The *amide*, m. p. 217—218°, and the *anilide*, m. p. 149—150°, were prepared. On reduction by Rosenmund's method, the chloride affords 1-*phenyl*-5-*methyl*-1 : 2 : 3-*triazole*-4-*aldehyde*, m. p. 52° (*hydrogen sulphite* compound, m. p. 158°; *semicarbazone*, m. p. 226—227°; *aminoguanidone nitrate*, m. p. 224°; *anil*, m. p. 256°; syn.-*oxime*, m. p. 162°).

Treatment of the oxime with acetyl chloride in pyridine affords *4-cyano-1-phenyl-5-methyl-1 : 2 : 3-triazole*, m. p. 63—64°, whilst it is reduced by sodium amalgam in alcohol to *1-phenyl-5-methyl-4-aminomethyl-1 : 2 : 3-triazole* (*hydrochloride*, m. p. 182—184°; *picrate*, m. p. 328°). The aldehyde condenses with ethyl cyanoacetate to form the *compound* $C_{15}H_{14}O_2N_4$, m. p. 126—127°, whilst treatment with ethyl acetate and sodium affords the corresponding *triazolylacrylic acid*, m. p. 189°. 1-Phenyl-5-methyl-1 : 2 : 3-triazole and *1-phenyl-4 : 5-dimethyl-1 : 2 : 3-triazole*, m. p. 98° (*picrate*, m. p. 131°), are obtained as by-products in the above reduction of the acid chloride. The use of insufficiently purified hydrogen leads to the formation of the *anhydride* of *1-phenyl-5-methyl-1 : 2 : 3-triazole-4-carboxylic acid*, m. p. 189°. *1 : 5-Diphenyl-1 : 2 : 3-triazole-4-carboxyl chloride*, yellow, m. p. 101°, obtained similarly (cf. Dimroth and Letsche, A., 1903, i, 127) (*amide*, m. p. 174°; *anilide*, m. p. 147—148°) is reduced analogously to *1 : 5-diphenyl-1 : 2 : 3-triazole-4-aldehyde*, m. p. 104—105° (*oxime*, m. p. 176°; *semicarbazone*, m. p. 224°; *aminoguanidone nitrate*, m. p. 205°; *anil*, m. p. 136—137°; ethyl cyanoacetate *condensation product*, m. p. 165—166°). Treatment of the sodium salt of ethyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate with phosphorus pentachloride and phosphoryl chloride at 140° yields *ethyl 5-chloro-1-phenyl-1 : 2 : 3-triazole-4-carboxylate*, m. p. 78°, which is hydrolysed by boiling concentrated hydrochloric acid to the corresponding carboxylic *acid*, m. p. 189—190°. The latter is converted into the acid *chloride*, m. p. 125—126°, by the action of phosphorus pentachloride and phosphoryl chloride at 140°. The *amide*, m. p. 182—183°, and *anilide*, m. p. 146°, are described. Treatment of 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid (cf. Dimroth and Letsche, *loc. cit.*) with thionyl chloride yields a resinous *product*, which affords, when treated with ammonia, the corresponding *diamide*, m. p. 228°. Condensation of 2-chloro-5-methyl-1 : 3 : 4-triazole with ethyl chloroformate in ether in presence of metallic sodium yields *ethyl 2-chloro-5-methyl-1 : 3 : 4-triazole-3-* (or 4)*-carboxylate*, m. p. 58—59°. Acid chlorides can only be obtained from carboxylic acids of 1 : 2 : 3-triazoles which contain a methyl-, phenyl-, or carboxyl-group, or a halogen atom, attached to the atom adjacent to that carrying the carboxyl-group. Acid chlorides could not be obtained from 1 : 3 : 4-triazolecarboxylic acids.

F. G. WILLSON.

Methylation of diketopiperazine and piperazine. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1925, **148**, 245—253).—Piperazine may be methylated by means of methyl iodide, giving 1 : 4-dimethylpiperazine dihydriodide, which, with more methyl iodide, yields *1 : 1 : 4 : 4-tetramethylpiperazinium di-iodide*, m. p. 278° (decomp.). Both substances combine with iodine, the compound with the former showing greater tendency to dissociation than that with the latter. Piperazine may also be methylated by methyl sulphate. The methylated base is then precipitated with mercuric chloride and the product on treating with hydrogen sulphide gives *1 : 1 : 4 : 4-tetramethylpiperazinium dichloride*, m. p. 276° (decomp.). Both the di-iodide and the dichloride give the same *sulphate*, m. p. 230°, which with aqueous barium hydroxide gives the corresponding *hydroxide*, m. p. 175° (decomp.). Glycine anhydride on treatment with methyl sulphate gives sarcosine anhydride, m. p. 145°, which by reduction with sodium and alcohol gives 1 : 4-dimethylpiperazine.

P. W. CLUTTERBUCK.

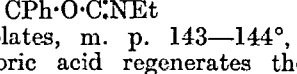
Pyrimidines. CIII. Discovery of 5-methylcytosine in tuberculinic acid, the nucleic acid of the tubercle bacillus. T. B. JOHNSON and R. D. COGHILL (J. Amer. Chem. Soc., 1925, **47**, 2838—2844).—Hydrolysis of tuberculinic acid (cf. Johnson and Brown, A., 1923, i, 160) with 25% sulphuric acid affords cytosine and 5-methylcytosine (cf. Wheeler and Johnson, A., 1904, i, 624), separation of the two bases being effected by fractional crystallisation of their picrates, although the picrate of the methyl derivative cannot be completely separated from that of cytosine. Cytosine picrate crystallises in slender, golden-yellow, blade-like, monoclinic crystals formed by twinning of individuals along a plane parallel to their length, whilst 5-methylcytosine picrate forms minute, lath-like, orthorhombic crystals of golden-yellow lustre, the two salts being readily characterised under the microscope. Identity with synthetic specimens was established by crystallographic examination.

F. G. WILLSON.

Dimethyl*iso*indigotins and a new hydrolysis of disulphisatides. A. WAHL and T. FAIVRET (Compt. rend., 1925, **181**, 790—792).—On treatment with hydrogen in the presence of finely divided platinum 7-methylisatin is not reduced, isatin yields isatide, and 5-methylisatin gives 5-methylisatide. 5-Methylisatin reacts with hydrogen sulphide, yielding *5 : 5′-dimethyldisulphisatide* (cf. A., 1925, i, 588). When heated with pyridine, 5 : 5′-dimethyldisulphisatide gives sulphur, *5 : 5′-dimethyliso**indigotin***, brown, *leuco*-compound, m. p. 330°, and *5-methyloxindole*, m. p. 168°, *benzylidene* compound, m. p. 182°. Oxindole and *7-methyloxindole*, m. p. 203—204°, *benzylidene* compound, m. p. 224°, were isolated from the reaction products of pyridine with disulphisatide and 7 : 7′-dimethyldisulphisatide, respectively (cf. A., 1923, i, 607; 1924, i, 322).

L. F. HEWITT.

Anhydrides of amino-acid derivatives. C. GRÄNACHER (Helv. Chim. Acta, 1925, **8**, 865—873; cf. A., 1924, i, 1118).—Hippuric ethylamide is converted by the action of phosphorus pentoxide in chloroform into *5-ethylimino-4-β-ethylamino-β-keto-ethyliminobenzyl-2-phenyloxazoline*,



yellow plates, m. p. 143—144°, from which 5% hydrochloric acid regenerates the probable intermediate *4-benzoyl-5-ethylimino-2-phenyloxazoline*, yellow needles, m. p. 112°, developing a green colour with ferric chloride, whilst 20% hydrochloric acid acts on either of these substances to open the oxazoline ring with production of *α-benzoylhippuric ethylamide*, NHBz·CHBz·CO·NHEt, m. p. 197—198°, which gives a violet-red colour with ferric chloride. Aqueous potassium hydroxide slowly hydrolyses this substance

to benzoic acid and hippuric ethylamide. For comparison, ethyl α-aminobenzoylacetate was obtained by reduction of ethyl benzoyl*iso*nitrosoacetate and converted by benzoylation into *ethyl α-benzoylhippurate*, NHBz·CHBz·CO_2Et, m. p. 128—129°. This gives a red colour with ferric chloride. Ethylamine converts it, not into the ethylamide, but into hippuric ethylamide and benzoic acid derivatives.

G. M. BENNETT.

Hydroxybenzylidene azides and indoxazens. H. LINDEMANN and A. MÜHLHAUS (Annalen, 1925, **446**, 1—13).—Both *o*- and *p*-hydroxybenzylidene halides react with sodium azide in neutral or acetic acid solution according to the scheme: $OH\cdot C_6H_4\cdot CHBr_2 \xrightarrow{-HBr} O{:}C_6H_4{:}CHBr \xrightarrow{+N_3H}$ $OH\cdot C_6H_4\cdot CHBrN_3 \xrightarrow{-HBr} O{:}C_6H_4{:}CHN_3 \xrightarrow{+N_3H}$ $OH\cdot C_6H_4\cdot CH(N_3)_2$, an intermediate quinonemethide (methylenequinone) compound being formed (cf. A., 1923, i, 686; 1924, i, 181). The hydroxybenzylidene azides are unstable, but may be handled without danger. On boiling in neutral or acetic acid solution, they lose the elements of azoimide and nitrogen, giving intermediate compounds of the form $O{:}C_6H_4{:}CH\cdot N{:}$, which tautomerise in the *p*-series into nitriles, $OH\cdot C_6H_4\cdot CN$, and in the *o*-series into indoxazens, $C_6H_4{<}^{CH}_{O-}{>}N$ (cf. Meyer, A., 1892, i, 992). Alkalis bring about molecular rearrangement of the indoxazens with formation of the isomeric nitriles (cf. Russanow, A., 1893, i, 95). By this series of reactions the following compounds were prepared: 3 : 5-*dibromo*-4-*hydroxy*-2 : 6-*dimethylbenzylidene azide*, m. p. 101° (decomp.); 3 : 5-*dibromo*-4-*hydroxy*-2 : 6-*dimethylbenzonitrile*, m. p. 189° (*acetyl* derivative, m. p. 161°); 3 : 5-*dibromo*-4-*hydroxy*-2 : 6-*dimethylbenzamide*, m. p. 270°; 3 : 5-*dibromo*-2-*hydroxybenzylidene azide*, m. p. 60°; 4 : 6-*dibromo*-*indoxazen*, m. p. 141°; 3 : 5-*dibromo*-2-*hydroxybenzonitrile*, m. p. 174° (*acetyl* derivative, m. p. 97°); 3 : 5-*dibromo*-2-*hydroxy*-4 : 6-*dimethylbenzylidene azide*, m. p. 64° (decomp.); 4 : 6-*dibromo*-3 : 5-*dimethylindoxazen*, m. p. 185°; 3 : 5-*dibromo*-2-*hydroxy*-4 : 6-*dimethylbenzonitrile*, m. p. 212° (*acetyl* derivative, m. p. 145°); 3 : 5-*dibromo*-2-*hydroxy*-4 : 6-*dimethylbenzamide*, m. p. 267°.

R. W. WEST.

Reactions of ββ′-dichloroethyl sulphide with amino-compounds. W. E. LAWSON and E. E. REID (J. Amer. Chem. Soc., 1925, **47**, 2821—2836).—The following alkylthiazanes, $R\cdot N{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}S$, were obtained by the action of the appropriate amine on ββ′-dichloroethyl sulphide in absolute alcohol in presence of sodium carbonate: n-*propyl*-, b. p. 82·5—83·5°/12 mm. (*hydrochloride*, m. p. 202°); iso*propyl*-, b. p. 74·5—75°/9 mm. (*hydrochloride*, m. p. 184—184·5°); n-*butyl*-, b. p. 118°/33 mm., 101—102°/19 mm.; iso*butyl*-, b. p. 93°/17 mm.; n-*amyl*-, b. p. 119°/15 mm., 104°/7 mm., d_4^4 0·9485, d_4^{25} 0·9332; and benzylthiazane, b. p. 152·5°/10 mm. (*hydrochloride*, m. p. 218°) (cf. Clarke, J.C.S., 1912, **101**, 1583). The following alkylthiazane-1-oxides were obtained analogously from the dichloroethyl sulphoxide: *methyl*-, m. p. 52° [*hydrochloride*, m. p. 241° (decomp.); *ethyl*- [*hydrochloride*, m. p. 177·5° (decomp.)]; and *benzylthiazane*-1-*oxide* [*hydrochloride*, m. p. 224° (decomp.)]. Similar condensations between primary amines and the dichloroethylsulphone afforded the following thiazane-1-dioxides: *methyl*-, m. p. 82°, b. p. 174·5—175°/19 mm. (*hydrochloride*, m. p. not below 280°); *ethyl*-, b. p. 175·5—176°/19 mm. (*hydrochloride*, m. p. 248—249°); n-*propyl*-, b. p. 177·5—178°/16 mm. (*hydrochloride*, m. p. not below 225°); iso*propyl*-, b. p. 173·5°/13 mm. (*hydrochloride*, m. p. not below 225°); n-*butyl*-, liquid, decomp. on distillation (*hydrochloride*, m. p. 195°); iso*butyl*-, m. p. 45°, decomp. on distillation (*hydrochloride*, m. p. 200·5°); n-*amyl*-, m. p. 41·5° (*hydrochloride*, m. p. 152°); and *benzylthiazane*-1-*dioxide*, m. p. 76·5°, decomp. on distillation (*hydrochloride*, m. p. 237—239°). Corresponding condensations with secondary amines proceeded without ring closure, with formation of bis-(dialkylaminoethyl) sulphides, sulphoxides, and sulphones. Bis-(β-dimethylaminoethyl) sulphide could not be isolated, as it decomposes when formed into *β-dimethylaminoethyl vinyl sulphide*; b. p. 168·5°/763 mm., and dimethylamine. The following were prepared: *bis*-(β-*diethylaminoethyl*), b. p. 139—140°/9 mm. (*dihydrochloride*, m. p. 247°); *bis*-(β-*di*-n-*propylaminoethyl*), b. p. 194°/19 mm., d_4^4 0·9007, d_4^{25} 0·8855 (*dihydrochloride*, m. p. 164·5°); *bis*-(β-*di*-n-*butylaminoethyl*), b. p. 205—206°/10 mm. (*dihydrochloride*, m. p. 130·5°); and *bis*-(β-*dipiperidylethyl*) *sulphide*, b. p. 174·5—176°/15 mm.; *bis*-(β-*dimethylaminoethyl*), liquid, decomp. when heated (*dihydrochloride*, m. p. 234°); *bis*-(β-*diethylaminoethyl*), similar (*dihydrochloride*, m. p. 222°); and *bis*-(β-*di*-n-*propylaminoethyl*) *sulphoxide*, similar (*dihydrochloride*, m. p. 164°); *bis*-(β-*dimethylaminoethyl*), b. p. 174—175°/15 mm. (*dihydrochloride*, m. p. 249°), d_4^4 1·0916, d_4^{25} 1·0755; *bis*-(β-*diethylaminoethyl*), (*dihydrochloride*, m. p. 202—202·5°); *bis*-(β-*di*-n-*propylaminoethyl*), b. p. 202—207°/10 mm. (*dihydrochloride*, m. p. 173°); *bis*-(β-*di*-n-*butylaminoethyl*), b. p. 215—220°/8 mm. (decomp.) (*dihydrochloride*, m. p. 162·5°), and *bis*-(β-*piperidylethyl*) *sulphone*, b. p. 247°/18 mm. Dichloroethyl sulphide, sulphoxide, and sulphone react with trimethylamine, with formation of *quaternary ammonium chlorides*, m. p. 135·5°, 239°, and 211·5°, the corresponding *chloroplatinates* having m. p. 253°, 240°, and 257°, respectively. The corresponding *pyridinium chloride* from the *sulphide* (*chloroplatinate*, m. p. 190°) was prepared, as well as the *pyridinium chloride* and *quinolinium chloride* from the *sulphone* (*chloroplatinates*, m. p. 191·5° and 243°, respectively). The sulphone was condensed with phenylalanine, with formation of *α-benzyl*-4-*thiazaneacetic acid*-1-*dioxide*, $CH_2Ph\cdot CH(CO_2H)\cdot N{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}SO_2$, m. p. 176°. None of the above compounds possesses vesicant action. The trimethylammonium salts exhibited the greatest toxicity, the sulphone derivative being more toxic than those of the sulphide and sulphoxide, the last two being about equally toxic (cf. Marshall and Williams, J. Pharmacol., 1920, **16**, 259), and observed results are in agreement with the theory that the vesicant action of ββ′-dichloroethyl sulphide is due to its reactions with constituents of the living cell.

F. G. WILLSON.

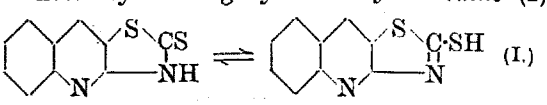
Aminobenzthiazoles. II. Naphthylamino-naphthathiazole derivatives. R. F. HUNTER (J.C.S., 1925, **127**, 2270—2274; cf. A., 1925, i, 1335).—Bromination of *s*-di-α-naphthylthiocarbamide, m. p. 196°, in chloroform yields 2-α-*naphthylamino*-β-*naphthathiazole tetrabromide*, red crystals which become paler at 190°, yellow at 200°, and colourless at 260°. On exposure to air, an orange *tribromide* is formed, which loses all its bromine when treated with sulphurous acid, giving 2-α-*naphthylamino*-β-*naphthathiazole*, m. p. 221°. Under different conditions of bromination the product obtained is a red *heptabromide*, $C_{10}H_6<^{NBr_2}_{SBr_4}>C{\cdot}NH{\cdot}C_{10}H_7,HBr$, or a red *tribromide* (softens at 260°, but is not melted at 280°). The tetra- and hepta-bromides, when digested with boiling alcohol and then for a few minutes with warm alkali, are converted into a *dibromo*-2-α-*naphthylamino*-β-*naphthathiazole*, m. p. 270—272° (sinters at 180°). Bromination of the thiazole base gives a *hexabromide*, which changes colour without melting at 238°. All these perbromides readily lose bromine on exposure to air or treatment with sulphurous acid or alcohol. In a similar manner, *s*-di-β-naphthylthiocarbamide, m. p. 194°, gives 2-β-*naphthylamino*-α-*naphthathiazole hexabromide*, which forms (i) dark red crystals, decomposing at 216° without melting, or (ii) purplish-red plates, m. p. 196° after changing colour at 140° and 194°. A red *tribromide*, m. p. 245°, is obtained under other conditions. 2-β-*Naphthylamino*-α-*naphthathiazole*, m. p. 223°, prepared from the hexabromide, gives on bromination the hexabromide, m. p. 198°. C. HOLLINS.

Supposed formation of 1 : 2 : 4-oxadi-imine rings from nitroso-compounds and methylene-arylamines. G. N. BURKHARDT, A. LAPWORTH, and E. B. ROBINSON (J.C.S., 1925, **127**, 2234—2236; cf. Ingold, A., 1924, i, 322; Farrow and Ingold, A., 1925, i, 155).—Since hydrolysis of *N*-hydroxy-*N*-*p*-chlorophenyl-*N'*-*p*-bromophenylformamidine,

$$C_6H_4Cl{\cdot}N(OH){\cdot}CH{:}N{\cdot}C_6H_4Br,$$

with aqueous-alcoholic alkali yields pure *p*-bromoaniline, it cannot be identical, as alleged (*loc. cit.*), with the additive product from *p*-bromonitrosobenzene and methylene-*p*-chloroaniline, for hydrolysis of the latter product is shown to give pure *p*-chloroaniline. There is thus no evidence for the supposed transient formation of cycloids ("oxadi-imines"), and the theory of alternate latent polaries affords an explanation of the facts observed. C. HOLLINS.

Use of rhodanine in organic syntheses. VI. Quinrhodine. C. GRÄNACHER, A. OFNER, and A. KLOPFENSTEIN (Helv. Chim. Acta, 1925, **8**, 883—892; cf. A., 1924, i, 765).—A by-product in the reduction of *o*-nitrobenzylidenerhodanine as previously described has now been isolated and found to contain a new heterocyclic ring system. *Quinrhodine* (I),



(I.)

bright yellow plates or brownish-red needles, m. p. 295°, cannot be obtained, as seemed likely, by the internal condensation of *o*-aminorhodanine, but owes its formation to the opening of the rhodanine ring by alkalis when, after reduction of the nitro-group, the quinoline ring closes first and then the rhodanine ring. The best method of preparation consists, therefore, in boiling the nitrobenzylidenerhodanine with alkali, reducing with ferrous hydroxide, and subsequently acidifying. The *potassium* salt ($+2H_2O$) is oxidisable to a *disulphide*, and is converted by benzyl chloride into the *benzyl thioether*, m. p. 145°. Fusion of quinrhodine with sodium hydroxide at 180° ruptures the rhodanine ring, yielding 3-*thiolcarbostyril*, m. p. above 350° (*methyl thioether*, m. p. 274° decomp., *benzyl thioether*, m. p. 234°, converted by ethyl iodide and sodium hydroxide into N-*ethyl*-2-*quinolone*-3-*benzyl thioether*, m. p. 138°), together with carbostyril (m. p. 199°).

N-*Methylquinrhodine*, m. p. 205°, N-*ethylquinrhodine*, m. p. 155°, N-*phenylquinrhodine*, m. p. above 285°, and N-*benzylquinrhodine*, m. p. 233°, are obtained by condensation of *o*-aminobenzaldehyde and the respective substituted rhodanines. Fusion of the *N*-ethyl compound with sodium hydroxide at 220° gives thiolcarbostyril. Ethylrhodanine condenses with 2 : 4-dinitrobenzaldehyde in acetic acid solution to yield 2 : 4-*dinitrobenzylidene*-N-*ethylrhodanine*, m. p. 133°, reduced by ferrous sulphate and ammonia to the *diamino*-compound, m. p. 223° (*diacetyl* derivative, m. p. 272°), from which a quinrhodine derivative could not be obtained. G. M. BENNETT.

Synthesis of galegine. E. SPÄTH and W. SPITZY (Ber., 1925, **58**, [*B*], 2273—2279; cf. Späth and Prokopp, A., 1924, i, 502; Barger and White, *ibid.*, 272; Tanret, *ibid.*, 622).—As a preliminary step in the synthesis of galegine,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}N{:}C(NH_2)_2,$$

the preparation of α-amino-γ-methyl-Δ^β-butene has been investigated. For this purpose, ethyl β-iodopropionate is converted by magnesium methyl iodide into *dimethyl*-β-*iodoethylcarbinol*, b. p. 81—83°/12 mm., from which the elements of water could not be conveniently removed by zinc chloride or zinc iodide or by replacement of the hydroxy-group by iodine and subsequent removal of hydrogen iodide; in all cases either much resin is formed or iodine separates in quantity. β-*iso*Amylenyl iodide is obtained in small quantity by direct distillation of the carbinol, but the process is not suitable for the synthesis of galegine in quantity. Better results are obtained by using *dimethyl*-β-*chloroethylcarbinol*, b. p. 62—63°/14 mm., prepared under definite conditions from methyl β-chloropropionate and magnesium methyl bromide. The chlorocarbinol is caused to react with potassium phthalimide in the presence of xylene at 169° and the product loses water when the temperature is raised to 218°, with formation of γ-*methyl*-Δ^β-*butenylphthalimide*, m. p. 100°, which, with barium hydroxide, affords α-amino-γ-methyl-Δ^β-butene. The picrate, m. p. 140°, of the synthetic base is identical with that derived from the product of the fission of galegine. The m-*nitrobenzoyl* derivative, m. p. 100°, and *chloroplatinate*, m. p. 191—192° (decomp.), of the bases are identical. α-Amino-γ-methyl-Δ^β-butene hydro-

chloride is transformed into galegine (picrate, m. p. 180—181°) by disodium cyanamide. The additive *compound*, m. p. 160·5—161·5°, of galegine and 2 : 4 : 6-trinitro-*m*-cresol and *di*-m-*nitrobenzoylgalegine*, m. p. 163—164°, are also described.

H. WREN.

Action of bromine on caffeine. Preparation of bromotheopylline. Y. YOSHITOMI (J. Pharm. Soc. Japan, 1925, No. 524, 884—888).—No dibromocaffeine is produced by the action of bromine on 8-bromocaffeine or in the presence of catalysts such as iodine, iron, ferric or aluminium chloride, or sulphur, or by heating a mixture of 8-bromocaffeine and dry bromine in a sealed tube at 100—150°. Under corresponding conditions, 7 : 8-dichlorocaffeine is easily prepared. By heating 8-bromocaffeine with phosphorus pentabromide in a sealed tube, no 3 : 8-dibromo-derivative is formed; 3 : 8-dichlorocaffeine is easily prepared by the same treatment. The affinity between bromine and caffeine is less powerful than that between chlorine and caffeine; thus, by heating with chlorine the bromine atom in 8-bromocaffeine is displaced by chlorine. Bromotheophylline is prepared by adding 10 g. of bromine in nitrobenzene to 10 g. of theophylline in 80 g. of nitrobenzene and 20 g. of carbon tetrachloride and heating at 110° for 2 hrs., followed by steam distillation.

K. KASHIMA.

Alkaloids of the group of *Sinomenium* and *Cocculus*. VI. Alkaloid of *Cocculus laurifolius*, DC. H. KONDO and T. KONDO (J. Pharm. Soc. Japan, 1925, No. 524, 876—882).—An alkaloid, *coclaurin* (cf. Greshoff, "I Verslag van het onderzoek naar de Plantenstoffen van Nederlandsch-Indie," Batavia, 1890; P. C. Plugge, Arch. exp. Path. Pharm., 1893, **32**, 266), has been isolated from an alcoholic extract of the stem and root of *Cocculus laurifolius*, DC., as colourless plates, m. p. 221°. It is easily soluble in alkali. An aqueous solution of the *hydrochloride* gives a violet or green coloration with ferric chloride in the cold or hot, respectively, but gives no coloration in alcoholic solution. It gives Liebermann's nitroso-reaction. It has $[\alpha]_D^{22}$ −17·01°, and contains one OMe-group, but no NMe-group. It gives a *hydrochloride*, m. p. 264°, and a *methiodide*, m. p. 155°. The alkaloid does not react with semicarbazide nor with hydroxylamine. By the Schotten–Baumann method, a *tribenzoyl* derivative, m. p. 207°, and a *triacetyl* derivative, m. p. 174°, are obtainable. Neither of these derivatives reacts as a base towards acids. From these results, the authors suggest the following formula for the base: $C_{16}H_{13}$(or $C_{16}H_{11}$)(:NH)(OMe)$(OH)_2$.

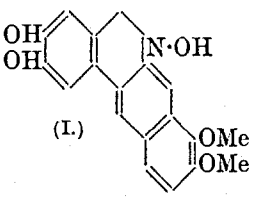
K. KASHIMA.

Series of feebly toxic alkaloidal derivatives. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1925, **181**, 887—888).—Pharmacological experiments with the nitrogen oxide derivatives of alkaloids of the nux vomica and of the tropan group (cf. A., 1925, i, 828) indicate that such derivatives ("genalkaloids") conserve the specific physiological action, but lose most of the toxicity, of the parent alkaloid. This probably holds for all active alkaloids. The effect may be due to slow partial reduction of the ·N:O group in contact with certain cells.

S. K. TWEEDY.

Syntheses of oxyberberine, palmatine, and tetrahydrojatrorrhizine. E. SPÄTH and H. QUIETENSKY (Ber., 1925, **58**, [*B*], 2267—2272).—The constitution of palmatine (Späth and Lang, A., 1922, i, 166) has been established only with respect to those of berberine and oxyberberine (Pictet and Gams, A., 1911, i, 483, 807). The uncertainty which has arisen regarding the latter (cf. Haworth, Perkin, and Rankin, A., 1924, i, 1100) has necessitated a fresh synthesis of oxyberberine which is effected from homopiperonylamine and meconinecarboxylamide; the results are not published in detail, however, since they have been anticipated by the independent work of Perkin, Rây, and Robinson (A., 1925, i, 695).

Berberine sulphate is converted by treatment with phloroglucinol and aqueous sulphuric acid at 100° into the phenolic base (I) which is isolated as the sparingly soluble *iodide*, $C_{19}H_{18}O_4NI$. It is converted by treatment with sodium methoxide and methyl sulphate into palmatine iodide, the identity of which is established by its transformation into tetrahydropalmatine. Partial methylation of the phenolic base gives a mixture of palmatine and jatrorrhizine which is readily separated into its components by treatment with alkali hydroxide; the portion soluble in alkali is reduced by zinc dust and sulphuric acid to tetrahydrojatrorrhizine, m. p. 216—217°, identical with the natural product; its purification is readily effected by means of the hydrochloride.



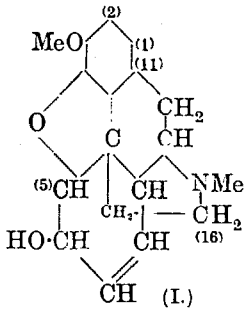
(I.)

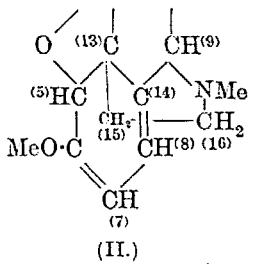
H. WREN.

Oxyacanthine. E. SPÄTH and A. KOLBE (Ber., 1925, **58**, [*B*], 2280—2285).—Oxyacanthine, to which the composition $C_{19}H_{21}O_3N$ or $C_{18}H_{19}O_3N$ has previously been assigned, is conveniently prepared by extracting the dried root rind of *Berberis vulgaris* with ethyl alcohol followed by treatment of the dried extract with hot, dilute hydrochloric acid. The precipitate obtained by adding sodium carbonate to the acid solution is exhaustively extracted with ether, which dissolves the oxyacanthine, but not berberine and other dark-coloured products. The crude base is purified through its hydrobromide or sulphate and obtained crystalline from much ether. It has m. p. 216—217°. Analyses and determinations of *M* in camphor indicate the composition, $C_{37}H_{40}O_6N_2$. The hydrochloride, $C_{37}H_{40}O_6N_2$,2HCl, m. p. 270—271°, $[\alpha]_D^{20}$ + 188·5° in water, and the *hydrobromide*, m. p. 273—275° (decomp.), are described. Three of the six oxygen atoms of the base are present in methoxy-groups, whereas a fourth is present in a hydroxy-group, since the base is soluble in alkali hydroxide and yields a *potassium* salt and a *methyl ether*. A methylenedioxy-group does not appear to be present. Oxyacanthine is converted by exhaustive methylation into *oxyacanthine methyl ether dimethiodide*, $C_{40}H_{48}O_6N_2I_2$, m. p. 255—260°, which is converted by silver chloride into the corresponding methochloride; the latter substance is reduced by sodium amalgam in aqueous solution to a base which

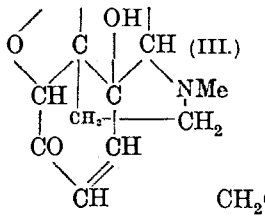
is characterised as the *dimethiodide*, $C_{42}H_{56}O_6N_2I_2$, m. p. 230—231°. Application of the same procedure to the new methiodide results in the production of trimethylamine and a nitrogen-free *compound*, $C_{36}H_{40}O_6$, m. p. 124—125°. Each nitrogen atom is therefore monocyclically attached in the molecule of the base and is united to a methyl group; the presence of two *iso*quinoline nuclei is suggested by the readiness with which the Emde degradation takes place. H. WREN.

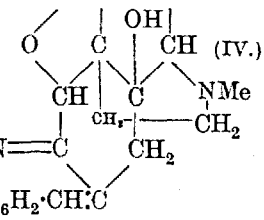
Constitution of codeine and thebaine. J. M. GULLAND and R. ROBINSON (Mem. Manchester Phil. Soc., 1924—25, **69**, 79—86).—The structures suggested earlier (J.C.S., 1923, **123**, 980, 998) are slightly modified, the bridge between carbon atoms 8 and 15 being replaced by an ethylene linking in position 7 : 8 (for complete numbering see *loc. cit.*). Codeine (I) and thebaine (II) are thus represented by the formulæ :


(I.)


(II.)

These contain the papaverine skeleton, which becomes apparent when the linking 12 : 13 is broken and the lower ring rotated through 180° about the axis 6 : 14. Codeine and the methylmorphimethines show strong evidence of unsaturation, and the existence of isomeric tetrahydrodeoxycodeines and of the isomerides thebainol and dihydrothebainone admits of a stereochemical explanation. The conversion of thebaine by hydrogen peroxide into hydroxycodeinone is usually represented by the change $-C(OMe):CH- \longrightarrow -CO\cdot CH(OH)-$. It is now shown, however, that hydroxycodeinone and its dihydro-derivative do not reduce Fehling's solution or ammoniacal silver solution, and are not changed by boiling 30% sulphuric acid; it is improbable, therefore, that they are α- or β-hydroxyketones. The remaining alternative is a γ-hydroxyketone structure. Hydroxycodeinone does not contain the grouping $\cdot CO\cdot CH_2\cdot$ which is present in dihydrohydroxycodeinone. Both condense with benzaldehyde, salicylaldehyde, and piperonal to give arylidene derivatives of dihydrohydroxycodeinone, reduction accompanying condensation in the case of hydroxycodeinone, to which is assigned the structure


(III.)


(IV.)

(III). From hydroxycodeinone and 6-aminopiperonal in the presence of alcoholic sodium ethoxide there is obtained a *compound*, $C_{26}H_{26}O_5N_2$, m. p. 243—244°, derived by loss of $2H_2O$ and addition of 4H. Dihydrohydroxycodeinone under the same conditions yields *dianhydro-6-aminopiperonal-dihydrohydroxycodeinone* (IV), $C_{26}H_{24}O_5N_2$, m. p. 282—283°.

C. HOLLINS.

Interactions of tellurium tetrachloride and aryl alkyl ethers. I. G. T. MORGAN and H. D. K. DREW (J.C.S., 1925, **127**, 2307–2315; cf. Rust, A., 1898, i, 137; Rohrbaech, A., 1901, i, 273; Lederer, A., 1915, i, 1056; 1916, i, 809, 810).—Lederer's view that in the reaction between anisole or phenetole and tellurium tetrachloride the tellurium enters the alkyl group, is shown to be erroneous. The products are of the type $RTeCl_3$, not R_2TeCl_2 as assumed by Lederer and previous workers; and their reduction products are ditellurides, RTe:TeR, not tellurides, R_2Te. The telluridichlorides, R_2TeCl_2, are obtained only when the reaction is forced.

Phenetole, refluxed for 2 hrs. with tellurium tetrachloride in chloroform, yields *p*-phenetyltelluritrichloride, $EtO\cdot C_6H_4\cdot TeCl_3$, m. p. 182—183°, which is reduced by potassium metabisulphite to bis-*p*-phenetyl ditelluride, m. p. 107—108°. The latter gives *p*-nitrophenetole, m. p. 60—61°, by the action of cold nitric acid. *Bis*-p-*phenetyltelluridichloride*, m. p. 108°, is obtained by heating phenetole with tellurium tetrachloride for 6 hrs. at 180—190°.

From resorcinol dimethyl ether are prepared in similar manner 1 : 3-*dimethoxyphenyl*-4-*tellurichloride*, m. p. 155—156°, and a mixture of this with *bis*-1 : 3-*dimethoxyphenyl*-4-*tellurichloride*, m. p. 204—205°. Reduction with metabisulphite leaves the dichloride unchanged, but converts the trichloride into *bis*-1 : 3-*dimethoxyphenyl* 4 : 4-*ditelluride*, m. p. 134—135°.

2-*Hydroxy*-1-*methoxyphenyl* 4-*telluritrichloride*, m. p. 157—159° (impure; decomp.), from guaiacol, is reduced by metabisulphite to *bis*-2-*hydroxy*-1-*methoxyphenyl* 4 : 4-*ditelluride*, m. p. 117—118° (decomp.).

The bis-*p*-anisyl ditelluride (Lederer's dianisyl telluride, *loc. cit.*), treated with methyl iodide, gives an equimolecular mixture of p-*anisyldimethyltelluriiodide* (*picrate*, m. p. 326—127°) and p-*anisylmethyltelluridi-iodide*, m. p. 109°. From the latter, by reduction with metabisulphite, is obtained *p*-anisylmethyl telluride.

The telluritrichlorides described are all yellow, the telluridichlorides colourless. The ditellurides are intensely coloured. C. HOLLINS.

Structure of proteins. Conversion of di- and tri-peptides into anhydrides. Reduction of gelatin. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1925, **148**, 254—263).—Purified gelatin on reduction with sodium and alcohol yields ammonia and a product from which was isolated by means of phenylcarbimide two compounds, one which on hydrolysis with hydrochloric acid gives a piperazine *compound* of leucine and proline, m. p. 181°, and a second which after hydrolysis gives a piperazine *compound* of glycine and oxyproline, m. p. 190°. The latter with diazomethane forms a *methyl* derivative, m. p. 195°. Leucylglycine, glycyltyrosine, and

leucylglycyl-leucine are converted into the anhydride when heated with glycerol. P. W. CLUTTERBUCK.

Alcoholytic cleavage of proteins. I. C. GRÄNACHER (Helv. Chim. Acta, 1925, **8**, 784—791).—Keratin (from white goose-feathers), heated with absolute ethyl alcohol or methylated spirit under pressure at 170—175°, is dissolved more rapidly than by 1% hydrochloric acid at 180°. The residue on evaporation of the solution is a pulverisable solid containing 15% of nitrogen of which only 0·7% is amino-nitrogen. Extraction with water and ether yields diketopiperazine (m. p. 280—282°) and a syrup which may be distilled at 5 mm. pressure. The viscous water-soluble oil of b. p. 130—140°/5 mm. gives no amino-acid reactions until boiled with concentrated hydrochloric acid. Benzoylglycyl-leucine-ethylamide (this vol., 78) and benzoyldiglycylglycine are recovered unchanged after prolonged heating at 170—180° with ethyl alcohol, whilst glycine anhydride is obtained from diglycylglycine under similar conditions. This evidence is considered to point to some other structure in the proteins than the generally assumed polypeptide linking of amino-acids. G. M. BENNETT.

Muscle albumin (myoalbumin). M. PIETTRE (Compt. rend., 1925, **181**, 737—739; cf. A., 1924, i, 228, 348).—Muscle extract is purified by saturation with ether, which precipitates 3·85% of bulky material, and is then treated with acetone, which precipitates 0·53% of globulin-like proteins. The mother-liquors are saturated with ether and when kept in the cold deposit 2·1% of myoalbumin, coagulating at 45—47°, yielding a clot, $[\alpha]_D$ −27° to −30° (for different species of animals), giving a limpid solution in water of high refractive index, not possessing marked anaphylactic properties. L. F. HEWITT.

Volumetric determination of nitrobenzene. I. M. KOLTHOFF (Chem. Weekblad, 1925, **22**, 558).—The nitrobenzene, dissolved in a mixture of alcohol and water, is reduced in presence of sodium hydroxide by addition of titanous chloride; after oxidation in air of the excess of titanous hydroxide, bromate and bromide are added, and the whole is acidified; after 5 min., potassium iodide is added and the liberated iodine titrated with thiosulphate. S. I. LEVY.

Qualitative test to show the absence of citrate or tartrate in mixtures. J. B. PETERSON (Ind. Eng. Chem., 1925, **17**, 1146).—A method is described for testing for the absence of citrates or tartrates in mixtures, based on the fact that the purple colour of the ferric salicylate complex is changed by the addition of minute quantities of citrate, tartrate, or any other substance capable of repressing the ferric ion. The absence of hydrogen tartrate in amounts not less than 1 in 8×10^4, 25×10^4, and $12{\cdot}5\times10^4$, respectively, can be shown by this method. L. L. BIRCUMSHAW.

Systematic detection of traces of aldehydes. E. C. CROCKER (Ind. Eng. Chem., 1925, **17**, 1158—1159).—See B., 1925, 1011.

Biochemistry.

Specific action of carbonic acid on the respiratory centre in man and rabbits. S. HETÉNYI, J. HOLLÓ, and S. WEISS (Biochem. Z., 1925, **160**, 242—245).—After injection of 20 c.c. of normal sodium hydrogen carbonate solution into man, a lowering of the acidity of the blood and of the alveolar carbon dioxide tension is found. In experiments with rabbits, injection of mixtures of hydrogen carbonate and carbonic acid of acidity either corresponding to, or somewhat more acid than, that of the animal's blood, displaces the p_H of the blood slightly to the alkaline side. P. W. CLUTTERBUCK.

Metabolism in rarefied air. I. Gas metabolism and protein metabolism. W. LAUBENDER (Biochem. Z., 1925, **162**, 459—468).—Experiments with guinea-pigs living in a chamber under reduced pressure (430—380 mm. of mercury) show that decrease in weight is smaller than in the control experiment; that during the first 2—6 hrs. there is a 20—40% increase in carbon dioxide elimination, the oxygen utilisation being, however, unaffected; that after the first 12—24 hrs. there is a 5—30% reduction in gaseous exchange; that there is a 14—59% increase in total nitrogen eliminated in the urine, and that during the second stage of the experiment the ammonia coefficient decreases. P. W. CLUTTERBUCK.

Respiration and glycolysis in animal tissues. R. O. LOEBEL (Biochem. Z., 1925, **161**, 219—239).—The glycolysis and respiration of the grey matter of rats' brains and of the spinal cord of frogs is compared with the carbohydrate metabolism of muscle and carcinoma cells. Narcotics inhibit respiration to a greater extent than glycolysis in nervous tissues, carcinoma cells, and growing epithelium. The effect is more pronounced with the higher members of a homologous series. Sodium fluoride, on the other hand, depresses glycolysis more than respiration.

The glycolytic behaviour of different sugars is similar in nervous and carcinoma cells, but differs sharply in the case of muscle. Lactic acid is produced from dextrose and mannose, to a lesser extent from hexosephosphoric acid, and not at all from glycogen, lævulose, maltose, or trioses. Respiration in absence of sugar decreases to about 10% or 20% of its original intensity in 2 hrs., but this is restored equally well by dextrose or lævulose. Although the trioses are unable to increase respiration, yet lactic and pyruvic acids will restore this when its intensity has fallen. C. RIMINGTON.

Gas and electrolyte equilibria in blood. VIII. Distribution of hydrogen, chloride, and hydrogen carbonate ions in oxygenated and reduced blood. D. D. VAN SLYKE, A. B. HASTINGS, C. D. MURRAY, and J. SENDROY, jun. (J. Biol. Chem., 1925, **65**, 701—728).—The activity coefficient of hydrogen carbonate ions in horse-serum, calculated from the experimentally determined apparent dissociation constant and the real constant (cf. Hastings, and Sendroy, this vol., 25), is 0·63, which gives 0·16 for the ionic strength of the serum; the latter value agrees closely with that calculated from analyses of serum; in the case of the cell contents, there is a discrepancy, at present not explained, between the activity coefficient demanded by the calculated ionic strength (0·62) and that found (0·40). A study of the distribution of ions between cells and serum in reduced and oxygenated blood indicates that for the range of p_H 7·0—7·6 the changes in distribution with changes in reaction are in agreement with those predicted by Van Slyke, Wu, and McLean (A., 1923, i, 1249); the actual ratios are related as follows: $[\alpha_H]_{cells} : [\alpha_H]_{serum} = 0{\cdot}77 \times \{[Cl]_{cells} : [Cl]_{serum}\} = 0{\cdot}62 \times \{[HCO_3]_{cells} : [HCO_3]_{serum}\}$, where α_H represents the activities of the hydrogen ions, and [Cl] and $[HCO_3]$ the molar concentrations of chloride and hydrogen carbonate. The fact that the difference in the magnitude of the latter ratios was not previously observed is accounted for by the previous lack of a method for determining the chlorides of the cells; this is now done with accuracy by the method of Van Slyke and Sendroy (A., 1924, ii, 271). C. R. HARINGTON.

Reconversion of methæmoglobin into oxyhæmoglobin. II. Perfusion experiments. III. Experiments on the living animal. K. SAKURAI (Arch. exp. Path. Pharm., 1925, **109**, 198—213, 214—232).—II. If the blood perfused through an isolated lung contains more than 70% of methæmoglobin, scarcely any conversion of the latter into oxyhæmoglobin can take place; if the concentration is 60% or less, such conversion takes place to the extent of 26% if ordinary air be breathed; the degree of conversion is increased by breathing hydrogen, by the addition of sodium thiosulphate to the blood, and by inclusion of the liver in the circulation; in the most favourable circumstances it is still less than 50%.

III. The toxic symptoms of poisons such as aniline and sodium nitrite, which exert their effect by formation of methæmoglobin, can be relieved to some extent, in cats, by intravenous administration of sodium thiosulphate; the favourable effect of thiosulphate could not be observed in rabbits.

C. R. HARINGTON.

Do ammonium salts exist in the blood? G. FONTÈS and A. YOVANOVITCH (Bull. Soc. Chim. biol., 1925, **7**, 1044—1055).—Only minimal amounts of ammonium salts (0·05—0·1 mg. per litre) are found in fresh venous or arterial blood, and it would appear that in the circulating blood no ammonium salts exist. The ammonia in the blood gradually increases with the time after withdrawal from the body. The biological consequences of the non-existence of ammonium salts in the circulating blood are discussed.

W. O. KERMACK.

Isolation of a new substance from blood and its bearing on determination of uric acid. G. HUNTER and B. A. EAGLES (J. Biol. Chem., 1925, **65**, 623—642).—By treatment of the protein-free filtrate from red blood-corpuscles with alcoholic mercuric chloride, fractional precipitation of the solution obtained on recovery from this precipitate with lead acetate and sodium hydroxide, removal of the lead from the precipitate with sulphuric acid, and treatment of the resulting solution with mercuric sulphate, there was obtained, from 5·5 litres of corpuscles, 0·7 g. of a *substance*, $C_6H_{11}O_3N_2$, darkening at 250°, m. p. 269—270°, $[\alpha]_D^{27\cdot5}$ −115°. The substance is neutral, takes up bromine and decolorises alkaline permanganate, gives Weyl's reaction, and is resistant to acid hydrolysis, being unchanged by heating at 140° for 4 hrs. with 20% sulphuric acid; with nitrous acid, it gives traces only of nitrogen; it is suggested that the compound is a simple pyrimidine nucleoside. The substance gives a blue colour with the reagents used for the determination of uric acid, and its presence accounts for the discrepancies observed between determinations by the method of Benedict (A., 1922, ii, 405) and that of Folin and Wu (A., 1919, ii, 308). (Cf. Bulmer, Eagles, and Hunter, A., 1925, i, 605.)

C. R. HARINGTON.

Sugar content of blood. B. K. HARNED (J. Biol. Chem., 1925, **65**, 555—560).—Precipitation of the proteins of blood with mercuric nitrate in nitric acid and removal of excess of mercury from the filtrate with hydrogen sulphide yields a solution entirely free from organic nitrogenous compounds; determinations of dextrose in such fluids by the method of Folin and Wu (A., 1920, ii, 337) give results in close agreement with those obtained by the recent method of Benedict (A., 1925, i, 994) and therefore probably represent the true concentration of dextrose. C. R. HARINGTON.

Dextrose content of human erythrocytes. P. A. TEDESCO (Folia med., 1924, **10**, 561—571; from Chem. Zentr., 1925, II, 939).—Human red blood-corpuscles are permeable to dextrose, yet their dextrose content is always less than that of the plasma. G. W. ROBINSON.

Determination of dextrose, non-protein nitrogen, uric acid, and total phosphorus in normal blood of man in tropical regions and in the blood of birds suffering from avitaminosis. P. J. T. VAN BERKHOUT (Arch. Néerland. physiol., 1925, **10**, 303—322).—See A., 1925, i, 453.

Action of calcium on the acid-base equilibrium in man. J. HOLLÓ and S. WEISS (Biochem. Z., 1925, **160**, 237—241).—Intravenous injection of hypertonic calcium chloride solution decreases the hydrogen carbonate content of the plasma and increases the alveolar carbon dioxide tension and acidity of the blood. Calcium chloride and lactate administered orally also decrease the hydrogen carbonate content of the plasma, but an effect on the tension of carbon dioxide and on acidity of blood could not be detected with certainty.

P. W. CLUTTERBUCK.

Influence of calcium salts on serum calcium of normal and thyroparathyroidectomised dogs. A. M. HJORT (J. Biol. Chem., 1925, **65**, 783—795).—A constant increase in the calcium of the blood-serum, following oral administration of calcium salts to dogs, could be obtained only by doses of soluble calcium salts in amounts equivalent to 0·2727 g. of calcium oxide, or more, per kg. of body-weight. Doses of this magnitude raised the concentration of calcium in the serum, and hence relieved the symptoms of tetany, in thyroparathyroidectomised dogs.

C. R. HARINGTON.

Action of metallic salts on the capacity of blood to decompose hydrogen peroxide. L. BLEYER (Biochem. Z., 1925, **161**, 91—103).—In comparing the action of different salts, the p_H of the solution cannot be neglected. In the majority of instances inhibition of the catalase occurs, this being least marked with the alkali chlorides, but no relation between inhibition and valency can be detected.

By graphic representation of the inhibition (ordinate) produced by different concentrations (abscissa), there is obtained for each salt a curve closely resembling the dissociation curve of an acid. The time curve of the catalytic action of sodium molybdate approximates to a parabolic function ($k=x/\sqrt{t}$). With catalase also present, no summation effect occurs, the velocity being less than that of the control. Ferric chloride in concentrations up to 0·0001*M* has a stimulating influence on catalase.

The reaction velocity in presence of lanthanum chloride, strontium nitrate, and potassium antimonite still corresponds with Morgulis' equation (A., 1921, i, 751); these substances do not therefore decrease the active concentration of the enzyme, although inhibition occurs in their presence. C. RIMINGTON.

Buffering properties of serum proteins. K. GOLLWITZER-MEIER (Biochem. Z., 1925, **163**, 470—475).—The relation of carbon dioxide combining power to carbon dioxide tension was determined for serum, serum ultrafiltrate, and ultrafiltrate residue. The results lead to the conclusion that, in the physiological range, the buffering of the serum depends chiefly on the serum proteins.

R. K. CANNAN.

Influence of protein concentration on conductivity of human blood-serum. D. W. ATCHLEY and E. G. NICHOLLS (J. Biol. Chem., 1925, **65**, 729—734).—Blood-serum was dialysed against 0·8% sodium chloride solution until free from other electrolytes and the conductivity of the resulting solution compared with that of a protein-free solution of similar sodium chloride content. An average of three experiments indicates a decrease of 1·58% in the conductivity at 25° for every gram of protein per 100 c.c. C. R. HARINGTON.

Blood proteins. II. Action of coagulation-inhibiting salts on plasma and serum. H. HUECK (Biochem. Z., 1925, **160**, 183—198).—Native serum has a higher refractivity than serum from defibrinated blood. Refractometric and interferometric methods show that the changes in the concentration of the serum exuding from spontaneously clotting blood are irregular during the first 4—5 hrs., but that the concentration then increases regularly up to 24 hrs. The view that plasma serum contains a higher protein concentration than serum of whole blood could not be confirmed. The refractivity of dilute sodium citrate solutions increases proportionately with increasing strength, but at higher concentrations the increase of refractivity becomes less and less. By addition of sodium citrate (0·2%) to whole blood, incorrect plasma values were obtained and addition similarly to serum did not give a purely additive increase in refractivity. The viscosity increase when increasing amounts of sodium citrate are added to serum does not keep pace with the increase in refractivity. Addition of isotonic sodium citrate to the serum has, however, corresponding effects on both refractivity and viscosity. When hirudin is not available, Starlinger's method is recommended for the determination of fibrinogen.

P. W. CLUTTERBUCK.

Relative viscosity of proteins of human blood-serum and their determination. W. STARLINGER and K. HARTL (Biochem. Z., 1925, **160**, 225—236).—A critical study of a number of methods for the determination of the relative viscosity of serum proteins. P. W. CLUTTERBUCK.

Abderhalden's reaction. A new blood reaction. H. SELLHEIM (Vox Medica, 1925, **1**, 128—141; from Chem. Zentr., 1925, II, 1078).—Abderhalden's reaction as modified by Lüttge and Mertz (B., 1925, 259) is discussed. Amongst the applications of the method are the study of nutrition, of cancer, and of changes during pregnancy, the examination of spinal fluid, and the determination of the degree of decomposition of meat.

G. W. ROBINSON.

Reversible hæmolysis. L. BOGENDÖRFER and B. HALLE (Biochem. Z., 1925, **160**, 199—209).—The methods of reversible hæmolysis of Brinkman and Szent-Györgyi are used to effect the combination of hæmoglobin and stroma of different origin and of different kinds of animals. Red blood-corpuscles after hæmolysis and reversion become more resistant to hypotonic solutions. The adsorption of hæmoglobin from solution by foreign stroma may be seen refractometrically. The authors support the view that hæmoglobin is adsorbed on the stroma.

P. W. CLUTTERBUCK.

Detection of enzymic processes conditioned by immunisation. III. E. KUPELWIESER and E. NAVRATIL. **IV.** E. KUPELWIESER and I. WILHEIM (Biochem. Z., 1925, **160**, 75—87, 88—100).—III. Sera obtained during the anti-anaphylactic condition from guinea-pigs which had received preliminary treatment with active horse-serum as antigen, were investigated by the refractometric method for the presence of specific proteolytic action on the antigen, with entirely negative results. (Cf. A., 1924, i, 806.)

IV. The possibility that the refractometric method failed to detect products of proteolytic action because the products were adsorbed on the intact substrate and thus did not go into solution, is dismissed in view

of the results of a series of adsorption experiments under similar conditions. P. W. CLUTTERBUCK.

Salkowski's method of preparing protein-free anti-toxin solutions. H. DOLD and E. FREUDENBERG (Biochem. Z., 1925, **162**, 169—170).—A criticism of Salkowski's preparations, which were found to be not entirely free from protein. H. G. REEVES.

Salivary glands. II. Occurrence of glycogen with reference to the excretion of sugar and glycogen. S. YAMAGUCHI (Beitr. pathol. Anat. allgem. Pathol., 1924, **73**, 123—141; from Chem. Zentr., 1925, II, 1055).—Glycogen was absent from the salivary glands of human and canine fœtuses, and from the excretory ducts of new-born and of adult rats. It was present only in small quantities in the case of pregnant rats. From experiments with pancreatectomy, and injection of sugar or adrenaline, the author concludes that the salivary glands play an important part in the excretion of glycogen and sugar. They can excrete these substances under the same conditions as the kidneys. The lachrymal glands and other organs (uterus, bronchi) may also participate to some extent. G. W. ROBINSON.

Distribution of injected sulphates in tissues. W. DENIS and S. LECHE (J. Biol. Chem., 1925, **65**, 565—570).—Considerable variations were observed in the sulphate content of normal tissues. Intravenous injection into dogs of large amounts of hypertonic sodium sulphate solution produced a marked and prolonged rise in the concentration of sulphates in the blood but no definite change in that in the tissues. C. R. HARINGTON.

Body-content of the hedgehog during hibernation. E. WEINLAND (Biochem. Z., 1925, **160**, 66—74).—Determination of the fat, glycogen, nitrogen, and water content of the hedgehog at various times during hibernation are tabulated. P. W. CLUTTERBUCK.

Mucoproteins of snails, *Helix aspersa* and *H. pomatia*. P. A. LEVENE (J. Biol. Chem., 1925, **65**, 683—700).—From the mucoprotein of the mucus of these two species there was obtained in each case, by treatment with alkali followed by precipitation with alcohol, a substance which is soluble only in strong mineral acids, gives a positive reaction for glycuronic acid, and reduces Fehling's solution only after hydrolysis; it is therefore a *mucoitinsulphuric acid*; on partial hydrolysis, it yielded mucosin (which on distillation with hydrochloric acid gave the theoretical amount of furfuraldehyde), and on complete hydrolysis chitosamine, and a volatile fatty acid which was probably acetic acid. By similar treatment of the mucoprotein of the foot of the snail, the glucoprotein of the body, or by direct extraction of the body, there was obtained, in addition to the above mucoitinsulphuric acid, a *polysaccharide* ("animal gum"), which on hydrolysis gave galactose and acetic acid, and, on oxidation with dilute nitric acid, yielded mucic acid, and therefore appears to be an acetylated polygalactose. C. R. HARINGTON.

Transformation products of the pigments of flesh and blood. VI. Kopratin, a substance derived from α-hæmatin by intestinal putrefaction, and the related porphyrin. O. SCHUMM (Z. physiol. Chem., 1925, **149**, 1—18).—If food containing blood pigments is eaten, or blood reaches the intestine from internal bleeding, together with α-hæmatin itself, another pigment which is derived from α-hæmatin by putrefaction appears in the fæces. This pigment, *kopratin*, may be separated from fæces by extraction with pyridine. On treatment of the pyridine extract with a little hydrazine hydrate, a solution is obtained having a well-marked absorption band at 545 μμ. It does not occur in the fæces of healthy individuals on a diet free from blood. It also appears to be produced outside the body during putrefaction of blood. The corresponding porphyrin is obtained by treatment of kopratin with hydrazine hydrate in glacial acetic acid solution. Methods of isolation of kopratin are described. H. D. KAY.

Bile pigments. XVII. Copper bilirubin. R. HAAS, H. MAURER, and W. KÜSTER (Z. physiol. Chem., 1925, **149**, 30—43).—Copper salts combine with bilirubin, in ammoniacal solution, to give a copper *compound* of bilirubin which may be precipitated from the reaction mixture with acetic acid. It occurs in two modifications, one obtained from hot ethyl benzoate, the other from hot pyridine solution. It is a very stable salt, and may be esterified direct with boiling methyl alcohol and hydrochloric acid without breaking up the bilirubin molecule. The copper is firmly united and is only very slowly precipitated by sodium sulphide and not at all by potassium ferrocyanide. Copper bilirubin may be benzoylated in pyridine solution, yielding a *benzoyl* compound which contains 4 mols. of pyridine very firmly attached. By reduction with sodium amalgam, copper bilirubin yields mesobilirubinogen. H. D. KAY.

Pigments. B. BLOCH and F. SCHAAF (Biochem. Z., 1925, **162**, 181—205).—Melanin is formed in the protoplasm of pigment cells (ectodermal and mesodermal melanoblasts) from a colourless precursor by means of an intracellular oxidation ferment, "dopaoxydase," which may be detected by the "dopareaction" (conversion of 3 : 4-dihydroxyphenylalanine into "dopamelanin"). It is sensitive to heat, drying, and hydrogen sulphide, but only slightly to hydrogen cyanide. It is very specific and its optimum p_H is 7·3—7·4. Pigment formation and the presence of the enzyme run parallel. The absorption spectrum of dopamelanin shows no characteristic bands, absorption beginning in the visible spectrum and increasing continuously with decreasing wave-length. Dopamelanin is a negative colloid and is best precipitated by acid, aluminium sulphate solution, or colloidal ferric hydroxide. Its solubility in alkalis, water, alcohol, and pyridine varies with the method of preparation and drying. It is very resistant to oxidation and reduction, and the products obtained by energetic reagents are not characterised. Dopamelanin is prepared by oxidation of 3 : 4-dihydroxyphenylalanine with oxygen in alkaline solution, carbon dioxide being eliminated. The original nitrogen of the amino-group was in part removed as

ammonia and in part converted into another form no longer determinable by Van Slyke's method. The amount of nitrogen obtained as ammonia is about half of the amino-nitrogen disappearing. This deamination occurs, therefore, without the presence of a deaminase and without the assistance of iron (the reaction follows the same course in the presence of potassium cyanide). The nitrogen content of dopa-melanin varies in different preparations from 5% to 8%, the purest product containing 5·23%. The proportion between the amino-nitrogen (Van Slyke) and the total nitrogen in both natural and artificial melanins is smaller the purer the preparation, the quotient in the purest artificial sample being 1/15·5. The author concludes that the small amino-nitrogen content of all specimens of melanin is due to adsorption during purification of intermediate products of oxidation.

P. W. CLUTTERBUCK.

Pigment studies in connexion with a case of "ringed" hair. K. KLINKE (Biochem. Z., 1925, **160**, 28—42).—Determinations of the sulphur, nitrogen, cystine, tyrosine, and tryptophan contents of a number of types of hair were made, including a case of "ringed" hair in which the hair cylinder is alternately lightly and darkly pigmented. The whole of the sulphur of normal human hair is present as cystine. Red hair contains, however, more sulphur than is represented by the cystine value. The colour of hair does not depend directly on the sulphur or the cystine content, but more probably on the tyrosine content. Whereas normal hair contains 4·3% of tyrosine, red and "ringed" hair contain 5·3—6·2%. White flaxen hair contains only 3·8% of tyrosine and 0·6% of tryptophan. The gas in the air-containing chambers of "ringed" hair contains 5·4% of oxygen and 2% of carbon dioxide. P. W. CLUTTERBUCK.

Reducing and iodine-combining power of urine. I. In normal individuals. H. K. BARRENSCHEEN and L. POPPER (Biochem. Z., 1925, **161**, 210—218).—The urinary substance described by Moor (A., 1924, i, 1134; 1925, i, 328) does not exist, the properties attributed to it being due to the accompanying pigments. In normal urine, the reducing power is parallel to the pigment content, but is unrelated to the iodine value. In the presence of glacial acetic acid, this latter value falls to the extent of about 9—29%, no alteration in reducing power occurring. The residual iodine uptake is related to the amount of urobilinogen present.

C. RIMINGTON.

Kidney and amino-acid excretion. E. SCHMITZ and P. SIWON (Biochem. Z., 1925, **160**, 1—19).—In the human subject, the exogenous amino-acid content of the urine is always less than the endogenous. Alteration in protein diet and administration of water and diuretics show that the endogenous amino-acid runs parallel with the functional activity of the kidney as measured by urinary volume.

P. W. CLUTTERBUCK.

Effects of calcium and potassium ions on urine secretion, as studied in the whole animal. L. BRULL and F. EICHHOLTZ (Proc. Roy. Soc., 1925, **B**, **99**, 57—70).—When a mixture of potassium and calcium chlorides is injected intravenously into an anæsthetised dog, the quantity of water secreted by the kidney is increased, but there is no constant increase in the concentration of chloride in the urine, such as was observed by Starling and Eichholtz in a heart-lung-kidney preparation (Eichholtz and Starling, Proc. Roy. Soc., 1925, **B**, **98**, 93). When, however, the pituitary body was removed, so that the kidneys had lost their power of concentrating the chlorides, results were obtained on the intact animal precisely similar to those of Starling and Eichholtz, the chloride in the urine secreted being constantly increased after injection of a mixture of calcium and potassium ions. W. O. KERMACK.

Secretion of inorganic phosphate by the kidney. II. Influence of the pituitary gland and of the wall of the third ventricle. L. BRULL and F. EICHHOLTZ (Proc. Roy. Soc., 1925, **B**, **99**, 70—91).—Excision of the pituitary body, or injury to the tuber cinereum, results in the loss by the kidney of the ability to secrete inorganic phosphates, whether or not denervation of the kidney has taken place. If, however, the inorganic phosphate in the blood is raised by injection of sodium phosphate, that ion appears in the urine when its concentration in the blood exceeds a certain critical value. Intravenous injection into an animal with intact pituitary and tuber cinereum, of sodium or potassium, or small quantities of calcium chloride, results in an increased secretion of urine, and an increase in the amount of inorganic phosphate secreted, although this increase is less than corresponds with the increase in the amount of urine. Large quantities of calcium chloride, on the other hand, cause a decrease, or even complete cessation of phosphate output. W. O. KERMACK.

Hydrolysis of phosphoric esters by the kidney *in vivo*. F. EICHHOLTZ, R. ROBISON, and L. BRULL (Proc. Roy. Soc., 1925, **B**, **99**, 91—106).—When a heart-lung-kidney preparation is perfused with defibrinated blood containing sodium glycerophosphate, inorganic phosphate appears in considerable, although variable, quantities in the urine. This is not due to the increase in inorganic phosphate of the circulating blood, nor to hydrolysis in the urine after secretion of organic phosphate, but it seems to be caused by hydrolysis in the kidney cells by the enzyme described by Robison (A., 1923, i, 730) as being present in the kidney, as well as in calcifying bone. Decrease of the p_H of the circulating blood results in a decrease in the inorganic phosphate in the urine. This is to be expected as a result of the high optimum p_H of the enzyme. When sodium glycerophosphate is injected into an intact animal from which the pituitary body has been removed (cf. preceding abstract), inorganic phosphate is excreted in the urine in high concentration, and the injected sodium glycerophosphate rapidly disappears from the blood. It is suggested that the normal secretion of phosphate by the kidney is dependent on the activity of the enzyme. W. O. KERMACK.

Botelho's reaction. F. FALUDI (Biochem. Z., 1925, **162**, 116—127).—The reaction is essentially a protein precipitation test; it is independent of the

albumin and globulin content, but depends on the total protein and the concentration of the precipitating reagent. If the percentage of protein is less than 6, a pronounced positive is obtained, but the reaction is not specific and in many cases a determination of the refractive index of the serum gives more trustworthy results. H. G. REEVES.

Nucleic acid of cancer tissue. R. WILLHEIM (Biochem. Z., 1925, **163**, 488—501).—Three separate preparations of nucleic acid and guanylic acid from large carcinomas were made by the method of Levene and Jacobs. Both the nucleic acid, $C_{48}H_{64}O_{32}N_{10}P_4$, and the guanylic acid, $C_{36}H_{45}O_{23}N_7P_2$, fractions differed grossly in composition, in particular in the P : N ratio, from the established composition of the substances isolated from the normal thymus. Hydrolysis of the nucleic acid fraction led to the identification of the presence of 1 mol. each of adenine and guanine, and 2 mols. of phosphoric acid. No pyrimidines were found, the carbohydrate presumed to be present could not be identified, and a phenolic substance was suspected. Hydrolysis of the guanylic acid fraction showed the presence of guanine and thymine, phosphoric acid, and, probably, a pentose. R. K. CANNAN.

Protein metabolism in experimental pancreatic diabetes. M. VON FALKENHAUSEN (Arch. exp. Path. Pharm., 1925, **109**, 249—275).—The ratio of amino-acid nitrogen, A.N., to total nitrogen, T.N., in the urine of normal dogs fed on a standard diet poor in nitrogen varies from 1·5% to 8%, but is constant for the same individual, and does not alter when the diet is withheld. After extirpation of the pancreas, and with low diet, A.N. does not markedly increase, but T.N. rises considerably, so that the ratio A.N. : T.N. falls. Amino-acids added to the diet are transformed to a greater extent by the diabetic than by the normal organism. Partial extirpation is followed for a short time by increased decomposition of proteins, with unaltered or lessened production of sugar from protein, resulting in absolute and relative increase of amino-acids in the urine. Tying or cutting the pancreatic ducts causes atrophy of the gland, affecting protein metabolism. In diabetes following pancreatectomy, insulin operates more slowly on the protein than on the carbohydrate metabolism; the absolute excretion of amino-acids is not greatly altered. The residual and amino-acid nitrogen in the blood increase after extirpation of the pancreas, the increase being afterwards partly lost; insulin causes a decrease, especially in the residual nitrogen. S. I. LEVY.

Calcium-ion concentration of the blood in puerperal eclampsia. R. VON BODÓ and S. LIEBMANN (Arch. exp. Path. Pharm., 1925, **109**, 178—184).—The blood-serum from cases of puerperal eclampsia, when perfused through the isolated frog's heart, caused no diminution in the contraction of the latter such as is brought about by blood-serum in which the calcium-ion concentration is reduced, *e.g.*, the serum from a parathyroidectomised dog. In eclampsia, therefore, the calcium-ion concentration is not reduced. C. R. HARINGTON.

Fat-cholesterol content of the blood in obesity and myxœdema. H. I. BING and H. HECKSCHER (Biochem. Z., 1925, **162**, 32—42).—The fat-cholesterol content of the blood of three patients suffering from myxœdema was definitely above normal up to a certain point. The increase was variable both as regards the individual and in different patients and administration of thyroid causes a diminution in the fat-cholesterol content. The amount of fat and cholesterol in the blood appears to depend on the fat content of the diet. Apparently thyroid feeding has no effect on the fat-cholesterol content of the blood in cases of nephritis. H. G. REEVES.

Physiological behaviour of acetylmethylcarbinol. II. Behaviour of acetylmethylcarbinol in the animal body. C. NEUBERG and A. GOTTSCHALK (Biochem. Z., 1925, **162**, 484—487).—Acetylmethylcarbinol and butylene glycol were injected subcutaneously into rabbits. No lactic, β-hydroxybutyric, or acetoacetic acid or acetone could be detected, but acetylmethylcarbinol is excreted partly unchanged and partly as the glycuronic acid compound in the urine and butylene glycol also as a glycuronic acid compound. Butylene glycol is not oxidised to any extent to acetylmethylcarbinol, since this did not appear in the urine. No toxic effects were observed. P. W. CLUTTERBUCK.

Chemical processes in "lipodiæresis" in the lungs. E. SCHMITZ and F. PEISER (Biochem. Z., 1925, **160**, 20—27).—An attempt to convert acetoacetic acid into β-hydroxybutyric acid by digestion with lung pulp, and butyric and β-hydroxybutyric acids into acetoacetic acid by perfusion through a surviving lung gave, in both cases, negative results. It would appear, therefore, that the lung does not play a similar part to the liver in this phase of fat metabolism. The use of foreign blood for the perfusion results in the rapid obstruction of the capillaries and œdema of the lung. P. W. CLUTTERBUCK.

Lactic acid in mammalian cardiac muscle. I. The stimulation maximum. L. N. KATZ and C. N. H. LONG (Proc. Roy. Soc., 1925, **B**, **99**, 8—20).—A comparison of the effects of lack of oxygen on stimulated mammalian heart and mammalian skeletal muscle shows that the former is far more sensitive than the latter, and is much less capable of going into "oxygen debt." At the same time, the mean maximum amount of lactic acid found after stimulation in heart muscle was 0·072%, whereas in skeletal muscle the mean stimulation maximum was 0·252%. The greater sensitiveness of active heart muscle to lack of oxygen would appear to be due to its greater sensitiveness to an increase in hydrogen-ion concentration along with its smaller buffering action as compared with skeletal muscle. W. O. KERMACK.

Lactic acid in mammalian cardiac muscle. II. Rigor mortis maximum, and the normal glycogen content. H. J. G. HINES, L. N. KATZ, and C. N. H. LONG (Proc. Roy. Soc., 1925, **B**, **99**, 20—26).—The maximum amount of lactic acid found in the heart muscle of a cat during rigor mortis or caffeine rigor is only about one-half of that found in skeletal muscle under similar conditions. In the

case of the heart muscle, the difference between the amount of lactic acid found and the normal amount of glycogen present is much greater than in the case of skeletal muscle, and this would indicate that in the former case there is normally present a larger amount of some lactic acid precursor other than glycogen, such as a hexosephosphate. The relatively low stimulation maximum of heart muscle (cf. preceding abstract) is not due to a deficiency of lactic acid precursor. In normal well-fed animals, heart muscle is poorer in glycogen than skeletal muscle.

W. O. KERMACK.

Lactic acid in mammalian cardiac muscle. III. Changes in hydrogen-ion concentration. L. N. KATZ, P. T. KERRIDGE, and C. N. H. LONG (Proc. Roy. Soc., 1925, **B**, **99**, 26—27).—During stimulation or in rigor mortis, heart muscle attains a higher p_H value than does skeletal muscle. The buffering value of skeletal muscle is greater than that of heart muscle. W. O. KERMACK.

Changes in composition of urine after muscular exercise. D. W. WILSON, W. L. LONG, H. C. THOMPSON, and S. THURLOW (J. Biol. Chem., 1925, **65**, 755—771).—See A., 1925, i, 1115.

Excretion of lactic acid in urine after muscular exercise. S. H. LILJESTRAND and D. W. WILSON (J. Biol. Chem., 1925, **65**, 773—782).—See A., 1925, i, 1115.

Connexion between creatine and carbohydrate metabolism. A. PALLADIN (Biochem. Z., 1925, **161**, 139—156).—The contradictory results of Mendel and Rose (A., 1911, ii, 1002) and of Wolf and Osterberg (A., 1911, ii, 1003) are reconciled by the finding that whereas in both dogs and rabbits addition of carbohydrate to the diet causes the disappearance of the creatine from the urine which is excreted in starvation, yet it is only in dogs that a similar result is achieved by the administration of protein in amounts in excess of that required to maintain nitrogen equilibrium. Probably rabbits are able to transform protein into carbohydrate with less facility. In both rats and guinea-pigs, creatine excretion rises when carbohydrate is withheld from the diet. Such excretion is prevented in dogs by administration of glycerol or lactic acid. Artificial lowering of temperature leads to creatine excretion which is also relieved by carbohydrate feeding. The muscle creatine is increased by a cold bath, rising to a sharp maximum at 12 hrs., then declining slowly. If carbohydrate is fed prior to the immersion, the increase is much reduced and of shorter duration. C. RIMINGTON.

Sugar catabolism in the human placenta. R. TATEYAMA (Biochem. Z., 1925, **163**, 292—296).—When placenta tissue was incubated in solutions of starch, glycogen, lactose, sucrose, or dextrose there resulted a greater production of acetaldehyde than in the absence of the carbohydrate. Alanine also led to acetaldehyde production. In the case of dextrose, addition of insulin further increased the yield of aldehyde. R. K. CANNAN.

Metabolism of salicylic acid. E. G. HOLMES (J. Pharm. Exp. Ther., 1925, **26**, 297—314).—When sodium salicylate is ingested by a normal individual in doses of 2—5 g., salicylic and salicyluric acids appear in the urine in the ratio approximately of 40 : 60, and it is estimated that more than 85% of the total salicylic acid taken is excreted. After ingestion of 1·5 g. of salicyluric acid the above ratio is 8 : 92. There does not appear to be any destruction of salicylic acid by the body. The distillation method of Hanzlik (cf. A., 1918, i, 142) is shown to be inapplicable to the determination of salicyluric acid, and a modification is described which yields better results. No evidence could be obtained of the production of any glycuronic compound. W. O. KERMACK.

Synthesis of hippuric acid in the human body. II. Glycuronic acid in urine after administration of sodium benzoate. G. BIGNAMI (Biochim. terap. sperim., 1924, **11**, 383—393; from Chem. Zentr., 1925, II, 944).—After administration of sodium benzoate to men, only a portion can be excreted as hippuric acid (at greatest, 21 g. from 20 to 42 g.) because not more than 13 g. of glycine is produced daily. Not more than 4·5 g. can be combined as glycuronic acid; the remainder appears unaltered in the urine, and, to some extent, also in the fæces. G. W. ROBINSON.

Synthesis of hippuric acid in the human body. III. Diuresis after administration of sodium benzoate. G. BIGNAMI (Boll. Soc. med.-chirurg. Pavia, 1924, **36**, 531—545; from Chem. Zentr., 1925, II, 944; cf. preceding abstract).—Administration of 50 g. of sodium benzoate causes diuresis both in normal and in sick individuals. G. W. ROBINSON.

The spleen in relation to metabolism. I. Effect of removal of the spleen on nitrogen and creatinine excretion. A. PALLADIN and L. PALLADIN (Biochem. Z., 1925, **161**, 104—113).—Removal of the spleen in rabbits leads to an increase in creatinine and a decrease in total nitrogen in the urine, with raised creatinine coefficient. These changes are not immediate, but develop gradually after the operation and are fully established in 1½—2 months. C. RIMINGTON.

Influence of radiation on metabolism. L. PINCUSSEN. **I. Alteration in blood potassium and calcium due to radiation.** I. MAKRINEOS. **II. Influence of sunlight on mineral metabolism.** L. PINCUSSEN (Biochem. Z., 1925, **161**, 61—66, 67—70).—I. Potassium and calcium determinations on the serum of normal human beings, after exposure to the rays of a quartz mercury lamp, and after certain dyes had been given (orally) prior to irradiation in order to sensitise the subjects, show that the serum potassium falls about 10% after irradiation, and this effect is greater when sensitisation is produced by methylene-blue, sodium anthraquinonedisulphonate, or sodium dichloroanthracenedisulphonate. With eosin, the results are negative, or a slight increase in the potassium figure occurs over that of the irradiated, non-sensitised subject.

The calcium results are less clearly defined. In most cases, no alteration occurred either with or without eosin sensitisation, but in the case of the other two dyes a slight tendency towards a rise in calcium content was noted. When expressed as a

quotient K/Ca the results show a fall of 25% below the normal on irradiation and a greater fall when methylene-blue or anthracene dyes are used. The fate of the potassium is unknown, but may be partly accounted for by renal excretion.

II. The urinary potassium, calcium, and magnesium excretion of rabbits was determined when the animals were kept, respectively, in complete darkness, in diffused light, and in bright sunlight. Throughout the experiments one of two chosen diets was supplied having widely different mineral contents. In both cases the effect of light was to increase the urinary K/Ca ratio considerably, whilst the ratio Ca/Mg fell 50%. C. RIMINGTON.

Effect of radioactivity on energy exchanges and metabolism of animal and plant cells. J. STOKLASA (Deut. med. Woch., 1925, **51**, 1057—1060; from Chem. Zentr., 1925, II, 1065).—The content of soil and air in radioactive substances may be positively correlated with suitability for plant growth and general healthiness for human beings in localities where such substances occur. Non-oxidative processes in cells are favoured by β-radiation, oxidative processes by α-radiation. G. W. ROBINSON.

Antagonism of potassium to *X*-rays and radium. G. A. NADSON and A. J. ŽOLKEVIČ (Biochem. Z., 1925, **163**, 457—463).—That potassium is antagonistic to the action of *X*-rays and radium on the growth of cells is suggested by experiments on the growth of treated and untreated seeds of *Sinapis alba* and of young yeast colonies. R. K. CANNAN.

Substance which reduces intraocular pressure. L. K. WOLFF and S. E. DE JONGH (Biochem. Z., 1925, **163**, 428—437).—The substance, which has been called "*antitonon*," is found in the serum of dogs in hypoglycæmic or other convulsions. It is colloidal, does not give protein, carbohydrate, or alkaloidal reactions, contains no sulphur or phosphorus, is stable to acids but unstable to alkali and to heat. Extracts of muscle and liver of animals in insulin convulsions were active; extract of brain was inactive. Its action is associated with an increased removal of aqueous humour. R. K. CANNAN.

Physiological action of furan. E. M. KOCH and M. H. CAHAN (J. Pharm. Exp. Ther., 1925, **26**, 281—285).—Although furan shows some anæsthetic and analgesic properties, it is too toxic to be of practical use. W. O. KERMACK.

Intoxication. VII. Effect of caffeine. VIII. Influence of oxygen. B. M. DAVIDSON (J. Pharm. Exp. Ther., 1925, **26**, 105—110, 111—121).—VII. In intoxication due to inhalation of ethyl chloride, caffeine exerts a stimulating effect during the stages prior to unconsciousness, and after cessation of the inhalation it accelerates the return of the reaction time to normal. It does not seem to shorten the actual time of recovery.

VIII. Some degree of anoxæmia appears to exist during anæsthesia and to be independent of the type of anæsthetic used. C. P. STEWART.

Absorption of certain gases by the skin. D. C. WALTON and M. G. WITHERSPOON (J. Pharm. Exp. Ther., 1925, **26**, 315—324).—Hydrogen cyanide is readily absorbed by the skin of dogs and guinea-pigs in amounts sufficient to cause death. Hydrogen sulphide is also absorbed by the skin of guinea-pigs, but death ensues only after large areas of the skin have been exposed to the pure gas. Carbon monoxide does not seem to be absorbed at all.

W. O. KERMACK.

Pharmacology of changes of concentration. III. Action of cations. L. JENDRASSIK and E. ANNAU (Biochem. Z., 1925, **162**, 207—227).—The action of potassium, calcium, and magnesium ions on the small intestine of cats and guinea-pigs is similar to that on the intestine of rabbits. The diminution effect on contraction of potassium and calcium ions is inhibited by atropine in the cat, but not in the rabbit. The effects of potassium and calcium are not additive. Magnesium inhibits the effect of calcium, but not of potassium. Decrease of the concentration of sodium chloride causes a short period of paralysis followed by a transient increased contraction, whilst high concentrations result in decreased amplitude. The behaviour of cæsium and still more of rubidium is similar to that of potassium. Addition of lithium causes successive transient periods of paralysis of contraction, increased contraction, and contraction with decreased amplitude of rabbit's intestine. The action of potassium on the isolated uterus of rabbits, cats, and guinea-pigs is similar to that on the intestine. Calcium concentrations above normal have a strong diminution effect on contraction of the uterus.

P. W. CLUTTERBUCK.

[Physiological activity of] benzyl compounds and the importance of substitution in the benzyl nucleus and the significance of side chains. H. H. JENSEN (J. Pharm. Exp. Ther., 1925, **26**, 123—169).—The following substances have been studied: 3 : 5-di(hydroxymethyl)-*p*-cresol, 3-*iso*propyl-6-hydroxymethyl-*m*-cresol, 5-hydroxymethyl-2-hydroxybenzaldehyde, and 2(or 3)-*hydroxymethyl*-4-*hydroxybenzaldehyde*. The last-named compound, obtained by the action of formaldehyde on *p*-hydroxybenzaldehyde, has m. p. 133·4° (corr.), and is slightly soluble in ether and almost insoluble in chloroform. The toxicity and physiological activity of all four compounds are less than those of the corresponding substances without the hydroxymethyl groups. The hydroxymethyl group appears to be chiefly responsible for the local anæsthetic action of benzyl compounds, and its position in the molecule to be of some importance. The introduction of a hydroxymethyl group reduces the antiseptic properties of benzyl compounds and the anthelmintic action of phenols. Bactericidal and anthelmintic properties of benzyl derivatives vary with the substituents in the following order of decreasing activity: hydroxyl, aldehydo, hydroxymethyl. The pharmacological action appears to correspond with that of the most active group in the molecule. C. P. STEWART.

Substance, from the putrefying stomach of a dog, resembling atropine in Vitali's test. T. SABALITSCHKA and W. BOLDT (Pharm.-Ztg., 1925, **70**, 1650—1651).—A substance was separated from

a putrefying dog's stomach and contents which could not easily be distinguished from atropine by Vitali's colour reaction, but was easily differentiated by the physiological test on the eye of a cat.

G. M. BENNETT.

Inactivation of atropine sulphate by rabbit serum. J. LA BARRE (J. Pharm. Exp. Ther., 1925, **26**, 259—279).—When atropine is added as sulphate to rabbit serum *in vitro*, about 30%, as determined by chemical or physiological methods, is inactivated in 2—6 hrs. This is confirmed by the fact that after ultrafiltration of the serum–atropine mixture about 60—65% of the original atropine is found in the filtrate. Further, tropine is formed during the inactivation in amounts approximately equivalent to the atropine which disappears. The inactivation of atropine by rabbit serum is therefore due to hydrolysis of the alkaloid, and not to adsorption by serum colloids as suggested by van Leeuwen and Zeijdner (*ibid.*, 1921, **17**, 121). W. O. KERMACK.

Tolerance to arsenic. E. KEESER and J. KEESER (Arch. exp. Path. Pharm., 1925, **109**, 370—377).—The hair of two dogs which had become tolerant to arsenic was found to contain considerable quantities of arsenic, and it is concluded that the hair and the whole ectoderm must play an important part in the excretion of arsenic. S. I. LEVY.

Effect of sodium arsenite on the blood-sugar concentration of the rabbit and dog. H. B. VAN DYKE (J. Pharm. Exp. Ther., 1925, **26**, 287—296).—When sodium arsenite solution is injected intravenously in sublethal doses into a rabbit, there occurs a hyperglycæmia accompanied by a decrease in the alkaline reserve. The hyperglycæmia is apparently due to a liberation of dextrose from the liver glycogen and is abolished by insulin. Sodium arsenite injected into a dog, causes a decrease in the alkaline reserve and often a slight hyperglycæmia.

W. O. KERMACK.

Combination of complex bismuth salts in the serum. H. BAUER and E. STRAUSS (Z. physiol. Chem., 1925, **149**, 19—29).—Bismuth circulating in the blood is mainly in a non-diffusible form, in loose combination with the euglobulin fraction of the serum proteins. It is also present in a diffusible form. The therapeutic action is probably associated with the non-diffusible part, the toxicity with the diffusible. Bismuth, added in the form of its complex organic compounds to blood-serum *in vitro*, is mainly taken up by the euglobulin fraction of the serum proteins, and becomes indiffusible. Part remains in simple solution as a diffusible salt. The two portions are in equilibrium, the position of which depends on the reaction of the serum. The presence of alkali favours salt formation, the presence of acid the formation of the protein complex.

H. D. KAY.

Absorption, excretion, and distribution of minute quantities of lead. B. BEHRENS (Arch. exp. Path. Pharm., 1925, **109**, 332—357).—By employing the radioactive isotope of lead, thorium-*B*, the determination of which by radioactive methods is extremely delicate, the distribution of lead injected into mice and cats may be quantitatively observed. The emanation from radiothorium was collected on platinum foil, and after equilibrium was established, the thorium-*B* was dissolved off with hydrochloric acid. The solution, either alone or with ordinary inactive lead chloride, was used for the injections. The organs to be examined were ignited, and the activity of the ash was compared with that of a suitable standard preparation.

Lead chloride introduced by the ear is very slowly absorbed, the maximum taken up being about 10% of that introduced after 10 hrs.; the amount absorbed is proportional to that introduced for small quantities (up to 0·25 mg. for the mouse), but diminishes for larger quantities. The metal is chiefly excreted in the fæces; the urine carries very little, and the exhaled air none. The amount excreted is proportional within limits to the concentration in the body. The lead is found chiefly in the liver, kidneys, bones, and gut; it is taken up from the blood first by the liver, and by the intestine and kidneys, and accumulates in the compact substance of the bones as it disappears from the liver. S. I. LEVY.

Intravenous silver therapy. IV. Silver-ion concentration in the process of disinfection in physiological media. V. Oligodynamic silver solutions. K. VON NEERGAARD (Arch. exp. Path. Pharm., 1925, **109**, 143—163, 164—177).—IV. The lethal effect of silver nitrate in aqueous solution on *Bacillus coli* is determined, not by the concentration of the salt in solution, but by its concentration in relation to the bacteria; the silver-ion concentration necessary to inhibit growth in distilled water is $1{\cdot}2\times10^{-7}$; in broth, it is $1{\cdot}8\times10^{-9}$. This marked difference is accounted for by the supposition that in broth (and also in physiological fluids) the toxic effect on the bacteria is exerted, not by silver ions as such, but by a loose compound of silver and sodium chloride; the power of the bacterial protein to adsorb silver ions is sufficient to dissociate this compound. This explanation is supported by the (potentiometric) observation that during the addition of silver nitrate to broth the silver-ion concentration does not even momentarily exceed the above-mentioned figure. The presence of bromide or iodide in therapeutic concentration must depress that of the silver ions to much below the bactericidal level.

V. Potentiometric determinations indicate that "oligodynamic" solutions, prepared by contact with silver, contain a concentration of silver ions of the order of $10^{-6}N$; the bactericidal agent in such solutions is therefore taken to be a definite ionised silver compound; an attempt was made to determine the nature of the anion of this compound by observing the depression of the silver-ion concentration on the addition of foreign salts with various anions; this has so far not been successful owing to the large amount of solution required. When a clean silver electrode is immersed in distilled water, it shows at first a high potential which slowly falls off; if the electrode has first been covered with a film of silver sulphide, the potential is at first low,

and rises fairly quickly. The fall of potential in the first case is ascribed to the gradual distribution throughout the solution of relatively insoluble dissociated silver salts, which are at first present only in a concentrated layer on the surface of the electrode; this process is regarded as indicating the mechanism of formation of an oligodynamic solution. The opposite effect in the second case is due to the suppression of the silver ions in the neighbourhood of the electrode, which continues until the excess of sulphide ions has been washed away.

C. R. HARINGTON.

Enzymes of the skin. III. Comparison of the enzymes of the skin of man and animals and the effect of light. N. SUGIHARA (Biochem. Z., 1925, **163**, 260—270).—The phenolase, diastase, gelatinase, and lipase activities of fresh living skins are compared. The skin of a number of animals showed much greater activities, particularly in respect to diastase, than did that of man. There was no parallel between the enzyme activities of the skin and of the blood. Suitable irradiation of the guinea-pig with natural or artificial sunlight led to an increase in skin phenolase, some decrease in lipase, and a notable decrease in diastase. *X*-Rays reduced the skin phenolase. Irradiation was without effect on the blood enzymes. R. K. CANNAN.

Enzymes of the human mammary gland. R. TATEYAMA (Biochem. Z., 1925, **163**, 297—307).—The enzyme activities studied were those of a nuclease, peptase (hydrolysis of glycyltryptophan), phosphatase, amylase, tributyrase, phenolase, and of a sucroclastic enzyme (production of acetaldehyde from sugars). Peptase activity was not increased in the lactating gland; the others, particularly the amylase, were increased. The difference between the tributyrase of the gland and of the blood is evidenced by the insensitivity of the former to quinine and atoxyl. R. K. CANNAN.

Influence of hydrogen-ion concentration on dextrin formation from starch by purified malt amylase. T. CHRZASZCZ, Z. BIDZINSKI, and A. KRAUSE (Biochem. Z., 1925, **160**, 155—171).—The optimal p_H for the action of malt amylase (probably for other enzymes also) is not fixed, but depends on a number of conditions, *e.g.*, temperature, the law of mass action, the protective action of starch, and on the buffering substances present. Over a temperature range of 20—75°, the optimal p_H shifts from 4·4 to 5·4. Conditions unfavourable to amylase action (high temperature, lowering of the active masses of reactants) shift the optimal p_H towards the alkaline side and conditions favourable to the reaction shift it to the acid side. The p_H zone for the reaction also is not of fixed size, but at lower temperatures (up to 40°) is large, extending on both sides of the optimum, whilst with higher temperatures it narrows and at 60° a sharp optimum is obtained. The reaction velocity constant is for each temperature dependent on the p_H. Acetate buffer mixture accelerates the reaction by 21—26% according to the temperature. The ratio K_2/K_1 and the temperature coefficient for temperature intervals of 10° decrease with increasing temperature and approximate to the values found for the saccharification process. Inactivation of amylase begins at temperatures above 30° and is almost complete above 60—65°, depending on p_H. P. W. CLUTTERBUCK.

Autolysis. V. P. RONA, E. MISLOWITZER, and S. SEIDENBERG (Biochem. Z., 1925, **162**, 87—115).—Glycogen decomposition during liver autolysis depends largely on the reaction of the medium. The optimum p_H is 6·7, and variation on either side greatly diminishes the amount of decomposition, particularly in acid solution (about p_H 3). The amount of glycogen decomposed usually exceeds the detectable reducing sugar formed during autolysis. The amount of inorganic phosphorus increases; this increase also depends on the p_H of the medium; it is at its maximum in neutral or faintly acid solution, but is practically negligible in strongly acid (p_H 6) or strongly alkaline (p_H 9) media. The production of inorganic phosphates is dependent on the enzymic decomposition of the nucleins and phosphatides, and is independent of the breakdown of protein and of glycogen. The phosphoric acid is responsible for the increase of acidity in the liver during autolysis. No indication of the formation of hexosephosphates is obtained. H. G. REEVES.

Autolytic decomposition of organic phosphorus compounds in the tissues. P. GYÖRGY (Biochem. Z., 1925, **161**, 157—177).—The increase in phosphate occurring in unhæmolysed blood is due to the fermentative decomposition of organic phosphorus compounds in the corpuscles. The effect is more rapid if the blood is hæmolysed; it is inhibited by sodium fluoride and oxalate, by heating to 80°, and by saponin. It disappears if the reaction is strongly acid, and is inhibited at $p_H > 8·4$. Potassium and lactates in small concentrations assist, whilst calcium and lactates in high concentrations retard the hydrolysis. Similar effects are exerted by these ions on autolysing extracts of liver, kidney, brain, and heart muscle.

It is suggested that the greater part of the urinary phosphate is derived from the breakdown of organic phosphorus compounds in the kidney cells.

C. RIMINGTON.

Diastase. II. Does α-diastase act like β-diastase? IIIa. Velocity of starch hydrolysis by α-diastase. V. SYNIEVSKI (Biochem. Z., 1925, **162**, 228—235, 236—244).—II. α-Diastase does not act like β-diastase. The small β-diastatic action of barley extract is attributed to the presence also of a small amount of β-diastase, and the small α-diastatic power of malt extract after heating to 60—61° is supposed to be due to the presence of a trace of α-diastase which still remains after this treatment (cf. A., 1925, i, 368, 369, 469, 470).

IIIa. The hydrolysis of starch by a pure diastatic enzyme is not a simple unimolecular process analogous to the sucrose hydrolysis by invertase, but is much more complex. P. W. CLUTTERBUCK.

Enzymic hydrolysis of sucrose-phosphoric acid into lævulose and dextrose-phosphoric acid. C. NEUBERG and S. SABETAY (Biochem. Z., 1925, **162**, 479—483).—This hydrolysis is effected by means of

an invertase solution prepared by the method of Willstätter and Racke. P. W. CLUTTERBUCK.

Affinity relationships of invertases. V. Specificity of invertase and raffinase. K. JOSEPHSON (Z. physiol. Chem., 1925, **149**, 71—93).—In an endeavour to throw further light on the identity or otherwise of invertase and raffinase, the inhibition by glucosides of the invertase and raffinase activity of preparations of invertase from the yeast "bottom yeast *B*" has been investigated. The results do not entirely agree with those previously given by others. The presence of 2 % of α-methylglucoside in the reaction mixture causes a decrease in the invertase activity to about one-tenth of the original velocity. The raffinase activity, however, is only diminished to one-half by this amount of α-methylglucoside. β-Methylglucoside, on the other hand, checks raffinase activity slightly more than invertase activity. The percentage inhibition of invertase activity by α-methylglucoside does not depend on the concentration of sucrose, whereas in the case of the inhibition of invertase or raffinase by salicin the concentration of the sugar is all-important. Raffinase activity is inhibited to a greater extent than invertase activity by salicin. Two types of inhibition phenomena are to be distinguished. First inhibition due to combination of enzyme with inhibiting agent, a combination of the same type as that between enzyme and substrate; secondly, inhibition due to changes in the stability of the intermediate enzyme-substrate complex, or due to the existence of some affinity between the enzyme and inhibitory agent of a different character from that between enzyme and substrate. Both types of inhibition may, however, exist at the same time in a reaction mixture, the inhibition of invertase activity by the simultaneous presence of dextrose and ethyl alcohol being a case in point. H. D. KAY.

Lipolytic enzymes in the blood of pregnant women. F. CLAUSER (Riv. ital. ginecol., 1924, **3**, 83—105; from Chem. Zentr., 1925, II, 1048).—Lipase is greatly decreased in the serum of pregnant women, but is as resistant to quinine and atoxyl as under normal conditions. The lipase in the blood of pregnant women is probably derived from the liver. G. W. ROBINSON.

Lipases of the internal secretory organs resistant to quinine and atoxyl. E. HERZFELD and W. ENGEL (Biochem. Z., 1925, **160**, 172—177).—The lipases detected in extracts of suprarenals, testes, ovary, corpus luteum, thymus, and hypophysis are resistant to quinine and atoxyl. Little difference in degree of resistance is seen in the enzyme from different organs except in the case of the lipases of the testes and ovary, the former being less resistant to quinine than to atoxyl, the latter less resistant to atoxyl than to quinine. P. W. CLUTTERBUCK.

Effect of members of the quinine group on the enzymic functions of the organism. III. Influence of some quinine and carbamide compounds on pancreatic lipase. I. A. SMORODINCEV and V. K. DANILOV (Biochem. Z., 1925, **161**, 178—194).—The hydrolysis of triacetin by pancreatic lipase both in presence and in absence of quinine and carbamide conforms to the laws of a unimolecular reaction. Quinine sulphate and hydrochloride accelerate, whilst carbamide nitrate and chloride inhibit the hydrolysis. Free carbamide is without action. A double salt of carbamide and quinine hydrochloride depresses the enzyme activity in small concentrations and entirely inhibits when above 0·6%. C. RIMINGTON.

Alterations in the enzyme activity of the blood. I. Influence on nuclease and lipase. L. PINCUSSEN. E. COELHO (Biochem. Z., 1925, **161**, 71—79).—Neither adrenaline nor pilocarpine alters the nuclease activity of the blood in rabbits, nor does potassium or calcium chloride injection, but the iodised preparations "Novoprotein" and "Yatren-casein" both inhibit the enzyme. Hence it appears that nuclease is derived from disintegrating cells, not from secretions.

The lipolytic activity, although unaffected by adrenaline or pilocarpine, is increased by calcium chloride, to which potassium chloride is antagonistic. "Novoprotein" increases, whilst "Yatren-casein" decreases the fat-splitting power. Lipase appears therefore to proceed from some internal secretion, and in support of this is the observation that in a rabbit suffering from pneumonia the lipolytic power of the serum was even below normal.

C. RIMINGTON.

Buffers in the study of proteases. I. Measurement of the p_H in the determination of pepsin by Gross' method. II. Influence of buffers on the digestion of caseinogen by pepsin. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1925, **7**, 1060—1067, 1068—1070).—In Gross' method (Berlin klin. Woch., 1908, **45**, 443), in which pepsin is determined by its action on caseinogen, the protein itself exerts a powerful buffering action, and the p_H of the solution is thereby kept constant. Determinations by electrometric and colorimetric methods, using methyl-violet and tropæolin-OO as indicators, are in good agreement. Addition of other buffers is without influence on the digestion of caseinogen by pepsin under the conditions used by Gross. W. O. KERMACK.

Influence of quinine preparations on the fermentative functions of the organism. IV. Influence of quinine salts on pepsin. I. A. SMORODINCEV and C. S. LEMBERG (Biochem. Z., 1925, **162**, 266—270).—Quinine, quinine hydrochloride, hydrobromide, dihydrobromide, and sulphate in concentrations of 0·000009—0·2% have neither accelerating nor inhibiting action on digestion of caseinogen by pepsin, nor does the presence of quinine affect the p_H of the mixture.

P. W. CLUTTERBUCK.

Activation and heat stability of enzymes. Relation between rennin and pepsin. J. WOHLGEMUTH and N. SUGIHARA (Biochem. Z., 1925, **163**, 253—259).—The observation of Hizume (cf. A., 1924, i, 798) that activators of salivary amylase exert a protective action against the destruction of the enzyme by heat is extended to rennin and its

activation by calcium. Although calcium does not activate pepsin, it protects the latter against heat destruction. If pepsin and rennin are not to be regarded as identical, they must at least possess a common nucleus. R. K. CANNAN.

Oxydases. I. Formation of crystals of indophenol-blue in the presence of different colloids. II. Oxydase reaction in surviving preparations. III. Oxydase reaction in spermatozoa. E. SERENI (Arch. fisol., 1924, **22**, 179—183, 185—189, 191—195; from Chem. Zentr., 1925, II, 1047).—I. The observation of Reed (J. Biol. Chem., 1915, **22**, 99) that in the presence of gelatin, gum arabic, and other colloids, indophenol-blue is obtained from α-naphthol and *p*-phenylenediamine, not as crystals, but as oval granules, is only partly confirmed. For example, ordinary crystals are obtained in the presence of blood-serum. Inorganic oxidising agents facilitate the formation of indophenol-blue without affecting its form. Similar results are obtained with dimethyl-*p*-phenylenediamine.

II. The granules obtainable by the oxydase reaction in sections of animal tissues decrease with the time of survival of such tissues.

III. Human spermatozoa show during ripening an increase in granules giving the oxydase reaction. G. W. ROBINSON.

Plant reductases. W. PALLADIN, P. PLATISCHENSKI, and E. ELLADI (Bull. Acad. Sci. Russie, 1915, **13**, 309—326; from Chem. Zentr., 1925, II, 1047).—Seeds and seedlings of peas, "hefanol," wheat seedlings, and dried yeast were examined for reductases by Lebedev's method. The reducing power, as shown by the decolorisation of methylene-blue by the sterile water extract, increases proportionately with growth from resting seeds to seedlings. G. W. ROBINSON.

Reductase (dehydrogenase) of yeasts. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1925, **149**, 44—51).—The co-reductase of yeast is able to induce reduction of methylene-blue in presence of washed muscle, and may therefore be identical with the co-reductase of muscle. It is not, however, identical with co-zymase of yeast. It is more easily removed from a bottom yeast than from a top (distillers') yeast. H. D. KAY.

Co-zymases in different fermentations. A. I. VIRTANEN (Ber., 1925, **58**, [*B*], 2441—2445).—Co-zymase-free lactic acid bacteria are activated by co-zymase extracts from yeast, muscle, and propionic acid bacteria, whilst the latter are similarly affected by the aqueous extract of lactic acid bacteria. Similarly, yeast is activated by dry preparations of *Bacillus casei* ε and propionic acid bacteria. In general, the co-zymases of animal and vegetable cells appear able to replace one another.

The ability of insulin to function as co-zymase towards lactic acid bacteria (Virtanen, A., 1925, i, 753), but not towards co-zymase-free yeast (Euler and Myrbäck, Chemie d. Zelle und Gewebe, 1925, **12**, 57), remains unexplained. H. WREN.

Apozymase and co-zymase. Mechanism of phosphorylation. C. NEUBERG and A. GOTTSCHALK (Biochem. Z., 1925, **161**, 244—256).—The condensation of hexose with phosphoric acid cannot take place in the absence of a co-enzyme. The poor esterification brought about by some dried top yeasts is due to a deficiency in zymase or apozymase; thus addition of co-zymase fails to increase their power.

Acetone preparations in the case of bottom yeasts resemble the dried extracts in their high esterifying ability, but the feeble power of acetone top yeasts can be greatly enhanced by addition of boiled yeast juice. The participation of two co-factors in esterification is indicated.

Boiled extracts of animal muscle are able to restore the esterifying power of washed acetone bottom yeasts. C. RIMINGTON.

Fermentation inhibitor. K. MYRBÄCK (Z. physiol. Chem., 1925, **149**, 52—59).—The thermolabile substance, found by Meyerhof in aqueous extracts of muscle, which inhibits fermentation of dextrose by dried bottom yeast, may be separated, and to a considerable extent purified, by adsorption on aluminium hydroxide or kaolin. It may be recovered from the washed sorbate by elution with phosphate buffer of 6·2. It does not dialyse through collodion. Of the four bottom yeasts investigated, all were strongly inhibited by the unboiled muscle extract, but both the top yeasts investigated showed, not only no inactivation, but also slight acceleration of fermentation when muscle extract was added. H. D. KAY.

Action of adrenaline and related substances on the self-fermentation of yeast. H. POPPER (Biochem. Z., 1925, **162**, 271—277).—Adrenaline (1/20,000) increases the self-fermentation of yeast (as measured by carbon dioxide evolution) by about 30%. This action is not specific for the hormone, since other polyhydric phenols, *e.g.*, pyrocatechol, resorcinol, and pyrogallol, act in the same way. Quinol is inactive. This action is, within limits, independent of the amount of polyhydric phenol added and of the duration of the experiment. It does not occur, however, when dextrose is added. So far as can be determined by the ferric chloride colorimetric test, little or none of the added phenol disappears during fermentation. P. W. CLUTTERBUCK.

Influence of oxygen on alcoholic fermentation by yeast. O. MEYERHOF (Biochem. Z., 1925, **162**, 43—86).—In sugar–phosphate solutions sown with yeast, simultaneous measurements of oxygen absorbed and carbon dioxide formed show that the oxidation of 1 mol. of sugar protects 4—6 mols. from fermentation. This agrees with observations based on the oxidation quotient of lactic acid and is not concerned with the oxygen intake, but depends entirely on the type of yeast employed. The relation between sugar absorption and decrease in sugar decomposition also holds if the reaction is hindered by hydrocyanic acid. In oxygen, the amount of fermentation is increased three- or four-fold in the presence of a little hydro-

cyanic acid, whilst it is slightly retarded in an atmosphere of nitrogen. Formation of alcohol is checked by oxygen absorption.

The effect of oxygen on fermentation depends on the maintenance by the respiration of circulation of the carbohydrate and on the influence of intermediate products, viz., ethyl alcohol, acetaldehyde, acetic acid, pyruvic acid, lactic acid, and methylglyoxal, which are formed. β-Hydroxybutyric acid, acetone, and aldol are without action. As in muscle, the main circulation of the carbohydrate is not through the end-products, but through pyruvic and lactic acids. H. G. REEVES.

Influence of ions on the sugar assimilation of oxygenated yeast. F. LIEBEN and D. LÁSZLO (Biochem. Z., 1925, **162**, 278—288).—Sugar assimilation of oxygenated shaken yeast suspensions (cf. A., 1922, i, 502, 1219) is increased by the anions SO_4'', CNS′, I′, and by the cations K·, Ca··, Mg··, but decreased by the anion F′, whilst the anions Cl′, NO_3', and the cation NH_4· are indifferent. The activity of the ions does not follow the Hofmeister series and the effect does not appear to be influenced by the power of the ions to cause swelling of the protein of the yeast. The effect is not caused wholly either by adsorption of the salts by yeast, or by change of p_H effected by the salts, but is due much more to the influence of the ions themselves. The effect is not obtained with higher external temperatures owing to the more rapid completion of fermentation and to the greater sensitivity of the yeast to salts, and to get the effect under these conditions, the duration of the experiment and the concentration of the salts must be decreased. P. W. CLUTTERBUCK.

Fixation of atmospheric nitrogen by yeast as a function of hydrogen-ion concentration. E. I. FULMER and L. M. CHRISTENSEN (J. Physical Chem., 1925, **29**, 1415—1418).—Yeast will grow on a synthetic medium with atmospheric nitrogen as the sole source of that element (A., 1923, i, 1158). Fixation of the nitrogen is now shown to be, at 30°, a function of the hydrogen-ion concentration. The medium contained 6 g. of cane molasses, with 0·5 g. of dipotassium phosphate as a buffer, in 100 c.c. (see Christensen and Fulmer, A., 1925, i, 1216, for method). Nitrogen is lost by the medium at first, an actual gain being shown only after 6—8 weeks. This probably accounts for the failure of previous investigators to observe fixation. Two optimal hydrogen-ion concentrations occur at p_H 6·0 and 7·9, the latter being the more effective. L. S. THEOBALD.

Physiological behaviour of acetylmethylcarbinol. I. Behaviour of acetylmethylcarbinol to yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1925, **160**, 250—255).—Acetylmethylcarbinol as well as diacetyl yields βγ-butyleneglycol on fermentation. P. W. CLUTTERBUCK.

Sulphur-containing sugar obtained by hydrolysis of adenylthiosugar. U. SUSUKI and T. MORI (Biochem. Z., 1925, **162**, 413—424).—From an alcoholic extract of yeast, a substance containing sulphur is isolated which on hydrolysis with dilute acid gives adenine and a thiosugar, claimed to be *methylthiopentose*. This gives the furfuraldehyde, Bial's, and phloroglucinol tests, a white precipitate with silver nitrate and gold chloride, an *osazone*, m. p. 159—160°, an uncrystallisable *triacetyl* derivative, a *dibenzoyl* derivative, m. p. 185°, and on reduction with amalgam gives a *thiosugar alcohol*, $C_6H_{14}O_4S$, m. p. 115—117°, which yields a *dibenzylidene* derivative, m. p. 135—136°. On evaporation of the thiosugar with concentrated nitric acid in presence of traces of vanadium, a 32% yield of oxalic acid is obtained, but if dilute (*d* 1·15) nitric acid be used (in absence of vanadium) a *monocarboxylic acid*, $C_6H_{12}O_6S$, m. p. 183—184°, is obtained. When the aqueous solution of the thiosugar is treated with bromine until no more is absorbed, then carefully neutralised and warmed with phenylhydrazine, the *osazone* of the corresponding sulphoxy-sugar, $C_{18}H_{22}O_3N_4$, m. p. 223—224° (decomp.), is obtained. Determination of the -SMe group gives positive but not quantitative results. P. W. CLUTTERBUCK.

Quantitative enzyme measurements in micro-organisms. I. Catalase content of bacteria. A. I. VIRTANEN and H. KARSTRÖM (Biochem. Z., 1925, **161**, 9—46).—The decomposition of hydrogen peroxide by bacteria follows the course of a unimolecular reaction. The velocity constant (k) is proportional to the number of cells, but independent of substrate concentration. The catalase activity (C. A.)$=k\div$number of cells. Trustworthy comparisons of the C. A. of different bacteria can be made and the influence of various conditions on this quantity determined.

The C. A. is a measure of catalase content, and is not raised by drying, warming, or by the action of protoplasmic poisons. The susceptibility of the enzyme towards hydrogen peroxide differs in different species; in no case, however, is there much destruction in a concentration of $N/100$. Similar differences appear in comparing the effect of temperature and growth on catalase content in different species. Old cultures show a greater catalase content than young ones do, but this appears to be due to autolysis of dead cells. The presence or absence of dextrose does not affect the C. A., whilst *Bacillus prodigiosus* and *B. lactis amari* have a higher C. A. after anaërobic as compared with aërobic growth, indicating possibly that catalase is also necessary in anaërobiosis or, alternatively, that, although then functionless, it is still produced by the cell. In young cultures, catalase is confined to the cells, whilst its presence in the medium in older ones may be accounted for by autolysis. C. RIMINGTON.

Metabolism of acid-fast bacteria. VI. Influence of c_H on the growth of acid-fast bacteria in simple artificial media. S. KONDO (Biochem. Z., 1925, **162**, 171—180).—Experiments were carried out with several members of this class of bacteria and it was found that the better the nourishment of the bacteria the easier it was for them to overcome an unfavourable hydrogen-ion concentration. H. G. REEVES.

Mechanism of lactic acid formation by bacteria. C. NEUBERG and G. GORR (Biochem. Z., 1925, **162**, 490—495).—The conversion of methylglyoxal into lactic acid by *Bacillus coli* is quantitative. P. W. CLUTTERBUCK.

Action of *Bacillus pestis* (Yersin) on carbohydrates. R. PONS (Ann. Inst. Pasteur, 1925, **39**, 884—887).—*Bacillus pestis* produces acid in maltose, mannitol, and dextrose media; it does not ferment lactose or sucrose. H. J. CHANNON.

Production of diphtheria toxin in Martin's broth. S. SCHMIDT (Ann. Inst. Pasteur, 1925, **39**, 875—883).—Martin's broth possesses many advantages over other broths employed for the production of diphtheria toxin. It is cheaply prepared and gives a large yield of toxin, which is constant in properties and has good antigenic power. Its clearness renders easy the reading of the end-point of an agglutination reaction. H. J. CHANNON.

Origin of carbamide produced by lower fungi. N. N. IVANOV (Biochem. Z., 1925, **162**, 425—440).—The carbamide formed by pure cultures of several lower fungi arises from arginine and not from other amino-acids. When arginine is the source of carbon and nitrogen during the growth of *Aspergillus niger*, half of the nitrogen appears as ammonia and half as carbamide. These urease-free cultures can be used for the determination of arginine in proteins and their degradation products. P. W. CLUTTERBUCK.

Protein of the protoplasm of *Myxomycetæ*. N. N. IVANOV (Biochem. Z., 1925, **162**, 441—454).—Partial acid hydrolysis of the protoplasm of *Myxomycetæ* results in a 16·25% yield of a protein, soluble in water and in 80—85% alcohol and containing 16·77% of nitrogen. This protein is similar in all its properties to that obtained from higher fungi. The total nitrogen content of the plastin of *Myxomycetæ* of different origin varies from 10% to 12·74% and the phosphorus content from 0·32% to 1·34%. Plastin often contains a carbohydrate insoluble in water which is hydrolysable to dextrose by acids and by taka-diastase. The protein content of plastin never exceeds 38·58%. P. W. CLUTTERBUCK.

Trehalose and trehalase in *Myxomycetæ*. N. N. IVANOV (Biochem. Z., 1925, **162**, 454—458).—*Myxomycetæ* usually contain trehalose, but trehalase is not always also present. *Reticularia lycoperdon* contains 2·19% of trehalose on the dry weight. Enzymes, *e.g.*, urease and trehalase, appear or disappear according to the needs of the plant, their presence or absence depending on the medium. P. W. CLUTTERBUCK.

Hormonal action of choline on the motor function of the alimentary tract. I. E. ABDERHALDEN and H. PAFFRATH (Pflüger's Archiv, 1925, **207**, 228—240; from Chem. Zentr., 1925, II, 934).—The total amount of choline yielded by a portion of intestine is unaltered by stimulation produced by stretching. The Auerbach plexus appears to regulate the formation, or at least the output, of choline. The significance of choline as the hormone of intestinal peristalsis is thus confirmed. G. W. ROBINSON.

Hormonal action of choline on the motor functions of the alimentary tract. II. E. ABDERHALDEN, H. PAFFRATH, and H. SICKEL (Pflüger's Archiv, 1925, **207**, 241—253; from Chem. Zentr., 1925, II, 934—935; cf. preceding abstract).—The authors have attempted to demonstrate the existence under different conditions of enzymes capable of effecting the synthesis of choline esters from choline and organic acids. In the place of organic acids, acetaldehyde was also used. The occurrence of such enzymes was not clearly proved, although there was evidence of a fermentative synthesis of acetaldehyde and choline to acetylcholine. The following new compounds were prepared: *n-hexoylbromoethanol*, b. p. 148—150°/11 mm.; *choline hexoate bromide*, $C_5H_{11}\cdot CO_2\cdot[CH_2]_2\cdot NMe_3Br$, hygroscopic, decomp. at 180—200°; *bromoethyl palmitate*, m. p. 61°; *choline palmitate bromide*, m. p. 72°; *bromoethyl stearate*, m. p. 76°; *choline stearate bromide*, m. p. 79°; *dicholine carbonate dibromide*, $CO[O\cdot CH_2\cdot CH_2\cdot NMe_3Br]_2$, crystals, m. p. 296° (decomp.); *dicholine orthophosphate dibromide*, $OH\cdot PO[O\cdot CH_2\cdot CH_2\cdot NMe_3Br]_2$, m. p. 166° (decomp.); *choline ethyl orthophosphate bromide*, $OH\cdot PO(OEt)(O\cdot CH_2\cdot CH_2\cdot NMe_3Br)$; *chloroethyl glycollate*, b. p. 156—160°; *chloroethyl lactate*, b. p. 218—220°; *chloroethylglycine hydrochloride*, m. p. 150°. The ester bromides were prepared by way of the bromoethyl esters (Fourneau and Page, A., i, 1914, 938). The effect of the different compounds obtained on the surviving intestine was investigated. The bromides of choline palmitate, choline stearate, dicholine carbonate, dicholine diphosphate, choline ethyl phosphate, and choline lactate equalled choline bromide in their effect. The ester bromides of *n*-hexoic acid and glycollic acid were twice and cholineglycine bromide 10 times as effective as choline bromide. Chloroacetylcholine is 300 times weaker in its effect than acetylcholine. G. W. ROBINSON.

Chemical properties of insulin. D. A. SCOTT (J. Biol. Chem., 1925, **65**, 601—616).—Insulin is inactivated by shaking in alkaline solution with carbon disulphide and benzoyl chloride, and by treatment with nitrous acid; formaldehyde in cold acid solutions causes partial inactivation; the effect increases with rise of temperature and is complete in alkaline solution; inactivation is also produced by other reducing agents; all these changes appear to be irreversible. Extraction of pancreas with acid alcohol, precipitation by ammonium sulphate, re-solution in acid alcohol, and re-precipitation, followed by a fractional precipitation at different acidities, and finally with trichloroacetic acid, gave a product which contained 25,000 units of insulin per g. The product has C 50·5, H 6·6, N 14·0, and ash 0·4%; it contains tryosine 10·0, tryptophan 0·81%; it gives positive reactions for protein, negative for carbohydrate and phosphorus. Figures are given for the nitrogen distribution by the method of Van Slyke. C. R. HARINGTON.

Chemical composition of insulin. E. GLASER and G. HALPERN (Biochem. Z., 1925, **161**, 121—127).—Insulin preparations were purified by dialysis,

then hydrolysed, and the nitrogen distribution determined by the method of Van Slyke. Besides melanin, ammonia, lysine, arginine, and histidine were present, but more than 50% of the total nitrogen occurred in the filtrate from the above bases. Evidence was obtained for the presence of leucine, whilst glutamic acid and aspartic acid appeared to be present. Cystine and tyrosine were absent, neither could choline be demonstrated in a sample of insulin picrate. Of the colour tests, only the Millon and Pauly reactions were positive.

C. RIMINGTON.

Dialysis and adsorption of insulin. E. DINGEMANSE (Biochem. Z., 1925, **163**, 412—421).—Insulin is completely retained by collodion membranes, whilst in acid solution traces penetrate parchment paper. Insulin preparations may be partly purified from protein by electrodialysis up to an activity represented by 0·05 mg. dry weight per unit. Kaolin partly adsorbs insulin from solutions of impure preparations of high dry weight per unit. Charcoal is an effective adsorbent for insulin in both acid and neutral solution. Only traces can be again removed by glacial acetic acid, 80% alcohol, or buffer mixtures of p_H 8. R. K. CANNAN.

Stability of insulin to heat and some of its chemical properties. E. DINGEMANSE (Biochem. Z., 1925, **163**, 422—427).—In *N*/100-hydrochloric acid insulin was little affected by boiling for 1 hr., but lost up to half of its activity after 2 hrs. After 2 hrs.' boiling in *N*/10-hydrochloric acid, the activity was much reduced, whilst the same period in boiling 25% acid led to almost complete destruction. Acetylation and benzoylation gave no definite products, but almost completely destroyed the activity of the insulin. R. K. CANNAN.

Biocatalysts concerned in carbohydrate breakdown. H. VON EULER, E. JORPES, and K. MYRBÄCK (Z. physiol. Chem., 1925, **149**, 60—64).—Highly purified specimens of the co-enzyme of yeast fermentation display no insulin-like activity on administration to rabbits or mice. H. D. KAY.

Effect of injection of secretin-like plant extracts on the intermediary metabolism of carbohydrates. M. DOBREFF (Biochem. Z., 1925, **161**, 80—90).—The hyperglycæmia of pigeons fed on a diet deficient in vitamin-*B* is markedly increased by injections of secretin-containing extracts of spinach. The blood-sugar curve reaches its maximum in 1½—2 hrs. after the injection. In normal animals (pigeon, dog) the effect is less pronounced. Anal injection of the plant extract fails to produce secretion of gastric juice in starving animals. In its action on the glycogen reserves etc. plant secretin appears to be antagonistic to insulin. C. RIMINGTON.

Photoactivation of vitamin-*A*, cholesterol, fats, and other substances by ultra-violet light. S. HAMANO (Biochem. Z., 1925, **163**, 438—444).—After irradiation for 24 hrs. with the mercury-vapour quartz lamp, a number of substances were found to affect a photographic plate in the dark. Cholesterol, cod-liver oil, butter, olive oil, oleic acid, camphor, borneol, menthol, and cinnamic acid were thus activated. Negative results were obtained with carbohydrates, amino-acids, saturated fatty acids, anthracene, naphthalene, cetyl alcohol, and salicylic and succinic acids. R. K. CANNAN.

Vitamin-*B*. P. A. LEVENE and B. J. C. VAN DER HOEVEN (Chem. Weekblad, 1925, **22**, 575—576).—After examination of the various methods of concentrating vitamin-*B* by adsorption, the silica-gel method was selected; this gives an extract 2000 times as strong as the original yeast, measured by the increase in weight of albino rats fed for 3 days on a diet including the extract, after being fed on vitamin-*B* free foods for 3 weeks. The product obtained was not homogeneous, and no conclusions could be reached as to the structure or even the qualitative composition of the vitamin. S. I. LEVY.

Cholesterol content of the tissues of pigeons suffering from cyanide poisoning and vitamin-*B* deficiency. N. MESSERLE (Z. physiol. Chem., 1925, **149**, 103—110).—Pigeons suffering from chronic hydrocyanic acid poisoning have more cholesterol in their tissues, both relatively and absolutely, than normal pigeons. Vitamin-*B* deficiency increases the cholesterol content to an even greater extent.

H. D. KAY.

Relation between water content and photosynthesis. R. H. DASTUR (Ann. Bot., 1925, **39**, 769—786; cf. A., 1924, i, 1392).—Apparatus for measuring the rate of carbon dioxide assimilation of leaves has been modified to allow of the leaf remaining attached to the plant without alteration of the conditions of temperature, atmospheric composition, humidity, etc., a new type of leaf chamber being devised for the purpose. If the rate of carbon dioxide assimilation by leaves of the same species be plotted against the water content, the points lie very nearly on a straight line, the slope of which is different for different species or varieties of the same species, those with a low water content assimilating more rapidly than those with a higher water content. It is held that one of the internal factors tending to terminate the life of the leaves, and ultimately of the plant, may be an inefficiency of the conducting system, leading to a shortage of water in the leaves and thus to decreased carbon dioxide assimilation.

C. P. STEWART.

Detection of acetaldehyde as an intermediate stage in the anaërobic respiration of higher plants. C. NEUBERG and A. GOTTSCHALK (Biochem. Z., 1925, **160**, 256—260).—When seeds germinate out of contact with air, a considerable amount of alcohol and traces of acetaldehyde are obtained. If calcium sulphite is added to the system, about 50 times as much acetaldehyde is obtained, but the amount of alcohol decreases. The decrease in amount of alcohol is only in part accounted for by the excess of acetaldehyde, the deficit chiefly resulting from the depression of the fermentation process by the sulphite. Acetaldehyde is considered to be the intermediate in alcohol formation. P. W. CLUTTERBUCK.

Cell respiration. IV. Oxidation mechanism of potato. A. VON SZENT-GYÖRGYI (Biochem. Z., 1925, **162**, 399—412).—The guaiacum reaction with potato results from the oxidation by oxydase of a pyrocatechol to an *o*-diketoquinone, which directly oxidises the guaiacum reagent without assistance from peroxides or peroxydases. In the oxydase system of the potato is present, besides the pyrocatechol, another substance, "tyrin," probably a respiratory pigment, the leuco-base of which is oxidised directly to the pigment by diketoquinone. Tyrin is present in warm-blooded tissues and its properties are discussed. P. W. CLUTTERBUCK.

Catabolism of starch in mesophyll and guard cells. S. STRUGGER and F. WEBER (Ber. deut. bot. Ges., 1925, **43**, 431—438).—In the mesophyll cells of the leaves of *Ranunculus ficaria*, the breaking down of starch is accelerated by the addition of 0·1*M*-calcium or potassium chloride to the nutrient medium; these salts, however, are mutually antagonistic in their effect on the starch breakdown in the guard cells, potassium chloride accelerating, and calcium chloride having an inhibitory effect. Calcium chloride inhibits also the opening of the stomata. H. J. CHANNON.

Melilotoside, the glucoside from which is formed coumaric acid, extracted from the flowers of *Melilotus altissima* and of *M. arvensis*. C. CHARAUX (Bull. Soc. Chim. biol., 1925, **7**, 1056—1059).—From the flowers of these plants *melilotoside*, $C_{15}H_{18}O_8,H_2O$, m.p. 240—241° (decomp.), $[\alpha]_D$ −64·10°, is obtained in yields of 0·5 g. and 0·28 g., respectively, of crude compound per 100 g. of dry flowers. It has a bitter taste, is readily soluble in hot and sparingly soluble in cold water, has marked acid properties, and forms a crystalline *lead* salt. When hydrolysed by emulsin, or by heating with dilute mineral acids, it yields 1 mol. of coumaric acid and 1 mol. of dextrose, and therefore is assigned the formula

$$CO_2H\cdot CH{:}CH\cdot C_6H_4\cdot O\cdot C_6H_{11}O_5.$$

W. O. KERMACK.

Plant phosphatides. II. Water-soluble phosphatides of *Aspergillus oryzæ*. V. GRAFE and H. MAGISTRIS (Biochem. Z., 1925, **162**, 366—398).—Water-soluble phosphatides are obtained by dialysis of *Aspergillus oryzæ* and are separated into several fractions: (1) The substance precipitable by lead acetate in neutral solution: a monoaminomonophosphatide, lead salt, $C_{48}H_{95}O_{15}NPPb_2$, P : N = 1 : 1·21, giving on hydrolysis oleic, palmitic, and phosphoric acids, betaine, glycerol, and dextrose; the same phosphatide is precipitated from neutral solution by cadmium chloride. Precipitated by benzene from its alcoholic solution, its composition becomes $C_{43}H_{88}O_{10}NP$, P : N = 1 : 1, and it gives the same products on hydrolysis. (2) The solution from (1) is made alkaline with ammonia and precipitated with more lead acetate. The lead salt of diaminomonophosphatide is obtained, composition $C_{29}H_{69}O_8N_2PPb_5$, P : N = 1 : 2·01, which on hydrolysis gives choline, betaine, palmitic and phosphoric acids, and glycerol. (3) Alcohol precipitation of the filtrate from (2) gives a monoaminomonophosphatide which on hydrolysis yields choline, a solid fatty acid, succinic acid, phosphoric acid, and dextrose. P : N = 1 : 0·96. (4) The filtrate from (3) contained either another phosphatide or a series of hydrolytic products, P : N = 1 : 5. On hydrolysis, choline, adenine, oleic, linoleic, palmitic, and phosphoric acids, glycerol, and dextrose were obtained. P. W. CLUTTERBUCK.

Influence of media on germination of seeds in absence of calcium. R. CERIGHELLI (Compt. rend., 1925, **181**, 728—730).—Under the conditions studied, namely, sterilisation or non-sterilisation of the seeds, immersion or non-immersion in water or in water-vapour, peas germinate and grow more rapidly in the presence of calcium salts. L. F. HEWITT.

***Mercurialis*. III. Physiological significance of the chromogen.** P. HAAS and T. G. HILL (Ann. Bot., 1925, **39**, 861—865; cf. A., 1925, i, 759).—The colourless chromogen extracted from *Mercurialis* is named "hermidin." It is readily oxidised by air to blue "cyanohermidin" and thence to yellow "chrysohermidin," the two stages of oxidation requiring equal amounts of oxygen. Chrysohermidin is reducible by an aluminium–mercury couple to cyanohermidin and thence to hermidin. A mechanism exists in *Mercurialis* for the reduction of cyanohermidin, and it is suggested that the chromogen plays some part in the absorption and transfer of oxygen in the plant. C. P. STEWART.

Plant cuticle. II. B. LEE (Ann. Bot., 1925, **39**, 755—768).—Cutin, unlike suberin, contains neither phellonic acid nor glycerol. It is a complex mixture of fatty acids both free and combined with alcohols, soaps, unsaponifiable material which probably contains higher alcohols, resinous and tannin-like substances. Hydroxy-acids are present in greater amount than normal fatty acids, a fact which may be due to oxidation during the deposition of the cuticle. C. P. STEWART.

Nitrogenous constituents of alfalfa (lucerne). H. B. VICKERY (J. Biol. Chem., 1925, **65**, 657—664; cf. A., 1925, i, 1370).—The precipitate obtained from "alfalfa filtrate" by mercuric acetate and sodium carbonate was decomposed and the resulting solution treated with phosphotungstic acid, yielding a filtrate which contained the asparagine and amino-acids. From this filtrate were isolated directly asparagine 0·411% and tyrosine 0·0027%, calculated on the weight of dry plant; after hydrolysis with 20% hydrochloric acid, there were further obtained aspartic acid 0·112, phenylalanine 0·019, serine 0·055, leucine 0·0472, valine 0·0658, and alanine 0·0265% of the dry plant. Assuming the aspartic acid to have been formed by hydrolysis from asparagine, the amount of the latter accounts for 77·1% of the amide nitrogen, and the sum of the substances isolated makes up 29·5% of the solids and 54·8% of the total nitrogen of the amino-acid fraction. Serine and alanine are here for the first time recorded as constituents of a plant juice. C. R. HARINGTON.

Absolute and percentual alkaloid content of various parts of *Lupinus luleus* L. during growth. T. SABALITSCHKA and C. JUNGERMANN (Biochem. Z., 1925, **163**, 445—456).—The total alkaloid (lupinine and lupinidine) and its distribution

in various parts of the plant were traced from the seed through 18 weeks of growth. The total alkaloid in the plant and in its various parts increases, after an initial decline in the first 2 weeks, to a maximum in 14 weeks. The variations in the concentrations of alkaloid in the various parts were less regular.

R. K. CANNAN.

Application of fluorescence phenomena in biological chemistry. R. FABRE (Bull. Soc. Chim. biol., 1925, **7**, 1024—1037).—The fluorescent properties of certain substances under ordinary or, more particularly, under ultra-violet illumination may be used for their qualitative and quantitative investigation. Details are given of the application of the method to the investigation of the elimination in the urine of such alkaloids as hydrastine or quinine, the alkaloid in the former case being oxidised to hydrastinine by agitation of the solution of the sulphate, in the presence of air, before examination. The method has further been applied to the detection of salicylic acid in the milk after administration of aspirin, and to the investigation of small quantities of hæmatoporphyrin such as are found in the Harder gland of the rat.

W. O. KERMACK.

Pyrotannic acid method for determination of carbon monoxide in blood and in air. R. R. SAYERS and W. P. YANT (U.S. Bur. Mines, Tech. Paper 373).—Blood is diluted to twenty times its volume, a mixture of tannin and pyrogallol is added, and the colour of the solution matched against the colours produced by bloods containing known amounts of carbon monoxide, or against artificial standards. Carbon monoxide in air is determined by shaking a sample of air with fresh blood and determining the amount of carbon monoxide in the blood as above, whence the partial pressure of carbon monoxide in the air may be calculated.

L. F. HEWITT.

Absorption of oxygen by pyrogallol. E. VON KOVÁCS-ZORKÓCZY (Biochem. Z., 1925, **162**, 161—168).—Determinations of the oxygen-absorbing capacity of pyrogallol by means of Barcroft's differential apparatus were carried out. In making the pyrogallol solutions, the alkali was varied, sodium, potassium, and barium hydroxides being used and the efficiency of the solutions compared. As a mean of some thirty experiments it was found that 2 g.-mol. of pyrogallol absorb 5 atoms of oxygen.

H. G. REEVES.

Micro-determination of base in blood and biological materials. W. C. STADIE and E. C. ROSS (J. Biol. Chem., 1925, **65**, 735—754).—A modification of the method of Fiske (A., 1922, ii, 408), in which an aliquot portion of the filtrate from the benzidine sulphate is titrated instead of the precipitate itself. Phosphates do not interfere with the method unless present in greater amount than 10 equivalents for every 100 equivalents of base; if present in greater amount, they are removed, after the incineration, by precipitation with ferric ammonium sulphate, the excess of iron being removed with ammonia. The error of the method is 1%.

C. R. HARINGTON.

Colorimetric determination of calcium-ion concentration. Ionic equilibrium in the organism. F. HAFFNER and R. SIMON (Arch. exp. Path. Pharm., 1925, **109**, 129—142).—The degree of decoloris ation of acid dyes which form undissociated calcium salts may be used as a colorimetric measure of the concentration of calcium in solution; moreover, the depressing effect of added citrate and phosphate on the decolorisation indicates that the process is dependent on the concentration of free calcium ions. For physiological purposes, the most suitable dye is dianil-brown-M.H., which is not affected by changes in p_H over the physiological range. This method indicates that in ordinary Ringer's solution the calcium chloride is 50% dissociated; the calcium-ion concentration of a solution remains unaltered during repeated perfusion through the surviving limbs and heart of a frog, although the p_H of such a solution undergoes marked change. Increasing alkalinity of the perfusion fluid causes a depression in the concentration of calcium ions, but an accentuation of their physiological effect, which indicates a sensitisation of the tissues by the increased hydroxyl-ion concentration.

C. R. HARINGTON.

Nephelometric determination of calcium and magnesium. II. L. KRISS (Biochem. Z., 1 25, **162**, 359—365).—The nephelometric determination of calcium and magnesium in presence of one another is attained by a combination of the methods of Feigl and Pavelka (A., 1924, ii, 784) for calcium together with magnesium and of Kleinmann (A., 1923, ii, 433) for calcium, and is used for their determination in blood.

P. W. CLUTTERBUCK.

Determination of cholesterol. L. SURÁNYI and A. KORÉNYI (Biochem. Z., 1925, **160**, 178—182).—Alcoholic cholesterol solutions containing increasing amounts of cholesterol are added to the same amount of distilled water, and the additional amount of alcoholic solution required just to redissolve the precipitated cholesterol is tabulated. The table is used for the determination of the amount of cholesterol in blood.

P. W. CLUTTERBUCK.

Micro-determination of blood-sugar. E. KOMM (Z. angew. Chem., 1925, **38**, 1094—1096).—With a pipette containing a minute crystal of sodium oxalate 0·4 c.c. of blood is transferred to a tube, diluted to 2 c.c., and treated with 1 c.c. of 10% sodium tungstate solution and 1 c.c. of 0·67*N*-sulphuric acid. After centrifuging, 2 c.c. of the clear liquor are transferred to a second similar tube, treated with 1 c.c. of Fehling's solution, heated to precipitate cuprous oxide, cooled, and centrifuged. The liquor is poured off and the precipitate washed several times with water under centrifugal action. The cuprous oxide is dissolved in 0·3 c.c. of 0·5% nitric acid, 0·6 c.c. of 25% ammonia solution is added, and the copper determined colorimetrically in the micro-colorimeter of Autenrieth and Königsberger; 1 mg. of copper corresponds with 0·69 mg. of dextrose. The results obtained agree closely with those obtained by Bang's method.

A. R. POWELL.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

FEBRUARY, 1926.

BIBLIOTECA

General, Physical, and Inorganic Chemistry.

Fine structure of Balmer lines. G. HANSEN (Ann. Physik, 1925, [iv], **78**, 558—600).—An examination of the fine structure of the Balmer lines of hydrogen with the aid of a Lummer–Gehrcke plate and the measurement of the intensities by means of a recording microphotometer. The sources of error in the apparatus are discussed and the necessary corrections effected. The ratio of the relative intensities of the long and short wave-length components of the doublets varies more with the pressure of the gas than with the current density. The frequency separations determined for the doublets H_α, H_β, H_γ, H_δ, H_ϵ are 0·316, 0·317, 0·328, 0·322, and 0·324 cm.$^{-1}$, respectively, for a pressure of 0·22 mm. The Sommerfeld–Kramers theory requires that the frequency separation of H_α should be 0·329 cm.$^{-1}$ for the field-free doublet. When the current density is maintained constant at 0·04 amp./cm.^{2} and the pressure is varied from 0·23 to 0·015 mm., the frequency separation of H_α increases from 0·316 cm.$^{-1}$, passes through the maximum of 0·320 cm.$^{-1}$ at a pressure of 0·09 mm., and falls again to 0·313 cm.$^{-1}$. This maximum is thus within 3% of that demanded by the theory. The general effects of varying the conditions of the discharge are discussed.

A. E. MITCHELL.

Measurement of the fine structure of hydrogen lines with the Lummer–Gehrcke plate. E. GEHRCKE (Ann. Physik, 1925, [iv], **78**, 461—464).—The work of van Cittert on this subject (A., 1925, ii, 909) is criticised. R. A. MORTON.

Interpretation of the hydrogen and helium spectra. J. C. SLATER (Proc. Nat. Acad. Sci., 1925, **11**, 732—738).—The anomalous Zeeman effect and the multiplicity of spectral terms may be due either to interaction between the valency electrons and the electrons of the core, or to peculiarities in the valency electrons themselves, the double levels in atoms having one electron being due to an assumed duality in the quantum laws. If so, the spectrum of hydrogen should resemble that of the alkalis, and that of helium the alkaline-earths. The evidence obtained from observations on the multiplicity of the lines and from the Zeeman effect is discussed in detail and is not unfavourable to the second alternative. E. B. LUDLAM.

Absorption and resonance radiation of excited helium. W. H. MCCURDY (Nature, 1926, **117**, 122).—Absorption was observed of the lines 5875, 4471, 4026, 3889, 3187, 5016, 3964, 3614, 6676, and 4921 Å. in excited helium, and the possibility of obtaining resonance of the line 3889 Å. has been demonstrated.

A. A. ELDRIDGE.

Spectrum of ionised lithium. Y. SUGIURA (J. Phys. Radium, 1925, [vi], **6**, 323—333).—The spark spectrum of lithium has been examined using a perforated cathode in a platinum tube coated with lithium chloride, the accuracy obtained being about 0·5 Å. Rays due to ionised lithium, Li II, have been identified and compared with those of helium; the two spectra are in good agreement with the law of spectroscopic displacement for the series $mD-nF$ and $md-nf$, but less strictly for the remaining series. The classification of the different series is discussed, and the lines 2924 and 5485 Å. are ascribed to the doublet and simple ray spectra, respectively, in contradiction to the conclusion of Mohler (A., 1925, ii, 615). The quantum defects corresponding with each term of the series are deduced from the observations and are in agreement with theoretical calculations, whilst the critical potentials calculated from the spectroscopic data agree with the direct measurements of Mohler (*loc. cit.*). The ionisation potential of ionised lithium, the term $1S$, is calculated to be 67·5 volts. W. HUME-ROTHERY.

Life-periods of the metastable s_3 and s_5 states of neon. H. B. DORGELO (Z. Physik, 1925, **34**, 766—774).—The neon lines $2s_3-2p$ and $2s_5-2p$, under suitable excitation conditions, exhibit self-reversal and other absorption phenomena. This behaviour shows that the s_3 and s_5 states must be metastable. Their life-periods have now been measured by observing the time interval, after the cessation of excitation, during which neon is still able to absorb the $2s_3-2p$ and $2s_5-2p$ lines. The intervals were determined by two procedures, one involving a toothed-wheel device, and the other depending on the control of the exciting currents. The period of the s_3 state is given as 5×10^{-4} sec., and that of the s_5 state as $4{\cdot}2\times10^{-3}$ sec. The s_4 state also has a period sufficiently long to produce similar absorption phenomena. The metastable states of neon are compared with those of mercury. S. BARRATT.

Maximum intensity and width of lines of the principal series of sodium. B. TRUMPY (Z. Physik, 1925, **34**, 715—721).—The intensity and width of the lines of the principal series of sodium, of term numbers 3—12, have been studied in absorp-

tion. The maximum absorption coefficient of the lines, and also their physical half widths, were determined by the usual methods of photographic spectrophotometry. The absorption coefficient is given as $8{\cdot}55\times10^{-7}$ for the line $1s-4p$, and as $2{\cdot}30\times10^{-7}$ for $1s-13p$, the intervening lines having intermediate values. The numbers are only approximate, as the length of the absorbing column could not be accurately fixed. The half width of $1s-4p$ is about seven times that of $1s-13p$, under identical observation conditions. The width of the lines is nearly independent of temperature and of the total gas pressure, but is very sensitive to the density of the sodium vapour. The Lorentz broadening due to "impact damping" cannot cope with the phenomena; the observed widths of the lines are far too great.

S. BARRATT.

Absorption of sodium vapour. J. HOLTSMARK (Z. Physik, 1925, **34**, 722—729; cf. preceding abstract).—Theoretical. An attempt is made to account for the very great increase in width of the absorption lines of sodium when the density of the vapour is increased. The atoms are treated as resonators of the "classical" type, and these do not vibrate freely, but are coupled together. This coupling causes the broadening. The theory leads to widths of the observed order. For small concentrations, the width of the lines should be proportional to the square root of the concentration of sodium vapour, in agreement with Trumpy's experiments.

S. BARRATT.

Wave-lengths and pressure-shifts in the spectrum of magnesium. M. PETERSEN and J. B. GREEN (Astrophys. J., 1925, **62**, 49—60).—Tabulated results are given of wave-length measurements of magnesium lines in an arc in air, and in an arc in a vacuum. Pressure shifts observed were less in magnitude than existing data, and increase with the series term. A. A. ELDRIDGE.

Spectrum of ionised calcium (Ca II). F. A. SAUNDERS and H. N. RUSSELL (Astrophys. J., 1925, **62**, 1—7).—Results are given of measurements in nearly all parts of the spectrum of Ca II from a large variety of sources; there exists a system of combination series similar to those of Mg II. The second and third members of the principal series have been found, and series of the types $2\pi-m\sigma$, $2\pi-m\delta$, and $3\varphi-m\varphi'$ detected, as well as other combinations.

A. A. ELDRIDGE.

Interpretation of the spectra of the alkaline-earths. G. WENTZEL (Z. Physik, 1925, **34**, 730—735).—Theoretical. Existing data are reviewed and discussed. L. F. GILBERT.

Regularity in the distribution of spectral lines of iron and intra-atomic magnetic field. H. NAGAOKA and Y. SUGIURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1924, **1**, 155—206).—If an iron arc is kept vertical, and there is a sufficiently high potential difference, *e.g.*, 56,000 volts/cm., between the electrodes, the Stark effect is observed. By examining the ultra-violet portion of the spectrum, between 2400 and 3000 Å., more than 200 lines showing the simplest of the Stark phenomena, namely, increase in intensity of the lines with slight displacement towards shorter wave-lengths, have been measured. On mapping out these lines according to the frequency, it has been shown that they form a number of triplets, quadruplets, and sextuplets, and also doublets which probably form part of more complex and anomalous separations. From the average separation in the quadruplets, on the assumption that it is due to the Zeeman effect produced by the atomic magnetic field acting on the electrons emitting light, this field has been calculated to be $7{\cdot}6\times10^{6}$ gauss, which is in accordance with the value found by Weiss (J. Physique, 1907, [iv], **6**, 661) from experiments on the magnetism of iron at high temperatures. From triplets with symmetrical distribution of intensity, the same agreement is not obtained, which is attributed to the possibility that the external magnetic field may produce an effect on lines already affected by the internal field when the plane of the electron orbit is oblique to the direction of the atomic field. It is suggested that the intricate nature of the spectral lines in ferromagnetic metals may perhaps be traced to the existence of an intra-atomic field, and it may ultimately be possible, by a combined study of the Zeeman and Stark effects, to arrange them in a spectral series. M. S. BURR.

Intensity measurements in the iron spectrum. J. B. VAN MILAAN (Z. Physik, 1925, **34**, 921—923).—The intensities in the multiplet $\bar{f}-\bar{d}$ were measured and satisfactory agreement was obtained with the Burger–Dorgelo summation rule. The ratio of the intensities indicates, however, that the formulæ hitherto suggested are only approximations.

E. B. LUDLAM.

Principal series of the copper arc spectrum. F. SIMEON and E. S. DREBLOW (Nature, 1926, **117**, 17).—The copper arc, examined with a large quartz spectrograph, shows the line 2024 Å. (reversed) only when the middle of the arc is projected on the slit of the instrument, the line 2025 Å. appearing at the poles only. The spark spectrum showed only the line 2025 Å. The observed wave-lengths of the two lines are 2024·19 and 2025·34 Å., giving $\Delta\nu$ 28·1 ($\pm1{\cdot}0$), Randall's calculated value being 32·7. It is concluded that the line 2024 Å. is a true arc line, and 2025 Å. a spark line, so that they do not constitute the second pair of the principal series.

A. A. ELDRIDGE.

Radiation emitted by optically excited zinc vapour. J. G. WINANS (Proc. Nat. Acad. Sci., 1925, **11**, 738—742).—Light from a water-cooled zinc arc was concentrated on zinc vapour in a silica tube and the resonance spectrum photographed. A scheme is given showing the change in energy levels of the electrons corresponding with each line. Also four bands were obtained, three of which formed a band system, but the fourth—the furthest in the ultra-violet—differed in character and in relative intensity compared with the lines. When the zinc vapour was illuminated by a water-cooled mercury arc, in

addition to resonance lines of mercury (impurity in the zinc tube), lines due to zinc were observed, which are due to collision between an excited mercury atom and a normal zinc atom. The strong cadmium line, 3261, also appeared, excited in the same way by impact, and showing that cadmium was present as an impurity. E. B. LUDLAM.

pp'-Group in the arc spectrum of zinc. R. A. SAWYER and N. C. BEESE (Nature, 1925, **116**, 936—937).—The rule that, in two-valency system spectra, the frequency of the first pp'-group is nearly a mean between the frequency of the first line of the principal series of singlets in the spectrum and that of the first line of the principal series of doublets of the once more ionised atom, is applied to cadmium and extended to zinc. The precise classification of the zinc line 2070·11 Å. is considered.
A. A. ELDRIDGE.

New lines between 3100 and 2200 Å. in the arc spectrum of lanthanum. S. PINA DE RUBIES (Anal. Fís. Quím., 1925, **23**, 444—449).—See A., 1925, ii, 612.

Wave-lengths and relative intensities in the molybdenum K-series X-ray spectrum. S. K. ALLISON and A. H. ARMSTRONG (Physical Rev., 1925, [ii], **26**, 701—713).—See A., 1925, ii, 1015.

Relative intensities of some X-ray lines in the L-spectrum of tungsten and the K-spectrum of copper. S. K. ALLISON and A. H. ARMSTRONG (Physical Rev., 1925, [ii], **26**, 714—723).—See A., 1925, ii, 1015.

Apparent shape of X-ray lines and absorption limits. F. K. RICHTMYER (Physical Rev., 1925, [ii], **26**, 724—735).—The effect of instrumental factors on the observed intensity distribution of X-ray lines and at absorption limits has been investigated as regards the height and width of the slit and the uniformity of energy distribution over the focal spot. When the results are corrected for the width of slit used, the K absorption limit of silver is sharp, its width falling within the limit of experimental error, 2×10^{-4} Å. The curves of the energy distribution in the $K\alpha$ doublet of molybdenum correspond with monochromatic lines of width $<0{\cdot}0003$ Å. and relative intensity 2. A. A. ELDRIDGE.

Relative intensity of X-ray lines. Y. NISHINA and B. B. RAY (Nature, 1926, **117**, 120—121).—A preliminary account of the method employed to obtain sensitivity curves applicable to measurements of the relative intensities of L- and M-series, in particular the L-series of tungsten. A. A. ELDRIDGE.

Regular relation between chemical elements with respect to the effect of an electric field on series lines. J. STARK (Ann. Physik, 1925 [iv], **78**, 425—433).—The Balmer series of hydrogen may be expressed by $\nu=2w-mw$. For heavy elements, instead of the single mw series, there are at least five series, ms, mp, md, mf, mf_2. The difference between the quantum number of a series line of an element and that of the hydrogen line having the same integer is called the hydrogen-difference of the line considered, *e.g.*, $ms-mw$, $mp-mw$. For lines of the sharp, intermediate, and diffuse series in the heavy elements, the Stark effect ($\Delta\lambda$) has the same sign as the hydrogen-difference, and within a series-type $\Delta\lambda$ is smaller for different elements as the hydrogen-difference is greater. For a single element within a series, the hydrogen-difference decreases with increasing term-number and $\Delta\lambda$ decreases. For equal hydrogen-differences, $\Delta\lambda$ is greater for the sharp than for the intermediate series, and again for this series greater than for the diffuse series. The same results are probably true for the other series. The important implications of these considerations are pointed out. R. A. MORTON.

Experimental basis of the Zeeman effect. E. BACK (Physikal. Z., 1925, **26**, 833—841).—A lecture reviewing the development of the Zeeman effect, and the interpretation of the experimental data.
F. G. TRYHORN.

Stark effect in hydrogen. M. KIUTI (Japan J. Phys., 1925, **4**, 13—38; cf. A., 1923, ii, 273).—The s-components of H_a, $\Delta\pm5$ and ±6, predicted by Kramers, have been found. The p-components, $\Delta\pm8$, seem to exist, but are very faint. The results for H_β also agree with Kramers' theory. Apparent central components on the red side of H_β belong to the many-lined spectrum. The second order effect for H_γ is only roughly in accord with the theory. In the many-lined spectrum, three pairs of line showed a strong effect, each line being accompanied by an isolated component; the effect of this spectrum on other lines and on the Fulcher bands is described.
E. B. LUDLAM.

Compton effect. G. HAGEN (Ann. Physik, 1925, [iv], **78**, 407—420).—The Compton–Debye theory of the change of wave-length occurring in the scattering of X-radiations requires that the change of wave-length should be dependent on the angle of scattering, but independent of the origin of the primary radiation and of the scattering medium. These relationships have been verified by determining the change of wave-length, for various angles of scattering, of X-rays from molybdenum, rhodium, silver, tungsten, and tantalum, when scattered by paraffin, magnesium, and lithium. The Compton effect was not observed in the scattering of X-rays from tantalum or tungsten by paraffin. F. G. TRYHORN.

[Compton effect.] F. KIRCHNER (Ann. Physik, 1925, [iv], **78**, 421—422; cf. preceding abstract).—The failure of Hagen to obtain the Compton effect in the scattering by paraffin of short-wave X-radiations from tantalum and tungsten may possibly be due to a confusion of the $K\alpha$ and $K\beta$ lines, as a result of inaccurate focussing of the apparatus.
F. G. TRYHORN.

Device for the study of the Compton effect. J. W. M. DU MOND (Nature, 1925, **116**, 937).—By the use of an X-ray tube in which both the scattering substance and the analysing crystal are contained in a small metal box mounted on the end of the anti-cathode, a photographic spectrogram of the Compton effect can be obtained with less than one-thousandth of the usual exposure. Very little

evidence has been obtained for any intensification of the Compton modified lines greater than that which a strict proportionality to the incident intensity would require. A. A. ELDRIDGE.

Influence of self-inductance and dilution on the persistence of spectral lines, the ultimate lines, and the quantum theory of optical spectra. A. T. WILLIAMS (Anal. Soc. cient. Argentina, 1924, **97**, 15—53).—The condensed spark spectra of solutions containing calcium, barium, strontium, magnesium, zinc, cadmium, manganese, or copper were examined. For the first three, weak lines which are unaffected by additional self-inductance appear only when the concentration is >1%. When self-inductance decreases the intensity of a line to that obtained with a non-condensed spark, the line persists at a dilution of 1—0·01%; strong lines persist in 0·001% solutions. For magnesium, zinc, and cadmium, there is practically no parallelism between the effect of self-inductance and that of dilution. Manganese lines markedly decreased in intensity by self-inductance disappear at a concentration <1·0%. Copper lines which disappear by the action of self-inductance usually disappear below 1% or 0·1%; these lines are absent if the non-condensed spark is employed. The typical ultimate lines of copper, magnesium, calcium, strontium, and manganese, but not those of barium, are but slightly affected by a change in the polarity of the solution. The series relations of the ultimate lines of the elements of the first and second columns of the periodic table are tabulated. The ultimate lines (doublets of the ionised atom) of magnesium, calcium, strontium, and barium correspond, respectively, with the ultimate lines (doublets of the neutral atom) of sodium, potassium, rubidium, and cæsium. The quotients V_i/V_r and V_i/V_r (where V_i is the potential necessary to displace completely a second electron after the first has been displaced by the potential V_i, and V_r the potential sufficient to translate inter-orbitally a second electron after the first has been completely displaced by the potential V_r) are constant for the corresponding lines of the similar series in the alkali metal group, in the sub-group magnesium, zinc, and cadmium, and in the sub-group calcium, strontium, and barium; they decrease when the temperature of thermal ionisation of the element rises. The ultimate lines in the arc and in the spark appear when the atoms are excited to a potential less than the corresponding ionisation potential. CHEMICAL ABSTRACTS.

Energy levels of the nitrogen molecule. R. T. BIRGE (Nature, 1926, **117**, 81).—A discussion. A. A. ELDRIDGE.

Critical potential of the *K* level of neon. F. HOLWÉCK (Compt. rend., 1926, **182**, 53—54).—The critical potential for the *K* level of neon, measured by the absorption method (cf. A., 1925, ii, 336), is 862±3 volts; this is probably more correct than the value given by the spectroscopic method, viz., 856 volts. S. K. TWEEDY.

Soft *X*-rays from iron, cobalt, nickel, and copper. C. H. THOMAS (Physical Rev., 1925, [ii], **26**, 739—748).—Up to 1500 volts, 46 critical potentials have been found for nickel, 48 for cobalt, and 46 for iron; in each case nine of these are designated ionisation potentials, the remainder being radiation potentials. For copper at 0—90 and 700—1200 volts, 25 critical potentials were found. General correspondence exists between the critical potentials of iron, nickel, and cobalt. A. A. ELDRIDGE.

Ionisation of hydrogen by slow electrons. H. KALLMANN and M. BREDIG (Z. Physik, 1925, **34**, 736—750).—The nature of the ions formed during the collision of hydrogen molecules with electrons moving under a potential difference of 15—30 volts was studied by the magnetic deviation method. H^+, H_2^+, and H_3^+ ions were detected, the H^+ and H_3^+ ions being probably formed secondarily from the H_2^+ ions, although some H_3^+ ions may be formed by the reaction of H^+ ions with molecular hydrogen. An effect corresponding with ions of the formula H_4^+ was also observed; this effect can be explained as a result of the decomposition of some H_2^+ to H^+ ions. L. F. GILBERT.

Ionisation of nitrogen by electron impact as interpreted by positive ray analysis. T. R. HOGNESS and E. G. LUNN (Physical Rev., 1925, [ii], **25**, 786—793).—At pressures below 10^{-5} mm., only N_2^+ ions were observed; with increase of pressure, the percentage of N^+ ions increased, reaching 60% at 0·006 mm. N_2^+ ions were formed by the impact of electrons of energy >17 volts; N^+ ions, by disruption of N_2^+ ions, above 24 volts. Thus, the critical potentials 16·95 and 24·6 volts correspond with the formation respectively of stable and unstable N_2^+ ions. Over the range 2·7—27 volts, the dissociation of an unstable N_2^+ ion is independent of its speed. N^{++} ions do not appear below 500 volts; N_2^- ions were observed. Helium increases the formation of N^+ ions. Apparently the negative bands are emitted by the stable ions. A. A. ELDRIDGE.

Action of visible light on electrodes. R. AUDUBERT (J. Phys. Radium, 1925, [vi], **6**, 313—322).—*E.M.F.* measurements have been made with cells containing aqueous electrolytes and two identical electrodes, one of which was illuminated by an arc or tungsten lamp. With pure metals when no contaminating surface films are present, the effect is instantaneous, and the illuminated electrode is anodic with platinum, copper, and mercury, and cathodic with gold or silver, but platinum is greatly influenced by the exact method of preparation. The photo-voltaic effect is diminished by an increase in the solution pressure of the cation of the electrolyte, and increases with the frequency of the exciting radiation. No effect is produced below a limiting frequency, which increases as the metal becomes more electro-positive, but platinum forms an exception to both rules. A positive polarisation of the electrode diminishes the photo-voltaic effect of platinum, copper, and mercury, and increases that of gold and silver. A negative polarisation acts oppositely, and by artificial polarisation the sign of the photo-effect may be reversed. Electrodes covered by thin films such as copper oxide or bromide, and silver sulphide

or chloride, show complex results differing from those for pure metals. The theory of Athanasiu (A., 1924, ii, 239) is criticised, and the results are ascribed to the existence of an electrical double layer at the liquid–metal surface, and to a photo-electric effect causing dissociation into free ions and electrons. According to the relative sign of the charge on the metal, either electrons or free ions leave the latter, and both positive and negative photo-voltaic effects are thus accounted for. W. HUME-ROTHERY.

Secondary emission from a nickel surface due to slow positive ion bombardment. A. L. KLEIN (Physical Rev., 1925, [ii], **26**, 800—806).—When positive ions from heated aluminium phosphate are accelerated on to a nickel target, the percentage saturated secondary electron emission increases approximately as the square of the primary ion energy. There are many reflected positive ions of energy 0—2 volts, and a group having about 0·9 of the primary energy. A. A. ELDRIDGE.

Peculiar effect in the bombardment of platinum with slow electrons. E. RUDBERG (Medd. k. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 12, 1—9).—Illumination of a platinum plate which is being bombarded with slow electrons results in a small decrease in the secondary emission, the magnitude of which is not influenced to any marked extent by the speed of the primary electrons. If the platinum has been previously heated at a fairly high temperature, the illumination effect is at first not perceptible, but gradually returns. The effect is not confined to any particular radiation and appears to be thermal in character.

J. S. CARTER.

Attempt to excite a mercury surface by electron bombardment. H. R. MOORE (J. Amer. Chem. Soc., 1925, **47**, 2932—2933).—The effects of a *P.D.* of 240 volts between a hot-wire filament (*e.g.*, platinum, tungsten) and a mercury surface in an evacuated vessel were observed (cf. Moore and Noyes, A., 1924, ii, 748), oxygen being admitted a fraction of a second before the filament current was turned off. Crinkling of the surface occurred when the oxygen was at pressures of 7—30 cm., even when admission was made 5 min. after stopping the filament current. This is probably due to the formation of a unimolecular layer of mercuric oxide which retains mechanically electrons received from the filament. Removal of the oxygen caused restoration of the surface; with readmission, the crinkling reappeared, often more pronounced. The surface layer of atoms probably suffers local alteration during the process, since the spilling of one drop of mercury renews the surface completely. Reversal of the field often produced positive results with oxide-coated platinum and thoriated tungsten filaments, showing that the phenomenon is "composite" and does not differentiate sharply between activation of the gas and excitation of the surface.

S. K. TWEEDY.

Equilibrium of the calcium chromosphere. E. A. MILNE (Month. Not. Roy. Astr. Soc., 1925, **86**, 8—28).—In an earlier paper (A., 1925, ii, 628), the equilibrium of the high-level calcium atoms in the sun has been discussed on the assumption that they are supported against gravity by radiation pressure and that the calcium with one positive charge possessed only two stationary states of equal statistical weight. The discussion is extended without these restrictions. The value for the mean life in the excited state is now found to be $1{\cdot}8\times10^{-8}$ sec. if there are only two stationary states, but if one of these states is double a further correction leads to the value $1{\cdot}3\times10^{-8}$ sec. The calculated value of the residual intensity in the infra-red lines is about ten times that in the hydrogen and potassium lines, and they ought to be ten times brighter than the hydrogen and potassium lines in the flash spectrum at low levels. E. B. LUDLAM.

Mobility of negative ions in petroleum, hydrogen, and hydrogen–chlorine flames. P. E. BOUCHER (Physical Rev., 1925, [ii], **26**, 807—819).—The mobility of negative ions in a hydrogen flame increases, and in a petroleum flame decreases, with rise of temperature. The mobility is decreased, to a progressively less extent, by the addition to the flame of chlorine, bromine, chloroform, carbon tetrachloride, ammonium chloride, or iodine. The mobility in a hydrogen–chlorine flame is increased by addition of sodium chloride, sodium carbonate, or potassium chloride. Temperature and potential changes probably affect the mobility of the ion by influencing the formation of clusters. A. A. ELDRIDGE.

Life-period of ionium. O. KOBLIC (Chem. Listy, 1925, **19**, 389—391).—The average life-period of ionium has been found to be 29,000 years from comparison of the intensity of a saturated current from the ionium of a sample of pitchblende containing 63—65% of uranium with that of a saturated current from ionium–thorium oxide, if the ratio of ionium to thorium in the latter is assumed to be 3 : 7 (Hönigschmidt). A. R. POWELL.

Absorption of β-rays by matter. (MME.) J.-S. LATTÈS and G. FOURNIER (Compt. rend., 1925, **181**, 1135—1136; cf. A., 1925, ii, 176, 622; this vol., 5).—The primary β-rays emitted by radium in equilibrium with its degradation products, like the secondary rays previously examined, obey the general law $\mu/\rho=a+bN$, where N is the atomic number of the absorbing element, and a and b are constants varying with the character of the rays. Values of a and b are given for three principal groups of the primary β-rays now examined. The ratio a/b is found to be constant for all cases examined, and is equal to 105. The general law may therefore be written $\mu/\rho=b(105+N)$. S. I. LEVY.

β-Ray spectra of radioactinium and its disintegration products. O. HAHN and (FRL.) L. MEITNER (Z. Physik, 1925, **34**, 795—806).—Radioactinium was separated from its decomposition products and its β-ray spectrum obtained. The spectrum was then obtained after successive intervals of time and thus the lines were determined which were due to the products, actinium-*X* and the active deposit. These lines were compared with those obtained from pure actinium-*X* with the active deposit, and finally

compared with those for the active deposit alone. The numbers of lines measured were, for radioactinium 49, for actinium-*X* 21, for the deposit 9, the investigation of the last being incomplete.

E. B. LUDLAM.

γ-Radiation of the actinium series and evidence that the γ-radiation emission follows the disintegration of the atom. (FRL.) L. MEITNER (Z. Physik, 1925, **34**, 807—818; cf. preceding abstract).—It is maintained that the γ-radiation does not come from the original nucleus, but results from the disturbance caused by the loss of an α- or a β-particle. The energies and the wave-lengths of the γ-rays from radioactinium, actinium-*X*, and actinium-*C*″ are calculated and show agreement with the values to be expected from the resultant atom, and not from the original atom. For γ-rays of great energy, the photo-electric emission of an electron takes place only in the level from which the work of emission is greatest, as from the *L* to the L_1 level. The calculation of the probability of absorption of *K*-radiation inside the atom, as estimated from the visual intensities of the lines, gives a value of the order of 10%.

E. B. LUDLAM.

Continuous spectrum and the γ-ray spectrograph of J. Thibaud. A. PICCARD (J. Phys. Radium, 1925, [vi], **6**, 334; cf. Thibaud, *ibid.*, 1925, **6**, 82; A., 1925, ii, 257).—The continuous background observed by Thibaud (*loc. cit.*) in the spectra of secondary β-radiation may be due to absorption of the radiation by the secondary radiator, consisting of a strip of metal. The use of a very thin strip of metal might overcome this defect.

W. HUME-ROTHERY.

Secondary γ-ray spectra: the origin of the continuous background and the variation of the relative intensity of rays. J. THIBAUD (J. Phys. Radium, 1925, [vi], **6**, 334—336; cf. preceding abstract).—The retardation of β-rays of known velocity by thin sheets of aluminium has been studied, and may be expressed by the equation $\Delta(RH)/RH = -0{\cdot}5x$, where x is the thickness of the sheet in mm. ($x < 0{\cdot}08$) and RH is in cm. gauss. The continuous background in the spectra of secondary β-radiation cannot be ascribed solely to retardation by the secondary radiator as suggested by Piccard (*loc. cit.*), but is due to a continuous γ-radiation of which the origin may be nuclear, but is probably due to degradation of the quantum by the Compton effect. With radium-*C*, the relative intensity of neighbouring γ-rays in the natural β-radiation is quite different from that in the artificially excited β-radiation.

W. HUME-ROTHERY.

Transmutation of elements. Lead. A. SMITS (Nature, 1926, **117**, 13—15).—The silica–lead lamp used is described and illustrated; in the lead employed, mercury or thallium could not be detected analytically, neither could either of these metals be detected spectroscopically in the various parts of the lamp. A comparison of the initial spectrum of the lead, the spectrum of mercury, and the spectrum of the lead after burning the lamp at 40 amp. and 80 volts for 10 hrs., indicated a transmutation of lead into mercury and thallium. Spectra showing a much stronger transmutation were obtained, all the mercury lines being present, when sparking was employed to obtain high current densities. Extended observation was difficult on account of the formation of a film of lead silicate, blackened by silicon, but the difficulty was overcome by modification of the apparatus.

In another method, lead was dispersed by sparking in a liquid dielectric; the lead in colloidal solution was converted into nitrate, the fine deposit of metallic lead being collected separately. The dispersed lead, but not the lead electrodes, gave a reaction for mercury when material volatile in air was heated in iodine vapour.

A. A. ELDRIDGE.

Absorption by scattering of hydrogen positive rays by passage through hydrogen and helium. R. CONRAD (Z. Physik, 1925, **34**, 73—99).—The absorption of hydrogen positive rays by passage through hydrogen and helium at a pressure of 0·05 mm. and for velocities of about 2×10^8 cm./sec., is chiefly caused by scattering. The coefficient of scattering is directly proportional to the pressure and inversely proportional to the fourth power of the velocity, for pressures below 2×10^{-4} mm.

E. B. LUDLAM.

Structure of tin. H. COLLINS (Chem. News, 1925, **131**, 403—405).—Speculative.

Magnetic evidence of the distribution of electrons in the inner M_{32} and M_{33} levels in atoms of the elements of the first transition group. D. M. BOSE (Z. Physik, 1925, **35**, 213—218).—From magnetic evidence, it is deduced that in the elements from scandium to iron the M_{33} level fills up and from cobalt to copper the M_{32} sub-group is formed. With the exception of cobalt and nickel, the calculated values agree with spectroscopic data.

E. B. LUDLAM.

Application of the correspondence principle to relative intensities in series spectra. F. C. HOYT (Physical Rev., 1925, [ii], **26**, 749—760).—A discussion of the representation of intensities in emission and absorption in terms of the probabilities of transition and of the estimation of the probability of spontaneous transition based on the correspondence principle. The relative probabilities of the transitions involved in the principal series of sodium are computed, and compared with experimental determinations.

A. A. ELDRIDGE.

Interpretation from the correspondence principle of the spontaneous appearance of spectral lines of the type *ms–md*. G. JOOS (Physikal. Z., 1925, **26**, 729—730).—Theoretical. An explanation of the appearance of the forbidden lines 1*s*—3*d* of potassium is put forward. The fact that the changes of k, the azimuthal quantum number, are not equal to ± 1 is connected with the assumption that the angular velocity of rotation of the perihelion depends on the angle made by the axis of the orbital ellipse and a fixed direction in the core. This idea implies that the core is not spherical.

R. A. MORTON.

Forces due to radiation. L. BRILLOUIN (Ann. Physique, 1925, [x], **4**, 528—586).—The mathematical theory of the forces exerted by a wave on a surface on which it is incident has been developed. These forces are given by the mean values of the tensor of the elastic forces and the flux of the "quantity of movement." Expressions for these as functions of the energy density in the medium and the wave velocity have been deduced for waves of compression in a fluid, and for longitudinal and transverse waves in an elastic solid. It is possible to base a theory of the solid state on these expressions, by regarding the thermal agitation in a solid as composed of a system of elastic waves passing in all directions, and exerting pressure on the walls. A. B. MANNING.

Relative sizes of atoms and ions. RITA BRUNETTI (Atti R. Accad. Lincei, 1925, [vi], **2**, 410—415).—It follows from the assumptions previously made to explain the displacement of the limit of the *X*-ray lines which occurs when an atom passes from the free state into the combined state, that the relative size of the atom and its ion should be related to the changes in the number of electrons in the shell as a result of combination. The formula which was derived for these changes has been tested by the insertion of experimental data for the spectral displacements and the lattice potentials for a number of alkali halides and the alkaline-earth sulphides. The results indicate that the ions of the alkali metals have smaller volumes than the free atoms, and that the volumes of the negative ions of the halogens and of metalloids are greater than those of the atoms. It is further shown that the explanation of the displacement of the limit of the *X*-ray lines as the result of ion formation followed by the introduction of the ion into the crystal lattice accounts for the regularities shown in Lothar Meyer's curve of atomic volumes, and for Grimm's curve illustrating the periodicity of ionic radii (A., 1922, ii, 635). F. G. TRYHORN.

Radii of atoms and ions. W. P. DAVEY (Chem. Reviews, 1925, **2**, 349—368).

Striated discharge in hydrogen. A. BRAMLEY (Physical Rev., 1925, [ii], **25**, 794—799).—The potential distribution, electron concentration, and mean electron energy at eleven points were determined at pressures of 0·625, 0·20, 0·09, and 0·02 mm. A. A. ELDRIDGE.

Critical potential of the negative band spectrum of nitrogen. E. E. WITMER (Physical Rev., 1925, [ii], **26**, 780—785).—The experimental results indicate that the negative band spectrum appears as a whole at the ionisation potential of nitrogen, or between that and 18 volts. A. A. ELDRIDGE.

Infra-red spectra of certain elements. J. C. MCLENNAN, H. G. SMITH, and C. S. PETERS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 39—50).—The spectra of nitrogen and carbon monoxide have been investigated in the region 6000—9000 Å., but no evidence was obtained in support of Nagaoka's suggestion (A., 1923, ii, 594) that these spectra should be approximately the same. New lines have been found in the arc spectrum of mercury in the near infra-red. A number of new lines have been observed in the arc spectrum of gold and tellurium in the red and near infra-red regions. J. S. CARTER.

Band spectra and electronic configuration of nitrogen and carbon monoxide molecules. H. NAGAOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1923, **1**, 125—133).—The data obtained by different investigators for the band spectra of nitrogen and carbon monoxide have been compared and show a close resemblance. Since the band spectra are probably due to molecules, this confirms the similarity of electronic configuration of the molecules of the two gases suggested by their striking resemblance in other physical properties. The line spectra, which are due to atoms, differ from one another. The possibility that the electrons of the molecule may be arranged as a space lattice, forming a face-centred cube with the two nuclei in the centre, is discussed. This arrangement, and also Langmuir's arrangement, would probably result in a ratio of specific heats of 1·67, instead of 1·40 as is actually the case. An arrangement of two cubes with a common edge, allowing the possibility of rotation of the molecule as a whole, is therefore suggested. M. S. BURR.

Flashing of certain types of argon–nitrogen discharge tubes. W. CLARKSON (Proc. Physical Soc., 1925, **38**, 10—15; cf. *ibid.*, 1924, **37**, 130).—The discharge tubes were filled with argon–nitrogen mixtures to pressures of 0·2—45·0 mm., and since the electrodes were only 1—2 mm. apart, the positive column was absent, and only the negative glow apparent. The observations are in general agreement with those obtained previously on neon and air discharge tubes. At pressures below 20 mm., the flash was the normal glow discharge, but at higher pressures the discharge was an arc. For a constant pressure, both the upper and low critical voltages for steady discharge, and the apparent critical voltages for continuous flashing, were constant for any one tube. Minor differences between tubes are discussed. C. J. SMITHELLS.

Band spectra of aluminium. G. ERIKSSON and E. HULTHÉN (Z. Physik, 1925, **34**, 775—787).—The spectrum of the aluminium arc in air and in hydrogen has been photographed under high dispersion. The arc in air shows intensive bands, degraded to the red, which are probably to be assigned to an AlO dipole molecule. In hydrogen, a weaker hydride band spectrum appears, degraded towards the red, with heads at 4067, 4241, 4354, and 4568 Å. This spectrum has been fully measured and analysed into a band system (ν_0=23,477). The moment of inertia of the unexcited AlH molecule is given as $1{\cdot}54\times10^{-40}$ g./cm.^{2}, and the distance between the atomic centres as $0{\cdot}984\times10^{-8}$ cm. S. BARRATT.

Absorption spectrum of manganese vapour in the visible and ultra-violet. R. V. ZUMSTEIN (Physical Rev., 1925, [ii], **26**, 765—770).—Thirty-one manganese absorption lines between 5394·07 and 1995·1 Å. are tabulated, with their intensities. The relatively small number of intense lines, and the

occurrence of groups consisting of one, two, or three lines, indicate that all the absorptions are from manganese in the normal state (1^6s term); $1^6s-{}^6d'$, $1^6s-{}^8p$, $1^6s-{}^6p$, and possibly 1^6s-4p and 1^6s-2p, combinations are represented. A. A. ELDRIDGE.

Band spectra of mercury. H. NAGAOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1922, **1**, 1—6).—A new form of lamp for exciting the mercury band spectra is described, and various methods of analysis of the fine structure of the bands are discussed. M. S. BURR.

Change in the infra-red absorption spectrum of water with temperature. J. R. COLLINS (Physical Rev., 1925, [ii], **26**, 771—779).—Maximum absorption of the bands was observed for 0° at 0·775, —, 0·985, 1·21, 1·45, and 1·96 μ; for 95° at 0·74, 0·845, 0·97, 1·17, 1·43, and 1·94 μ, rise of temperature being accompanied by an increase in the maximum absorption for the bands at 0·77, 0·98, and 1·21 μ. The results are in conformity with the supposed presence of molecules $(H_2O)_2$ and $(H_2O)_3$. A. A. ELDRIDGE.

Infra-red absorption spectra. Solutions of nitrogen pentoxide and nitrogen tetroxide in organic liquids. F. DANIELS (J. Amer. Chem. Soc., 1925, **47**, 2856—2866).—The absorption bands of nitrogen pentoxide between 2 and 7 μ are not shifted by the process of dissolution in organic liquids (*e.g.*, chloroform, dichloroethane). Slight shifts (0·05 μ) in the maxima may be attributed to concentration effects. Dissolution of nitrogen tetroxide in organic liquids, however, causes the absorption maxima to shift from 5·65 to 5·45—5·30 μ. The results do not support the radiation hypothesis of chemical action. It is considered that the relative position of the electron pair between the atoms of a molecule determines the infra-red absorption spectra of the latter. S. K. TWEEDY.

Infra-red spectra of solutions. O. REINKOBER (Z. Physik, 1925, **35**, 179—192).—The substances examined were water, methyl, ethyl, and propyl alcohols, glycerol, and concentrated solutions of ammonium chloride in these solvents. The region was from 2 to 9·5 μ. The reflexion spectra of the aqueous solution of ammonium chloride and of potassium nitrate were also examined in the same region. The frequency of internal vibration of the cation increases in solution, the opposite of the effect for the anion. The effect was the same in the different solvents. E. B. LUDLAM.

Light absorption and emission phenomena in anthracene. N. S. CAPPER and J. K. MARSH (J. Amer. Chem. Soc., 1925, **47**, 2847—2850).—Whereas pure, white, sublimed anthracene exhibits no selective absorption in phenetole and in chloroform solutions, recrystallised anthracene slightly tinted yellow by chrysogen exhibits absorption bands at 475, 445, 418, and 397 μμ, the last two being very weak (cf. Morton, Chem. News, 1872, **26**, 199). The bands at 475 and 445 μμ are, therefore, due to chrysogen, and Taylor and Lewis' deduction that dianthracene should absorb light at 707 μμ becomes erroneous (cf. A., 1924, ii, 580). The absorption observed by these authors at this wave-length may be due to the solvent, phenetole, since many benzenoid substances show well-marked absorption at this wave-length (Russell and Lapraik, J.C.S., 1881, **39**, 168) and fluorene and phenanthrene lose all visible fluorescence on careful purification. Pure anthracene polymerises as readily as the yellow-tinted specimens. This is due to absorption of light in the region of the four most characteristic bands (310—375 μμ) and not of light of wave-length 445 and 475 μμ (Taylor and Lewis, *loc. cit.*). The absorption and fluorescence spectra of chrysogen are similar to those of anthracene, but occur at higher wave-lengths. Apparently the green fluorescence of chrysogen depends for its stimulation on the potential emission of fluorescent light by anthracene. The fourth fluorescence band of pure anthracene in the red region, found by Morton, was not observed. S. K. TWEEDY.

Influence of different nuclei on the absorption spectra of substances. J. E. PURVIS (J.C.S., 1925, **127**, 2771—2776; cf. *ibid.*, 1914, **105**, 590, 1372).—The ultra-violet absorption spectra of a number of substances containing benzene nuclei have been examined in alcoholic solution. The bands of phenyl, benzyl, thymol, and camphor salicylates are comparable with those of salicylic acid, differing chiefly in position and strength, *i.e.*, only one of the nuclei shows specific absorption. The salicylates of theobromine, caffeine, phenazone, and quinine show much larger variations, but least in the quinine compound. *o*-Acetoxybenzoic acid approaches the behaviour of benzoic acid, showing that the replacement of the hydrogen of hydroxyl by another radical not possessing any specific absorption tends to nullify the effect of the hydroxyl group. The same influence is observed in the *o*-acetoxybenzoates of theobromine and quinine. In the specific absorption of the benzoate, citrate, and hydrochloride of caffeine, the basic nucleus is the chief agent. The results indicate that the specific and general absorption depend on the nature of the base, the nature of the acid, and the presence of hydrogen in hydroxyl, the vibration of the hydrogen evidently being an important factor in the absorption. M. S. BURR.

Absorption of light by hæmatoporphyrin. III. L. KAJDI (Biochem. Z., 1925, **165**, 475—496).—The change of the position of the absorption bands of acid hæmatoporphyrin does not depend on the concentration of acid if alcohol is present in fairly large concentration. The absorption bands of alkaline hæmatoporphyrin also change their position with changing concentration of solvent. If hæmatoporphyrin is dissolved in aqueous alkali, ethyl or amyl alcohols, ether, alcoholic acid or alkali, and the solutions are placed in sunlight, a new band (sometimes two) appears in the red. Solutions in aqueous acid do not give new bands under these conditions. By contact with rubber, the many-banded spectrum of hæmatoporphyrin, whether dissolved in pure alcohol, in acetic acid and alcohol, or in aqueous alkali, changes into a two-banded spectrum, with or without exclusion of air, in dark or in light. The substance contained in the rubber causing this change can be

extracted by alcohol. Hæmatoporphyrin solutions in which new bands have appeared by the action of sunlight, on contact with rubber give a two-banded spectrum which cannot be reverted to its original form by re-exposure to sunlight.

P. W. CLUTTERBUCK.

Photographic spectrophotometry. H. B. DORGELO (Physikal. Z., 1925, **26**, 756—794).—A summary of recent work with bibliography. The following matters, amongst others, are discussed: the laws of darkening of photographic plates, intensity measurements in groups of lines, light sources and distribution of energy throughout the spectrum, photomicrometric apparatus. R. A. MORTON.

Spectro-chemistry of compounds containing nitrogen. K. VON AUWERS and R. KRAUL (Z. physikal. Chem., 1925, **118**, 304).—Corrigenda to a previous paper (A., 1925, ii, 847).

L. F. GILBERT.

Three-dimensional method of representing quantum transitions in band spectra. H. B. LEMON and C. M. BLACKBURN (Astrophys. J., 1925, **62**, 61—64).—A three-dimensional representation of transitions corresponding with radiations in band spectra constructed for the case of the first negative Deslandres system associated with carbon is described.

A. A. ELDRIDGE.

Fluorescence of cadmium vapour. A. D. POWER (Physical Rev., 1925, [ii], **26**, 761—764).—The freshness of the vapour primarily determines the intensity of the lines 3262 Å. ($1S-2p_2$), 4678 Å. ($2p_3-1s$), 4800 Å. ($2p_2-1s$), 5086 Å. ($2p_1-1s$), and 2289 Å. ($1S-2P$), when excited by light of wave-length <3300 Å. The presence of thallium and indium as impurities was revealed by fluorescence lines, but not by the spark. A. A. ELDRIDGE.

Polarisation of fluorescent light from solutions of dyes. P. FRÖHLICH (Z. Physik, 1925, **35**, 193—206).—The degree of polarisation is considerable only for liquids of high viscosity, but it is not the same for different solutions of the same viscosity. Freezing the solution does not alter the degree of polarisation. In some cases, the solvent also fluoresces and the light emitted is polarised. In all cases examined, the degree of polarisation was different for different wave-lengths of the exciting light. E. B. LUDLAM.

Luminescence spectra of Geissler tubes. A. BJELOPOLSKI (Bull. Acad. Sci. Russie, 1918, [6], 1033—1046; from Chem. Zentr., 1925, II, 266—267).—The spectrum obtained in the wide portions of a Geissler tube is so weak that it cannot be photographed unless the tube be heated by long-continued passage of a current. The discharge may, however, be deflected electromagnetically and concentrated on a screen. Spectra are thereby obtained which can be photographed. The spectra obtained in this way from tubes containing hydrogen resemble those obtained in the capillary portions of tubes filled with methane or benzene. Their lines coincide with those of the second hydrogen spectrum of Frost (Astrophys. J., 1902, **16**, 100), Watson, and Hasselberg (Mem. Acad. St. Pétersbourg, [8], **31**, Nr. 14). The hydrogen tubes used were 10—24 yrs. old.

G. W. ROBINSON.

Excitation of spectra of gases by chemical reaction. H. FRÄNZ and H. KALLMANN (Z. Physik, 1925, **34**, 924—950).—The mechanism and energetics of the production of luminosity in chemical reactions between gases are discussed, in particular the excitation of the mercury resonance line by the action of chlorine on sodium in the presence of mercury and its non-appearance when bromine is used. The work of Haber and Zisch (A., 1922, ii, 461) is confirmed and extended. The action of all three halogens respectively on mercury vapour produces only band spectra; the bands with chlorine are the same as those observed in the electrical discharge through mercuric chloride; those with bromine and iodine are different from the spectra excited electrically in the bromide and iodide. Traces of impurity in the sodium affect the spectra in a marked manner when very little chlorine is present. E. B. LUDLAM.

Utilisation of luminescent and catalytic substances [*e.g.*, for *X*-ray screens]. P. L. G. MARCOTTE.—See B., 1926, 29.

Apparatus for direct registration of transparency curves of absorbing substances and of spectral effects. C. MÜLLER (Z. Physik, 1925, **34**, 824—832).—The apparatus consists of a monochromator, photo-electric cell, and string galvanometer combined with a special sliding form of rotating sector. The special advantage of the arrangement is that points on the curves of absorption, sensitivity, intensity, and the zero point can be obtained in any desired order. Thus four transparency curves with five comparison lines for 50 wave-lengths can be registered in 30 min. With appropriate changes, the method can be extended to measurements in the infra-red and to *X*-rays. E. B. LUDLAM.

Effect of ultra-violet light and *X*-rays on the stability of matter. A. L. FOLEY (Proc. Indiana Acad. Sci., 1925, **34**, 185—193).—Silica tubes containing carbon monoxide, krypton, neon, argon, bromine, chlorine, carbon monoxide, helium, hydrogen, iodine, nitrogen, oxygen, sulphur dioxide, water, or xenon, also glass tubes containing the above substances (with the exception of the first three), or the following elements in an atmosphere of nitrogen: aluminium, antimony, arsenic, barium, bismuth, cadmium, copper, magnesium, manganese, selenium, sulphur, or tin, in addition to control tubes, were exposed to ultra-violet light (silica tubes) or *X*-rays (glass tubes), the contents being periodically observed with the aid of an electrodeless discharge and photographs of the spectra. The results demonstrate the inadequacy of present knowledge of spectra; the electrodeless discharge gives results differing from those obtained in tubes containing electrodes. Mercury lines were usually present, but diminished in the presence of aluminium, arsenic, copper, or tin. Exposure of metals to *X*-rays liberates little or no gas. With continued discharge, changes in the spectra were observed similar to those previously

ascribed to phenomena connected with the presence of electrodes. CHEMICAL ABSTRACTS.

Energy levels of the nitric oxide molecule. H. SPONER (Nature, 1926, **117**, 81).—Evidence is adduced showing that the third positive group of nitrogen bands belongs to the nitric oxide molecule. The excitation potentials of the levels of the nitric oxide molecule are 5·44 and 13·96 volts; hence the ionisation potential must be greater than 14 volts. A. A. ELDRIDGE.

Dielectric constants of liquids. I. Measurement of dielectric constants of liquids. Y. MATSUIKE (Sci. Rep. Tohôku Imp. Univ., 1925, **14**, 445—452).—An apparatus is described for the measurement of dielectric constants of liquids by means of the resonance of two high-frequency oscillating circuits in one of which the liquid under examination forms the dielectric of a fixed condenser. The dielectric constants of six liquids have been determined at 25° and the results are in fair agreement with those of other observers. A. E. MITCHELL.

Molecular volume and molecular refraction of mixtures of liquids. W. HERZ (Z. anorg. Chem., 1925, **149**, 270—272).—The rule formulated by Lorenz and Herz (A., 1925, ii, 356) connecting the molecular volume at absolute zero and the molecular refraction, also the generalisation $V_0 p_k/T_k$=constant, where V_0 is the molecular volume at 0° Abs., T_k the critical temperature on the absolute scale, and p_k the critical pressure, have been extended to mixtures of liquids. R. CUTHILL.

Molecular and atomic volumes. VIII. Metaheulandites. W. BILTZ and F. SPECHT (Z. anorg. Chem., 1925, **150**, 10—19; cf. A., 1925, ii, 1141).—For measuring the volumes of partly dehydrated zeolites, a liquid is necessary which cannot replace the zeolithic water or enter the lattice, but which, nevertheless, wets the particles. Mercury was found suitable and a pyknometer was used which had a swan neck to prevent the solid rising to the open mouth. With a natural heulandite, the volume found was the same as when petroleum was used. When the heulandite was dehydrated, no change in volume occurred until the water content had fallen from 5·5 to 3 mol.; further dehydration caused at first a slow, and then a rapid, fall in volume. Zeolithic water thus causes no expansion of the lattice. When the volume was measured in petroleum, the decrease began with the beginning of dehydration, because this liquid can partly or wholly replace the zeolithic water. A. GEAKE.

Molecular and atomic volumes. IX. Hexahydrates of chromic and chromous chlorides. E. BIRK and W. BILTZ (Z. anorg. Chem., 1925, **150**, 20—25; cf. preceding abstract).—The molecular volumes of the three hexahydrates of chromic chloride and of chromous chloride hexahydrate were measured in petroleum. The molecular volume of the most stable of the chromic salts, the dark green dichlorotetra-aquochromic chloride dihydrate,

$$[CrCl_2(H_2O)_4]Cl,2H_2O,$$

is 145·2, that of the grey hexa-aquochromic chloride, $[Cr(H_2O)_6]Cl_3$, is 148·1, and that of the least stable, the light green monochloropenta-aquochromic chloride monohydrate, $[CrCl(H_2O)_5]Cl_2,H_2O$, is 151·4. The molecular volume thus falls with increasing stability, as for organic isomerides, the difference for each pair being 2%. The molecular volume of chromous chloride hexahydrate is 129·6, and this corresponds with a volume of 14·5 for each mol. of water. The molecular volumes of the water in the chromic chloride hexahydrates are 14·7, 15·2, and 15·7, respectively, and the chromous chloride thus corresponds with the dark green chromic salt and may be formulated $[CrCl_2(H_2O)_4],2H_2O$. A. GEAKE.

Mechanically-enforced double refraction of amorphous liquids in relation to molecular configuration. D. VORLÄNDER and R. WALTER (Z. physikal. Chem., 1925, **118**, 1—30).—Experiments in which a large number of organic liquids and a number of aqueous solutions, principally of salts of organic acids, were subjected to mechanical forces by being placed inside a stationary metal cylinder in which a coaxial solid metallic cylinder of slightly smaller dimensions was rotated at a high speed, show that the organic liquids acquire a normal, and the aqueous solutions an anomalous, double refraction. The values of the specific double refraction, $[D]=D/\mu\eta$, where D is the observed double refraction, μ the rotational velocity, and η the viscosity, are tabulated. In general, when η is less than 5 no double refraction is induced. Consideration of the $[D]$ values for a series of fatty acids and their triglycerides shows that there is some connexion between the optical properties and length of carbon chain. With increasing number of carbon atoms, the $[D]$ values increase at first slowly, then rapidly, and finally attain what is apparently an upper limiting value. Introduction of side chains or lengthening of those already present causes a diminution in $[D]$. With benzene compounds, the $[D]$ values increase in passing from *o*- to *m*- to *p*-compounds.

The double refraction is greater for those substances possessing an ethenoid linking than for the corresponding saturated compounds. The mechanically produced double refraction of colloidal solutions is discussed, and it is shown that there is some connexion between $[D]$ and size of particles. J. S. CARTER.

Rotatory dispersion of nicotine. T. M. LOWRY and B. K. SINGH (Compt. rend., 1925, **181**, 909—911).—The rotatory dispersions of nicotine over the range 4046—6708 Å. are given by the formula $\alpha/\alpha_1 = 0{\cdot}2379/(\lambda^2-0{\cdot}06)$, where α_1 is the rotation for the mercury line 5461 Å., and are therefore "simple" (cf. Lowry and Dickson, A., 1914, ii, 786). S. K. TWEEDY.

Diamagnetic and paramagnetic rotation of the plane of polarisation. R. LADENBURG (Z. Physik, 1925, **34**, 898—906).—As a result of thermal agitation, the number of electrons rotating in opposite directions in the magnetic field is not equal; the consequent rotation of the plane of polarisation is calculated from the dispersion theory and from Langevin's theory of paramagnetism. E. B. LUDLAM.

Optical rotation of arabic acid and the alkali arabates. M. A. RAKUSIN (Biochem. Z., 1925, **160**, 285—287).—Arabic acid, prepared from gum arabic of $[\alpha]_D$ −24·8°, had $[\alpha]_D$ −27·86°; lithium arabate $[\alpha]_D$ −17·81°; ammonium arabate $[\alpha]_D$ −19·81°; sodium arabate $[\alpha]_D$ −21·67°; potassium arabate $[\alpha]_D$ −23·06°. E. C. SMITH.

Relationship between optical rotatory powers and relative configurations of optically active compounds. II. Relative configurations of optically active mandelic acids and β-phenyllactic acids. G. W. CLOUGH (J.C.S., 1925, **127**, 2808—2813).—On the basis of the rule previously deduced (A., 1918, ii. 255) that the introduction of the same substituent into similarly constituted, optically active compounds possessing the same relative configurations produces alterations of the same character in their optical rotatory powers, the configurations of the optically active forms of mandelic and β-phenyllactic acids have been investigated. The molecular rotations of the following compounds have been determined: *l*-mandelic acid and its ethyl ester, methyl *l*-phenylbenzoyloxyacetate, methyl *l*-β-phenyl-lactate, methyl *d*-α-acetoxy-β-phenylpropionate, and methyl *l*-α-benzoyloxy-β-phenylpropionate. These results, combined with those of other investigators, indicate that *l*-hexahydromandelic acid and *l*-mandelic acid belong to the "*d*"-series (*loc. cit.*) of α-hydroxy-acids. The configurations of *l*-benzoin, the related optically active glycols, and amygdalin can thus be confirmed with reference to that of *d*-tartaric acid. *d*-β-Phenyl-lactic acid may also be classed with the "*d*"-series of α-hydroxy-acids. It is therefore possible to assign configurations to the glycols from this acid, and also to the four optically active phenylglyceric acids, provided it is assumed that *cis*-addition of hydroxyl occurs on oxidation of the cinnamic acids. M. S. BURR.

Calculation of Verdet's constant in the molecular theory of magnetic rotatory polarisation. R. DE MALLEMANN (Compt. rend., 1925, **181**, 1139—1141).—The constant A in its simplest form is expressed by $15{\cdot}82\times10^{-7}M(n-1)^2/dn$ for the sodium *D*-line. The calculated values show very good agreement with the values obtained experimentally by Perkin for a number of aliphatic compounds. The values of p, the number of effective electrons, assumed for the calculation, are for every case examined less by 4 than the accepted values of n, the number of valency electrons; hence the compounds examined appear to contain one atom of carbon less than they do in fact, and the free atom of carbon would have a zero value. S. I. LEVY.

Valency theories and the magnetic properties of complex salts. D. M. BOSE (Nature, 1926, **117**, 84).—If Z is the atomic number of the inert gas which terminates any transition group of elements, all those co-ordination compounds in which $Z=Z'(=N-E+2P$, where N is the atomic number of the co-ordinating atom, E its primary valency in the given compound, and P is 4, 6, etc., according as the complex compound is fourfold, sixfold, etc.) are diamagnetic, whilst the others are paramagnetic; the result is in agreement with that of Baudisch and Welo (A., 1925, ii, 943, 1031). Further, the number of Bohr's magnetons contained in any co-ordination compound of the first transition group of elements is $Z-Z'$, so far as magnetic properties have been studied. A. A. ELDRIDGE.

Elements with anomalous valencies. M. GOMBERG (Chem. Reviews, 1925, **2**, 301—314).

Co-ordination and co-valency. J. A. V. BUTLER (Trans. Faraday Soc., Dec., 1925, advance proof).—Co-ordination as an effect associated with compound formation is to be distinguished from co-valency; it consists in the congregation around an ion of a number of units with unshared electron pairs forming a new and distinct group of electrons outside the filled or partly filled groups in the simple ion. The attachment of the co-ordinated group is not due to the tendency of the simple ion to attain the configuration of the next higher inert gas. The maximum number of co-ordination valencies are deduced on the basis of the Main-Smith and Stoner sub-groups and agree with those given by the Sidgwick rule. Using this definition of co-ordination, it is shown that orthophosphoric, sulphuric, and chloric acids are true co-valent compounds, whilst the oxy-acids of the transitional elements, vanadic, chromic, and manganic acids, are co-ordinated. These co-ordinated acids give reversible oxidation potentials, indicating that the processess of oxidation and reduction involve the simple gain and loss of electrons. This behaviour is quite different from that of the oxy-acids of the non-metals. F. G. SOPER.

Nature of the chemical linking. Structure of silicon tetrachloride. G. Joos (Physikal. Z., 1925, **26**, 734—737).—Silicon tetrachloride may be regarded as four chlorine ions disposed tetrahedrally about a central silicon atom bearing four charges. The distance of each chlorine ion from the centre is taken from crystal data as 2·59 Å., and on this basis a value of 2847 cal./mol. is computed from electrostatic forces for the free energy. Spectroscopic and thermochemical data lead to a value of 2301 cal./mol. Accurate agreement requires the sphere including the four chlorine ions to be 7% greater than the value assumed from crystal data. The degree of agreement is regarded as justifying the idea of polar binding in this compound. R. A. MORTON.

Regularity in the rare earths. G. VON HEVESY (Z. anorg. Chem., 1925, **150**, 68; cf. A., 1925, ii, 938).—A numerical correction. A. GEAKE.

***X*-Ray analysis.** P. GÜNTHER and I. N. STRANSKI (Z. physikal. Chem., 1925, **118**, 257—275).—To test the possibility of the quantitative determination of alloys by means of the intensity of their *X*-ray spectrum, the influence of cobalt on the emission spectrum of nickel was investigated. It is shown that the ratio intensity Ni$K\alpha$/intensity Ni$K\beta$ is scarcely changed in the presence of cobalt and that the ratio intensity Co$K\alpha$/intensity Ni$K\alpha$ for a 50% alloy is nearly 1. Owing to the absorption of the Ni$K\beta_1$ line, the ratio intensity Co$K\beta_1$/intensity Ni$K\beta_1$ is greater than 1. It is deduced that where the presence of a

second element strengthens or weakens the radiation in an approximately equal manner, quantitative data on the composition can be obtained from the emission spectrum. H. TERREY.

Discovery of eka-manganese elements. (FRL.) I. TACKE (Z. angew. Chem., 1925, **38**, 1157—1160; cf. A., 1925, ii, 939).—A description of the chemical separation of the elements masurium and rhenium in the work previously described. W. T. K. BRAUNHOLTZ.

X-Ray examination of the inner structure of strained metals. IV. α-Iron plastically strained in extension, compression, and torsion. A. ONO (Mem. Coll. Eng. Kyushu, 1925, **3**, 267—286; cf. A., 1925, ii, 746).—The *X*-ray diffraction pattern of α-iron strained plastically in extension, compression, or torsion is in every case a series of rings having regularly oriented bright spots decreasing in intensity from the inner ring to the outer. The position of these spots has been analysed and shown to be due to the existence of two different kinds of symmetry in the strained crystal lattices. In the first kind, the rotation of the lattice during strain takes place about one of the axes in a definite direction, and in the second kind the lattice rotates about an axis which may occupy any position in a definite plane. In α-iron strained in extension, the symmetry is of the second kind, with the axis (110) more or less parallel to the direction of extension, whereas in the same metal strained by compression the symmetry may be of the first kind with the axis (111) in the direction of compression, or of the second kind with the axis of rotation (011) lying in the cross-sectional plane. In twisted α-iron, the second kind of symmetry exists with the plane (110), and probably also the plane (211), in the horizontal position. A. R. POWELL.

X-Ray examination of the inner structure of strained metals. V. Mechanism of crystal rearrangement and the cause of strain-hardening. A. ONO (Mem. Coll. Eng. Kyushu, 1925, **3**, 287—305).—Mathematical. The mechanism of the crystal rearrangement of a strained metal is investigated by assuming that slip and rotation are the causes of distortion and that the direction of slip is constant for each kind of lattice. The calculated results agree closely with those deduced from *X*-ray diffraction patterns. The resistance to slip of a metal increases with a diminution in the grain size, and this agrees with the fact that fine-grained metals are usually much harder and stronger than those in which the crystals are relatively large. A. R. POWELL.

Constitution of iron. F. WEVER.—See B., 1926, 15.

Allotropy of chromium. A. J. BRADLEY and E. F. OLLARD (Nature, 1926, **117**, 122).—A sample of chromium was found by *X*-ray examination to be a mixture of two allotropes. In the predominating form the atoms are arranged on two hexagonal lattices, giving an almost hexagonal close-packed structure, the axial ratio c/a being 1·625 instead of 1·633, and the distance between neighbouring atomic centres 2·714 and 2·705 Å. A. A. ELDRIDGE.

X-Ray determination of arrangement of atoms in the gold-copper and palladium-copper mixed-crystal series. C. H. JOHANSSON and J. O. LINDE (Ann. Physik, 1925, [iv], **78**, 439—460).—The lattice structures of the compounds Cu_3Au and CuAu have been ascertained. Tammann's view (A., 1919, ii, 398) that slowly cooled mixed-crystal series always exhibit regular structure has been criticised by Masing (A., 1922, ii, 37) and others. It is now confirmed that regular arrangement of atoms does not normally occur in mixed-crystal series. In the gold-copper series, the quickly cooled alloys show the normal conductivity-composition curve with a minimum at 50% (Mathiesen). With the slowly cooled alloys, the conductivity reaches maximum values at points corresponding with the compounds CuAu and Cu_3Au. *X*-Ray photographs show that near the maxima there are superimposed structure effects, whilst in regions removed from the maxima these lines do not occur. Højendahl's theory of conductivity in mixed crystals (A., 1924, ii, 647) as extended by Borelius (A., 1925, ii, 749) is supported. An increase in electrical conductivity is not necessarily due to a change in the lattice type, but it is always bound up with an increase in regular arrangement of atoms. R. A. MORTON.

Lattice parameter and density of tungsten. W. P. DAVEY (Physical Rev., 1925, [ii], **26**, 736—738).—Earlier values for the lattice parameter ($a=3·155\pm0·001$) and d ($19·32\pm0·02$) of tungsten (99·999% pure) have been confirmed. A. A. ELDRIDGE.

Arrangement of micro-crystals in rolled platinum plate. S. TANAKA (Mem. Coll. Sci. Kyōtō, 1925, **9**, 197—217; cf. *ibid.*, 1925, **8**, 319).—The examination by means of *X*-rays of platinum foil rolled in one direction only shows that the normal to the trapezohedral face of the micro-crystals is inclined about 10° to the direction of rolling, in the plane containing the direction of rolling and the normal to the rolled surface. E. B. LUDLAM.

X-Ray examination of some ammonia catalysts. R. W. G. WYCKOFF and E. D. CRITTENDEN (J. Amer. Chem. Soc., 1925, **47**, 2866—2876).—Various iron oxides and catalysts have been investigated by the *X*-ray powder method. The unit cube of magnetite has an edge of 8·37 Å.; if excess of ferrous iron is present, it appears as a separate phase, which disappears when an equivalent amount of alumina, silica, or zirconia (promoters) is added. With alumina, ferrous aluminate is formed and enters into solid solution, whilst the composition of the oxide tends towards that of ferroso-ferric oxide. The unit cube of magnetite containing potassium aluminate differs but little in size from the unit cube of ferroso-ferric oxide, and it is impossible to say whether or not solid solution occurs. Promoters maintain a large surface of iron in catalysts by inhibiting sintering of the reduced metal, so that the crystals of the latter grow only very slowly. α-Iron obtained by the reduction of magnetite has a unit cube of edge 2·859 Å.; if promoters are added before reduction,

iron is obtained with unit cells differing in size by less than 0·1% from those of pure iron.

S. K. TWEEDY.

Crystal structures of sodium and potassium trinitrides and potassium cyanate and the nature of the trinitride group. S. B. HENDRICKS and L. PAULING (J. Amer. Chem. Soc., 1925, **47**, 2904—2920).—The rhombohedral unit of sodium trinitride (d 1·853) contains 1 mol. and has $\alpha=38°\,43'$ and $a=5·481$ Å.; the sodium atom is at (0, 0, 0) and the nitrogen atoms at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, (u, u, u), and $(\bar{u}, \bar{u}, \bar{u})$, where $u=0·423$. The tetragonal unit of potassium trinitride (d 2·038) contains 4 mol. and has $a=6·094$ and $c=7·056$ Å.; the potassium atoms are at $(0, 0, \frac{1}{4})$, $(0, 0, \frac{3}{4})$, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$, whilst the nitrogen atoms are at $(0, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, 0)$, $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$; $(u, \frac{1}{2}+u, 0)$, $(\frac{1}{2}-u, u, 0)$, $(\bar{u}, \frac{1}{2}-u, 0)$, $(\frac{1}{2}+u, \bar{u}, 0)$; $(\frac{1}{2}+u, u, \frac{1}{2})$, $(u, \frac{1}{2}-u, \frac{1}{2})$, $(\frac{1}{2}-u, \bar{u}, \frac{1}{2})$, and $(\bar{u}, \frac{1}{2}+u, \frac{1}{2})$, where $u=0·135$. The unit for potassium cyanate, which is very similar in structure to potassium trinitride, has $a=6·070$ and $c=7·030$ Å.; the true structure was not deduced. The trinitride ion consists of a linear arrangement of three nitrogen atoms; two alternative electronic configurations are given. The azide group probably has the same collinear structure. The acid fluoride ion has a structure similar to that of the trinitride and cyanate ions.

S. K. TWEEDY.

Preparation and crystal structure of ferrous oxide. R. W. G. WYCKOFF and E. D. CRITTENDEN (J. Amer. Chem. Soc., 1925, **47**, 2876—2882).—A ferrous oxide was prepared by saturating electrically fused magnetic oxide with iron, the uniform interior product being freed from excess of iron by electromagnetic separation. The oxide, which is free from ferric iron, is practically non-magnetic (susceptibility=0·00052 per g.). The crystal unit, which is a cube of edge 4·29 Å., contains four molecules and has the sodium chloride structure giving a calculated d of 5·99. When much magnetite is present, the unit cube is slightly larger, but there is no evidence of solid solutions being formed at the ordinary temperature.

S. K. TWEEDY.

Hydroxides of aluminium and iron. I. J. BÖHM (Z. anorg. Chem., 1925, **149**, 203—216; cf. A., 1924, ii, 310).—The naturally-occurring hydroxides have been compared with artificially prepared hydroxides by the X-ray method of Debye and Scherrer (A., 1917, ii, 437). Bonsdorff's aluminium hydroxide (Ann. Phys. Chem., 1833, **27**, 275) is identical with hydrargillite. Aluminium hydroxide gels precipitated from cold solutions give no interference effects, but those from hot solutions give the same figure as bauxite, especially if allowed to age under boiling water. Bauxite gives a characteristic figure, which from its analogy to that of ruby mica indicates the formula of bauxite to be Al_2O_3,H_2O, and this hydrate has been prepared artificially. Sols of aluminium hydroxide give the bauxite figure after long boiling.

All the naturally-occurring hydroxides of iron except ruby mica consist of impure göthite. Ferric hydroxide gels appear to contain no crystalline hydroxide, unless they are heated with 2N-potassium hydroxide at 150°, when the göthite figure appears. Ferric hydroxide sols give a figure corresponding with a basic salt, but the deposit from old sols consists of göthite.

R. CUTHILL.

Incandescence of certain metallic oxides. J. BÖHM (Z. anorg. Chem., 1925, **149**, 217—222).—The change undergone by the oxides Sc_2O_3, Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2, Nb_2O_5, and Ta_2O_5 when they are ignited, which is apparent as sudden incandescence and results in the oxides becoming insoluble in acids, is shown by X-ray methods to be accompanied by a change in structure from amorphous to crystalline. The behaviour of explosive antimony is due to the same cause.

R. CUTHILL.

X-Ray analysis of some mixed crystals of the silver halides. R. B. WILSEY (J. Franklin Inst., 1925, **200**, 739—746).—An X-ray analysis has been made, using the Hull powdered crystal method, of the series of mixed crystals of silver chloride with silver bromide, and of silver bromide with silver iodide. The silver chloride-silver bromide mixtures showed the simple cubic structure (sodium chloride type) characteristic of the pure components, with a lattice spacing lying between those of the two components, and showing a linear relationship to the molar composition of the mixed crystals. Most of the silver bromide-silver iodide mixtures showed the existence of two mixed crystals, one the simple cubic type characteristic of pure silver bromide, but with an enlarged lattice spacing, and the other the diamond cubic or hexagonal type of the silver iodide crystal, with a slightly diminished lattice constant. In mixtures up to and including 70 mol.% of silver iodide, the simple cubic structure predominated, its lattice spacing increasing with the percentage of silver iodide fused in the mixture. Silver iodide appears to go quite readily into the silver bromide lattice, the calculations indicating that the largest simple cubic structure observed contained as much iodide as bromide. Judging by the effect on the lattice constant of the silver iodide structure, very little silver bromide entered the silver iodide lattice. Beyond 70 mol.% of silver iodide its own structure predominated in the mixture, and the lattice spacing of the simple cubic structure diminished, owing to a smaller fraction of the silver iodide entering the silver bromide lattice. The prediction of Trivelli (Rec. trav. chim., 1923, **42**, 714) that the incorporation of silver iodide would be found to enlarge the silver bromide lattice was verified. It seems likely that this enlargement is connected in some way with the increased speed obtainable in photographic emulsions of silver bromide containing small percentages of silver iodide.

F. G. TRYHORN.

Isomorphism of the molybdates of the rare-earth metals with those of calcium, strontium, barium, and lead. F. ZAMBONINI (Atti R. Accad. Lincei, 1925, [vi], **2**, 377—383; cf. A., 1925, ii, 1133).—Values of the angles and intensities of X-ray reflexions from crystals of the molybdates of lanthanum, cerium, praseodymium, neodymium, and samarium are tabulated.

F. G. TRYHORN.

Influence of the lanthanide contraction on the lattice dimensions of the cubical platinum metals. T. BARTH and G. LUNDE (Z. physikal. Chem., 1925, **117**, 478—490).—Precision measurements of the lattice constants of rhodium, iridium, palladium, and platinum were made by Wyckoff's method (Z. Kryst., 1923, **59**, 55). The increase in the lattice constants in passing from rhodium to iridium and from palladium to platinum only partly compensates for the decrease in the lattice constants of the rare earths in the same vertical series.

The length of the side of the unit gold cell, as determined by the Debye–Scherrer method, is 4·05 Å.

L. F. GILBERT.

X-Ray reflexions from mercuric iodide. R. J. HAVIGHURST (Amer. J. Sci., 1925, [vi], **10**, 556—558; cf. A., 1925, ii, 17).—From measurements by the powder method, and by the reflexion of the tungsten *K*-series from single crystal faces, the values $c=12{\cdot}34$, $a=6{\cdot}16$ Å. are computed for the dimensions of the elementary cell, containing 4 mols. of mercuric iodide. A smaller unit cell, containing 2 mols., is obtained by the rotation of the x and y axes of the crystal through 45°. For this cell, $c=12{\cdot}34$, $a=4{\cdot}356$ Å. All the lines obtained by the powder method are accounted for by this cell. Calculated for this unit d is 6·405, as compared with the experimental value of 6·30. F. G. TRYHORN.

Arrangement of atoms in tetragonal crystals of the mercurous halides, and the calculation of the optical double refraction of mercurous chloride. E. HYLLERAS (Physikal. Z., 1925, **26**, 811—814).—A determination of the crystal structure of the mercurous halides by the Debye–Scherrer method gave the following results for the cell dimensions: mercurous chloride, $a=6{\cdot}30$, $c=10{\cdot}88$; bromide, $a=6{\cdot}61$, $c=11{\cdot}16$; iodide, $a=6{\cdot}95$, $c=11{\cdot}57$ Å. The elementary cells contain eight mercury and eight halogen atoms. The crystal lattice of these substances may be regarded as similar to that of sodium chloride in which each sodium atom is replaced by two mercury atoms, so oriented that the line joining them coincides with the *c*-axis, and its mid-point takes the place of the sodium atom. Each chlorine atom in the sodium chloride lattice is replaced in the mercurous halide lattice in an analogous manner by two halogen atoms, The parameters α and β were determined from measurements of the intensities of the *X*-ray reflexions. For all three compounds, α is between 42° and 45°, and β between 54° and 60°. The optical double refraction of mercurous chloride was calculated by applying the Born theory to the above crystal structure. The values of the parameters $\alpha=45°$, $\beta=60°$ gave satisfactory values for the principal refractive index, but values about 20% too low for the secondary index. Complete agreement between calculated and observed figures was obtained when $\alpha=45°$ and $\beta=54{\cdot}30°$.

F. G. TRYHORN.

Varieties of thorium oxide and their catalytic action in the dehydration of alcohol. G. R. LEVI (Atti R. Accad. Lincei, 1925, [vi], **2**, 419—422).—An *X*-ray examination has been made of specimens of thorium oxide prepared by different methods. The hydroxide precipitated and dried at temperatures up to 120° is amorphous, as is the oxide prepared by heating the hydroxide to 340°. By heating the hydroxide to 1050°, or the nitrate or oxalate to 750°, the oxides obtained are crystalline and identical in structure. The formation of the so-called "meta" oxide as a distinct variety by heating the nitrate or oxalate is disproved. The catalytic activity of thorium oxide in dehydrating alcohol is approximately equal for the crystalline and the amorphous forms.

F. G. TRYHORN.

Measurement of the four magnetic transverse effects. E. H. HALL (Physical Rev., 1925, [ii], **26**, 820—840).—A detailed description is given of the measurement of the Hall, Ettingshausen, Nernst, and Leduc effects, together with tabulated results for gold, palladium, nickel, and cobalt at various temperatures between 17° and 86°. A. A. ELDRIDGE.

The magneton. W. GERLACH (Physikal. Z., 1925, **26**, 816—824).—A lecture summarising the present state and the theoretical and experimental development of the magneton theory.

F. G. TRYHORN.

Magneton number in complex compounds of some paramagnetic elements. D. M. BOSE (Z. Physik, 1925, **35**, 219—223).—The number of Bohr magnetons in complex compounds of ferric iron, chromium, nickel, and copper is found to be equal to the difference between the atomic number of the noble gas at the end of the series, krypton, 36, and the "effective" atomic number of the central atom as defined by Sidgwick. E. B. LUDLAM.

Magnetic properties of phosphors. E. RÜPP (Ann. Physik, 1925, [iv], **78**, 505—557).—An examination of the susceptibilities of a number of phosphors with partly diamagnetic and partly paramagnetic heavy metal atoms has been made, and the susceptibilities are co-ordinated with the central molecules and phosphorescent centres, the metal content, the phosphorescence bands, the temperature range of the phosphorescence, the susceptibility at low temperatures, the variation of susceptibility with the field strength, and the atomic magnetism of the heavy metal atoms. It is found that the central molecules of the mass (–CaS–, –CaO–) are more paramagnetic than the simple molecules (CaS, CaO) and that the central molecules are associated with a partly diamagnetic, as in the bismuth, copper, and silver phosphors, and a partly paramagnetic, as in the manganese, nickel, and tin phosphors, constituent. In the sulphur phosphors, it is likely that this constituent is the sulphide of the heavy metal. Various bands of one and the same heavy metal phosphor correspond with various sulphur compounds of the same metal, and lead to the conclusion that the same metal may be uni-, bi-, or ter-valent in the same phosphor. A method for the determination of the susceptibility of a finely divided substance has been developed, and depends on the observation of its Brownian movement, when dispersed in a suitable medium, with and without a

magnetic field. The magnetic moment of an individual centre of phosphorescence has been measured.
A. E. MITCHELL.

Influence of grain size on the magnetic properties of silicon-iron sheet. O. VON AUWERS.—See B., 1926, 15.

Comparison of a new ferro-nickel [permax] of remarkable magnetic properties with permalloy. H. TSCHERNING.—See B., 1926, 58.

Permanent magnets. F. STÄBLEIN.—See B., 1926, 57.

Electrical symmetry of nickel molecules. A. PERRIER and E. BOREL (Arch. Sci. phys. nat., 1925, [v], **7**, 289—298; cf. *ibid.*, 1923, **5**, 333).—A preliminary account of the technique of the determination of the longitudinal magnetic effects of electric currents in nickel at the ordinary temperature. Determinations are made by the ballistic method of the variations in magnetisation of a long tube of thin nickel as a result of the sudden passage of a heavy current. Details are given of the method of overcoming the simultaneous effects of the transverse magnetic field arising from the passage of the current through the nickel tube. The chief difficulties in the measurements are due to the deformability of the nickel tube, and to the magnetic properties of the nickel, which cause a lag in the action of the transverse magnetic field. F. G. TRYHORN.

Contact rectification by metallic germanium. E. MERRITT (Proc. Nat. Acad. Sci., 1925, **11**, 743—748).—Germanium possesses high thermo-electric power and resembles silicon chemically and in crystal form; consequently germanium may be expected to act as a rectifier for alternating currents, silicon being one of the best rectifiers known. This has been found to be the case, although the rectifying action is less marked than with many other materials; on the other hand, the contacts are quite stable and the action is uniform over the surface. Characteristic curves for several typical contacts are given, bismuth presenting a contrast to most other metals, the rectifying contacts being inferior. The effect of temperature was examined and curves are given. E. B. LUDLAM.

Unipolarity phenomena in compressed powders. F. TREY (Physikal Z., 1925, **26**, 849—862).—Theories of the rectifying action of certain crystals are discussed in the light of experiments whereby artificial detectors, mainly consisting of precipitated and compressed metallic sulphides, have been compared with their natural analogues. The natural and artificial sulphides of silver, cobalt, and tin, and also silver iodide, conduct electrolytically. When silver sulphide is pressed between equal electrodes, the current is transmitted equally well in either direction. If, however, unequal electrodes are used, *e.g.*, one is a point of wire positively charged, the negative ions will only be able to render up their charges by contact. The smallness of point of contact will cause an accumulation of ions; a polarisation and hence unipolarity effects will be observed. The investigation of the natural and compressed lead sulphides gave complicated results. A definite polarisation of a surface layer of moisture was observed, but the detector action could not be explained in this way.

The precipitated and compressed lead sulphide and also powdered lead glance transmit the current equally well in either direction and obey Ohm's law. On heating these preparations to 150°, a strong unipolarity effect is observed. It is shown that although lead sulphate and lead oxide exhibit polarisation, the real detector mechanism of lead sulphide is not bound up with surface effects. A possible explanation is based on an analogy with alloys of copper and silver. The pure metals show no rectifying action, whilst alloys may do so. Lead sulphide may function as a heterogeneous system. Iron sulphides behave similarly to lead sulphides. Compressed powders and ores of copper sulphide obey Ohm's law. The sulphides of bismuth have resistances too great to be amenable to investigation. R. A. MORTON.

Optical properties of amethyst quartz. C. V. RAMAN and K. BANERJI (Trans. Opt. Soc., 1924—5, **26**, 289—292).—Diffraction fringes are produced by the passage of unpolarised light through a section-plate of amethyst quartz cut normally to the optic axis, the plate, because of sectional repeated twinning, acting as a phase-changing diffraction grating.
A. COUSEN.

Bending of crystals. C. H. BOSANQUET (Proc. Physical Soc., 1925, **38**, 88—91).—Crystals of rock salt, 15×5×1—2 mm., can be bent into a semicircle in hot water or brine. Three alternative mechanisms are suggested for the deformation, (*a*) irrotational slip along cleavage planes, (*b*) alteration in the lattice spacing, (*c*) break up of the crystal into undistorted fragments with different orientations. These theories are tested by obtaining *X*-ray reflexions from the surface of a bent crystal rocked through a small angle. The reflected lines were curved and drawn out, showing that the orientation of the lattice varies in the crystal, but no change in lattice spacing could be detected within the accuracy of measurement (±1%). It is concluded that the third is the true explanation, and that the spaces between the crystal fragments are filled with amorphous sodium chloride.
C. J. SMITHELLS.

Influence of strain on the Thomson effect. H. E. SMITH (Proc. Physical Soc., 1925, **38**, 1—9).—The influence of strain on the Thomson effect in wires was investigated by Nettleton's method (*ibid.*, 1916, **29**, 16). For pianoforte steel, charcoal iron, constantan, and nickel, the Thomson coefficient decreases with tension (becomes less negative) until the elastic limit is reached, after which it increases. Thereafter the removal and re-application of tension produce a cyclic variation in the coefficient, even in wires stressed beyond the elastic limit. The coefficient for tungsten was determined within the elastic limit, and has a positive value, increasing with tension, and also following a cycle. Brass and German silver showed no change in the Thomson effect with variation in tension.
C. J. SMITHELLS.

Endurance properties of non-ferrous metals. D. J. MCADAM, JUN.—See B., 1926, 16.

Determination of the configuration of geometrically isomeric carbon compounds. A. LANGSETH (Z. physikal. Chem., 1925, **118**, 49—64).—The data for a large number of structural isomerides show that there is a close correspondence in the relation between the physical properties of the isomerides, $\begin{matrix}A\cdot C\cdot B\\ \|\\ D\cdot C\cdot E\end{matrix}$ and $\begin{matrix}B\cdot C\cdot A\\ \|\\ D\cdot C\cdot E\end{matrix}$, and that shown by the corresponding benzene derivatives, and . In a similar way, the relations between the physical properties of the oximes, $\begin{matrix}A\cdot C\cdot B\\ \|\\ N\cdot OH\end{matrix}$ and $\begin{matrix}A\cdot C\cdot B\\ \|\\ OH\cdot N\end{matrix}$, correspond with those exhibited by and . J. S. CARTER.

Influence of temperature on the mol. wt. of copper. A. JOUNIAUX (Bull. Soc. chim., 1925, [iv], **37**, 1525—1533).—The molecular condition of copper at various temperatures is deduced by the cryoscopic method from results of Sahmen, Heycock and Neville, and others, appropriate corrections being introduced where mixed crystals are formed. Between 400° and 650° Abs., the molecule is complex, association diminishing until the normal mol. wt. is reached. The metal is monatomic between 650° and 1356°, the m. p. Above the m. p., complexity increases very rapidly, until at 2583°, the b. p., the molecule is octoatomic. The latter conclusion is reached from the results of Ruff and Bergdahl and of Greenwood on the vapour pressure of copper at temperatures approaching the b. p., the constants in Dupré's relation being thereby evaluated and used in connexion with Clapeyron's equation. The mol. wt. given by the quotient of the mol. latent heat, calculated by Trouton's rule, and the atomic latent heat of vaporisation is approximately eight times the atomic weight. A point of inflexion is found on the dilatation curve of copper at 1600° Abs., in the region where marked association occurs.

C. H. D. CLARK.

Quantitative relationship between the mol. wt. of metals and their density in the liquid state. —A. JOUNIAUX (Bull. Soc. chim., 1925, [iv], **37**, 1534—1536; cf. preceding abstract).—From a survey of the results obtained with different metals, it is concluded that a relationship between mol. wt. and liquid density exists. When the specific volume of a liquid metal is a linear function of the temperature over a specified range, the degree of association is constant within the limits in question. A study of cases where the relationship is not a linear one indicates that the second differential coefficient of the specific volume with respect to temperature is positive or negative, according as the molecule is monatomic or polyatomic, respectively.

C. H. D. CLARK.

Electrical conductivity of certain light aluminium alloys and copper conductors as affected by atmospheric exposure. E. WILSON.—See B., 1926, 16.

Influence of an electrostatic charge on the surface conductivity of a plate of rock salt. P. VAILLANT (Compt. rend., 1925, **181**, 915—917).—The superficial conductivity of a plate of rock salt increases when positively charged and decreases when negatively charged. The positive ions thus have greater mobilities than the negative ions, indicating that the conducting ions are $H^{\cdot}$ and OH' and not those of sodium chloride. The influence of the electrostatic charge decreases as the humidity of the atmosphere increases. The conductivity is very small in a dry atmosphere, but increases greatly when the plate is charged. (Cf. Perkins, J. Phys. Radium, 1923, [vi], **4**, 246.) S. K. TWEEDY.

Relationship between hardness and the thermal and optical properties of elements. P. LASAREV (Bull. Acad. Sci. Russie, 1918, [6], 1259—1260; from Chem. Zentr., 1925, II, 259; cf. A., 1924, ii, 517).—The proportionality between hardness and atomic concentration (*i.e.*, the reciprocal of atomic volume) follows from the assumption that the mutual attractive force of the atoms of different elements is the same function of the distance between them. G. W. ROBINSON.

Influence of admixtures on the pyrophoric properties of finely divided metals. II. N. I. NIKITIN (J. Russ. Phys. Chem. Soc., 1925, **56**, 120—127; cf. A., 1924, ii, 556).—The loss of pyrophoric properties occurring when finely divided metals are heated is due to incipient recrystallisation of the metal. In the case of reduced iron, the presence of 2% (20%) of alumina in intimate admixture enables the metal to resist the tendency to crystallise and thus to retain its pyrophoric property even after being heated to 650° (700°). A mixture of finely divided metallic cobalt with manganese oxide, prepared by reducing the mixed oxalates of the two metals, undergoes crystallisation only with difficulty; even when less than 1% of manganese is present, maintenance of a temperature of 365° for 45 min. fails to destroy the pyrophoric properties of the cobalt, whilst a mixture containing 48% of manganese inflames in the air after being heated at 410°. Recrystallisation of copper and lead appears to take place at very low temperatures, since preparation of these metals by reduction at 125° results in non-pyrophoric powders. T. H. POPE.

Heat of combustion of salicyclic acid. E. BERNER (J.C.S., 1925, **127**, 2747—2750).—The heat of combustion of carefully purified salicylic acid determined in a bomb calorimeter is 5233·8 cal. (15°) per g. (vac.) at constant volume, or 5237·4 cal./g. when weighed in air against brass weights. The ratio of the heats of combustion of benzoic acid and salicylic acid is 1·2073 (vac.). M. S. BURR.

Heats of combustion of standard substances. W. SWIENTOSLAWSKI (J. Chim. phys., 1925, **22**, 583—588).—Polemical against Jaeger and Steinwehr (A., 1925, ii, 126). The value of the heat of combustion of benzoic acid calculated from the data of

Fischer and Wrede is nearly 0·2% below that found by Dickinson and others. The benzoic acid used by the former, and by Swientoslawski and Popov (A., 1915, ii, 315), was impure. The determination of the calorific value of Fischer's apparatus by Jaeger and Steinwehr (Ann. Physik, 1906, [iv], **21**, 23) contained a systematic error which raised the value for benzoic acid by approximately 0·3%. L. S. THEOBALD.

Freezing points. H. FOOTE and G. LEOPOLD (Amer. J. Sci., 1926, [v], **11**, 42—46).—F. p. determined at atmospheric pressure have usually been obtained under conditions tending to saturation with air, and methods proposed to eliminate the effects of variable amounts of air disregard the experimental fact that saturation may be rapidly accomplished. It appears preferable to regard the f. p. as the temperature at which solid and liquid are in equilibrium with dry air under a pressure of 1 atm. The effect due to the solubility of air on the m. p. of ice is 0·0023°, which, with the lowering due to pressure alone (0·0075°), makes the f. p. of air-saturated water 0·0098° below the temperature of the triple point. The f. p. of organic liquids are in general affected to a greater degree by the presence of dissolved air than is the f. p. of water. A. COUSEN.

Allotropy of zinc. D. STOCKDALE (J.C.S., 1925, **127**, 2951—2956).—Measurements have been made of the difference in *E.M.F.* between two zinc electrodes immersed in a fused mixture of zinc chloride, oxychloride, and bromide, at temperatures from 300° to 330°, a difference of temperature of about 10° being maintained between them. After allowing for lag, the breaks in the *E.M.F.*-temperature (or time) curve indicate that zinc undergoes an allotropic change at 315°, but the experiments are not entirely conclusive. This result, however, is in agreement with the observations that certain of the physical properties of zinc are discontinuous between 310° and 330°. M. S. BURR.

Densities at the absolute zero and the total expansion of the liquid state of organic compounds. W. HERZ (Z. anorg. Chem., 1925, **149**, 230—234).—The equation of van Laar ("Die Zustandsgleichung von Gasen und Flüssigkeiten," Leipzig, 1924, p. 140) $d_0/d_k=2(1+\gamma)$, where d_0 is the density at 0° Abs., d_k is the density at the m. p., b. p., or critical point, and $2\gamma=1+0{\cdot}038\sqrt{T_k}$, T_k being the (absolute) critical temperature, is used to determine the densities of a number of organic compounds at 0° Abs. The difference between the molar volumes at 0° Abs. and the critical point represents the total expansion of the liquid state lying between these temperatures. Its value increases in ascending a homologous series, or when one element in a compound is replaced by a heavier one. It is nearly the same for isomeric compounds of similar character. R. CUTHILL.

Vapour-pressure measurements on pure ozone. E. H. RIESENFELD and M. BEJA (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 7, 1—27; cf. A., 1922, ii, 637, 761).—The vapour pressure of ozone over the temperature interval −169° to −108·5° is satisfactorily represented by the equation $\log p=-\lambda_0/4{\cdot}571T+1{\cdot}75\log T-\varepsilon T/4{\cdot}571+C$, p being the pressure in mm. of mercury, T the absolute temperature, $\lambda_0=3500$, $\varepsilon=0{\cdot}05797$, and $C=5{\cdot}783$. At −169° and −108·5°, the vapour pressures are 4·8 and 840·8 mm., respectively. The b. p. of ozone is $-115{\cdot}5\pm0{\cdot}5°$. The heat of vaporisation varies with the temperature according to the equation $\lambda=\lambda_0+3{\cdot}499T-0{\cdot}05817T^2$, the values at 0° Abs. and the b. p. being 3500 and 2547 cal./mol., respectively. The value of the conventional chemical constant, pressure being measured in atm., is 2·9 (oxygen 2·8). J. S. CARTER.

Vapour pressures of metals; new experimental method. W. H. RODEBUSH and A. L. DIXON (Physical Rev., 1925, [ii], **26**, 851—858).—By the use of a quasi-static method, the vapour pressure of mercury at seven temperatures, from 170·4° (6·29 mm. of mercury) to 202·8° (18·90 mm.), has been determined, and that of lead at eight temperatures, from 1391° Abs. (5·70 mm. of mercury) to 1508° Abs. (19·70 mm.). The latter results are in agreement with the equation $\log p(\text{mm.})=-10372/T-\log T-11{\cdot}35$. The heat of vaporisation of lead at the m. p. is calculated to be 46,300 cal., and the chemical constant C_0 is −1·40, in agreement with the value −1·588 required by the quantum theory of monatomic gases. A. A. ELDRIDGE.

Mercury vapour pressure at low temperatures. F. E. POINDEXTER (Physical Rev., 1925, [ii], **26**, 859—868).—By the use of a modified form of Buckley ionisation gauge, the vapour pressure of mercury between $1{\cdot}210\times10^{-3}$ mm. at 19·73° and $3{\cdot}00\times10^{-9}$ mm. at −79·61° has been determined and tabulated for twenty-seven temperatures; the results correspond with the equations: $\log p(\text{liquid})=8{\cdot}86-3{\cdot}44(10^3/T)$; $\log p\,(\text{solid})=9{\cdot}35-3{\cdot}55(10^3/T)$. The heat of vaporisation of mercury is computed for sixteen temperatures from the vapour-pressure curve. The heat of fusion is calculated to be 600 cal. A. A. ELDRIDGE.

Vapour pressures of solid and liquid cyanogen. J. H. PERRY and D. C. BARDWELL (J. Amer. Chem. Soc., 1925, **47**, 2629—2632).—Vapour pressures of solid cyanogen have been measured from −93° to the triple point, and of liquid cyanogen from the triple point to −7°; the derived equations for the pressures in mm. are $\log P=(-1695{\cdot}122/T)+9{\cdot}65530$ for the solid, and $\log P=(-1818{\cdot}554/T)-5{\cdot}0813\log T+22{\cdot}30083$ for the liquid. The triple point is at −27·90° and 552·2 mm., and the normal b. p. is −21·17°. The latent heats of sublimation, vaporisation, and fusion are 7750, 8331—$10{\cdot}133T$, and 1904 (triple point) cal./mol., respectively. A. GEAKE.

Cause of change of physical properties of highly dried liquids, and influence of temperature on rate of drying. S. B. MALI (Z. anorg. Chem., 1925, **149**, 150—156; cf. Baker, J.C.S., 1922, **121**, 568).—Drying reduces the vapour pressures of carbon disulphide, toluene, benzene, and carbon tetrachloride by an amount which is the greater the higher the temperature at which the drying has been

carried out. The refractive index also appears to change at the same time. R. CUTHILL.

New statistical definition of entropy. M. PLANCK (Z. Physik, 1925, **35**, 155—169).—The new definition based on quantum considerations is: entropy $S=k\log P$, where P is the number of stationary states of the system the energy of which does not exceed a definite value E. The equation is not derived from considerations of probability, and is applicable to systems of few degrees of freedom. For systems of several degrees of freedom it leads to the formula for the free energy, $F=-kT\log P+E$.
E. B. LUDLAM.

Viscosity of ammonia gas. R. S. EDWARDS and B. WORSWICK (Proc. Physical Soc., 1925, **38**, 16—23).—The viscosity of ammonia was determined at 15°, 100°, and 184° by transpiring the gas through a capillary tube previously calibrated with air. By extrapolation, the values of η_0 and η_{100} were found to be $94{\cdot}4\times10^{-6}$ and $129{\cdot}5\times10^{-6}$ C.G.S. units, respectively. The value of Sutherland's constant C, in the equation $\eta=KT^{3/2}/(C+T)$ was found to be 377. The mean collision area of the ammonia molecule calculated from this value is $6{\cdot}33\times10^{-16}$ cm.^{2} The results agree closely with those of Rankine and Smith.
C. J. SMITHELLS.

Kinetic theory of compressibility of solutions and binary liquid mixtures. II. K. C. KAR (Physikal. Z., 1925, **26**, 737—739).—The author's equation (A., 1925, ii, 970) is in agreement with the empirical equation of Gilbaut (A., 1898, ii, 111). The equation is verified for a large number of salt solutions; *e.g.*, a 3·51% solution of ammonium chloride in water at 18° under 8 atm. pressure has an observed compressibility of $43{\cdot}6\times10^{-6}$, whereas the calculated value is $42{\cdot}8\times10^{-6}$. The compressibility of chloroform and carbon disulphide mixtures (not miscible) is given accurately by the equation, but for acetic acid–water mixtures the theoretical and observed curves differ, owing to the fact that the deduction of the formula demands dilute solutions as a necessary condition. R. A. MORTON.

Viscosity of sulphur dioxide, and of mixtures of it with hydrogen. M. TRAUTZ and W. WEIZEL (Ann. Physik, 1925, [iv], **78**, 305—369).—A simple apparatus is described for the rapid and accurate determination of the viscosities of gases at various temperatures. By determining the rate of flow of air, hydrogen, and carbon dioxide through tubes of various lengths and diameters, it was found that rim effects in these tubes are directly proportional to the rate of flow and to the density of the gas, and inversely proportional to the fourth power of the radius. It is further shown that these relationships correspond with the Hagenbach correction (*ibid.*, 1860, **109**, 385). The independence of the rim effect on the length of the tube permits the use of quite short lengths in the measurements of gas viscosities. A detailed consideration is given of various corrections which must be applied to viscosity measurements. The chief of these are those for expansion of the capillary tube, barometric fluctuations, and for the deviation of the gas under measurement from the ideal state. Appendices are given containing mathematical discussions of the theory of the transpiration method of measurement, and of the above corrections. Measurements were made of the viscosities of sulphur dioxide, and of numerous mixtures of it with hydrogen, at a series of temperatures between 17° and 199°. The viscosity of sulphur dioxide changes from 1221×10^{-7} at 14° to 2071×10^{-7} at 199°, the temperature coefficient being practically constant over this range. The Sutherland formula (Phil. Mag., 1893, [v], **36**, 507) does not apply to this gas. The viscosity curve of mixtures of sulphur dioxide and hydrogen exhibits a maximum, which, as the temperature increases, flattens, and is displaced towards mixtures richer in sulphur dioxide. At 17°, a mixture containing approximately 70 molar % of hydrogen has a maximum viscosity, whilst at 199° the maximum occurs with the mixture containing 50 molar % of hydrogen. The increase of viscosity of mixtures on the addition of hydrogen is roughly proportional, up to the maximum, to the mole fraction of hydrogen. The temperature coefficient of the viscosity of these mixtures approximates to that of pure sulphur dioxide, until sufficient hydrogen has been added to give a maximum viscosity. Beyond this maximum, the addition of further hydrogen slowly reduces the temperature coefficient to that of pure hydrogen. A comparison of these results with those for other gas mixtures suggests that the appearance of a maximum in the viscosity curve is dependent on the critical temperatures of both gases. F. G. TRYHORN.

Theory of atmolysis. J. SAMESHIMA (Japanese J. Chem., 1925, **2**, 33—44).—The rate of separation of the components of an ideal gas mixture when atmolysed under ideal conditions has been calculated. In the case of a two-component system, the following relations are deduced: $t=c(1/a-1/b)+1/b-x/a-(1-c)/b\,.\,c^{-b/a}\,.\,x^{b/a}$, or $t=(1-c)(1/b-1/a)+1/a-y/b-c/a(1-c)^{-a/b}\,.\,y^{a/b}$, and $y=(1-c)c^{-b/a}\,.\,x^{b/a}$, where a and b are the volumes of the pure gases which pass through a porous plate in unit time, c is the volume of the first gas in unit volume of the gas mixture, t the time from the beginning of atmolysis, and x and y are the volumes of the two gases in the remainder after time t.

For a system of n components: $t=(c_1/a_1+c_2/a_2+c_3/a_3+\ldots+c_n/a_n)-(x_1/a_1+1/a_2\,.\,c_2c_1^{-a_2/a_1}\,.\,x_1^{a_2/a_1}+1/a_3\,.\,c_3c_1^{-a_3/a_1}\,.\,x_1^{a_3/a_1}+\ldots1/a_n\,.\,c_nc_1^{-a_n/a_1}\,.\,x_1^{a_n/a_1})$ etc., and $x_2=c_2c_1^{-a_2/a_1}\,.\,x_1^{a_2/a_1}$, $x_3=c_3c_1^{-a_3/a_1}\,.\,x_1^{a_3/a_1}$, $\ldots\,x_n=c_nc_1^{a_n/a_1}\,.\,x_1^{a_n/a_1}$, where a is the volume of each pure gas that flows through a porous plate in unit time, c is the initial volume of each component of the mixture, and x is the volume of each component in the remaining gas after time t, different components being shown by different suffixes. The relation between the composition of the gases and t and those between the composition and volume of the gases are shown diagrammatically. L. L. BIRCUMSHAW.

Elastic properties of alloys. P. CHEVENARD and A. PORTEVIN.—See B., 1926, 59.

Boron-aluminium alloys. P. HAENNI.—See B., 1926, 58.

Artificial ferronickels and meteoric iron containing nickel. M. PESCHARD.—See B., 1926, 58.

Compounds and alloys of titanium and aluminium. W. MANCHOT and A. LEBER (Z. anorg. Chem., 1925, **150**, 26—34; cf. A., 1908, ii, 40; 1910, ii, 302).—Alloys of titanium and aluminium containing up to 37·3% of titanium were prepared by heating potassium titanifluoride with aluminium; uniform alloys containing more titanium could not be obtained. Titanium was determined by dissolving in hydrochloric acid and titrating with methylene-blue or bromine; aluminium was determined by difference, qualitative analysis showing that the alloys were pure, except for slight traces of iron and silicon. Cooling curves were followed by melting the alloys in a crucible completely surrounded with aluminium oxide powder, this being found preferable to an atmosphere of an inert gas. In general, the curves showed two halts, one corresponding with the compound Al_3Ti and the other with aluminium; the former increased with increasing titanium content, whilst the latter diminished and disappeared when the alloy contained 37·3% of titanium, corresponding with the compound Al_3Ti. No depression of the m. p. of aluminium was found, the m. p. rising with increasing titanium content from that of aluminium (658°) to a maximum of 1355° for the compound. Microscopical examination of the alloys revealed only two components, the compound usually appearing as needles. By dissolving the aluminium in cold 5% hydrochloric acid or sodium hydroxide the pure compound remains, *d* 2·74; the composition was confirmed both volumetrically as above and by gravimetric determination of titanium and aluminium. A. GEAKE.

Distillation of amalgams. A. MIETHE and H. STAMMREICH (Z. anorg. Chem., 1925, **149**, 263—269).—The amount of foreign metal carried over in the distillation of dilute amalgams under reduced pressure is shown to be negligible provided that care is taken to prevent local overheating and to keep back spray. Distillation of a mixture of colloidal gold and mercury gave a distillate which showed no trace of gold.

R. CUTHILL.

Solubility of cetyl alcohol in liquid sulphur dioxide. W. F. SEYER and R. W. BALL (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 149—151).—Saturated solutions of cetyl alcohol in liquid sulphur dioxide contain 0·42% of the alcohol at 5·3°, 7·70% at 22·2°, 31·18% at 23·5°, 57·46% at 25·5°, and 78·93% at 30·9°. J. S. CARTER.

Derivation of adsorption isotherms. A. GORBATSCHEV (Z. physikal. Chem., 1925, **118**, 357—360).—An addendum to a previous paper (A., 1925, ii, 959). L. F. GILBERT.

Transformation of water of hydration into water of adsorption by mechanical disintegration of crystal hydrates. T. HAGIWARA (Japanese J. Chem., 1925, **2**, 27—32).—By triturating microcrystalline aluminium hydroxide with quartz, heating the crystals at varying stages of disintegration in the electric furnace, and measuring the loss of weight of water, it is found that the greater the degree of disintegration the more easily is the water of hydration given up, and that with very fine particles the water takes on the characteristics of water of adsorption. This is in direct agreement with von Weimarn's theory (J. Russ. Chem. Soc., 1907, **39**, 651; Kolloid-Z., 1909, **4**, 198). Analogous results have also been obtained with göthite crystals.

L. L. BIRCUMSHAW.

Adsorption of barium chloride by colloidal hydrated manganese dioxide in aqueous solutions. W. CHLOPIN and A. BALANDIN (Z. anorg. Chem., 1925, **149**, 157—166).—This adsorption is not in agreement with the Freundlich isotherm, but appears to be due to the reaction, $MnO_2,H_2O+BaCl_2=BaMnO_3+2HCl$, accompanied by adsorption of one of the resultants by the manganese dioxide. At high salt concentrations, the former effect predominates, at low salt concentrations the latter. The enrichment of radium in barium may be explained in terms of adsorption by manganese dioxide (cf. Ebler and Bender, A., 1913, ii, 546; 1914, ii, 18).

R. CUTHILL.

Negative adsorption. VIII. Behaviour of kaolin towards aqueous solutions of alcohol and salts. M. A. RAKUZIN and A. N. NESMEJANOV (Biochem. Z., 1925, **160**, 288—290; cf. A., 1924, ii, 853).—Kaolin causes no increase of concentration by the removal of water from aqueous solutions of ethyl alcohol and metallic chlorides. E. C. SMITH.

Influence of thin surface films on the evaporation of water. E. K. RIDEAL (J. Physical Chem., 1925, **29**, 1585—1588).—Contrary to the results obtained by Hedestrand (A., 1925, ii, 102), it is found that the rate of evaporation of water from a surface is considerably diminished by the presence of a unimolecular film of fatty acid on the surface, and that an increase in surface concentration or film pressure retards the rate of evaporation. In Hedestrand's air-streaming method, it was assumed that the concentration gradient of water vapour in the stagnant layer is always small enough for any real change in the rate of evaporation of water from the liquid surface to be detected by a change in the rate at which water vapour is swept from the surface of the stagnant layer by the air stream. This is shown to be incorrect. An apparatus is described by means of which the rate of removal of water vapour from the neighbourhood of the water surface is increased, so that the ratio between the rate of removal and true rate of evaporation is increased, and thus any effect due to the presence of a thin film on the water becomes apparent. Rates of evaporation for water surfaces covered by unimolecular films of lauric, stearic, and oleic acids at various pressures are given. Different acids retard the rate of evaporation to different extents, and both condensed and expanded films behave similarly in this respect.

L. L. BIRCUMSHAW.

Phenomena of capillary chemistry. R. DUBRISAY (Compt. rend., 1925, **181**, 1142—1143; cf. A., 1923, ii, 741; 1924, ii, 731; 1925, ii, 961).—Ten drops of benzene solutions of various fatty acids were allowed to flow from burettes into water and alkaline solutions at various temperatures, the volumes occupied in each case being recorded. With water, the volumes increased with falling temperature; with

alkaline solutions, the reverse was the case. This agrees with the author's view that the influence of fatty acids on the tension at a benzene–water interface is greater as the alkali salts become less soluble in water, since soaps are more soluble in hot than in cold water. S. I. LEVY.

Superficial solutions. A. MARCELIN (Ann. Physique, 1925, [x], **4**, 460—527).—A full account of work already published (cf. A., 1924, ii, 390, 594; 1925, ii, 772).

Kinetic phenomena at liquid surfaces. L. KARCZAG and P. ROBOZ (Biochem. Z., 1925, **162**, 22—27).—The Brownian movement, in water and various liquids, of a series of substances including powdered metals and metalloids, inorganic and organic compounds, has been examined. Two types of motion are recognised, viz.: (1) the kinetic type without definite arrangement; (2) the static type in which definite forms are recognisable. Organic substances, *e.g.*, benzoic acid, acetylphenylhydrazine, and leucine, exhibit movements of the first type, which may be further subdivided into two groups distinguished as centrifugal and centripetal. Inorganic compounds are chiefly precipitated, whilst metals and metalloids exhibit centripetal motion. Inorganic compounds have no influence on the kinetic motion, but organic compounds, especially those which belong to the centrifugal type, exert a pronounced retarding effect. Kinetic phenomena at the inner boundary surface of two liquids are not controlled by hydrostatic pressure. The motion is largely governed by the dielectric constant of the medium; when the dielectric constant is less than that of water a marked restraining influence is evident. H. G. REEVES.

Electric phenomena and ionic permeability of membranes. V. Membranes of amphoteric character. A. FUJITA (Biochem. Z., 1925, **162**, 245—257).—If two solutions of an electrolyte of different concentrations are separated by a gelatin (or coagulated egg-white) membrane, the potential difference is the same as when the liquids are freely in contact only if the gelatin is isoelectric. If the gelatin is negatively charged, the more dilute solution is more positively charged than where there is free contact, whereas if the gelatin is positively charged, the reverse is the case. With agar membranes, the more dilute solution is always a little more positively charged than when there is free contact. The influence of the membrane disappears only in presence of considerable amount of hydrochloric acid. P. W. CLUTTERBUCK.

Comparison of methods of measuring polarity of surfaces. N. K. ADAM, R. S. MORRELL, and R. G. W. NORRISH (J.C.S., 1925, **127**, 2793—2795).—The polarities of glass, stearic acid, paraffin wax, two non-veiling varnishes, and one veiling varnish, have been compared by reference to (1) the catalytic activity of the surface for the combination of ethylene and bromine or ethylene and chlorine (Norrish, *ibid.*, 1923, **123**, 3006), (2) the measurement of the work W required to separate the surface from water in contact with it, W being related to the angle of contact θ of water with the solid surface by the relation $W = T(1+\cos\theta)$, where T is the surface energy of water (Adam and Jessop, A., 1925, ii, 962). There is a considerable difference between the results obtained by the two methods. Glass has less catalytic activity than either stearic acid or the veiling varnishes, but very much greater attraction for water; and stearic acid, which has only a slightly greater attraction for water than paraffin wax, has a very much greater catalytic activity. It is supposed that in certain cases, *e.g.*, with veiling varnishes, the reacting gases may penetrate some distance inwards, so that more catalytically active groups are reached. In the case of paraffin wax, no polar or catalytically active groups can be reached by penetration. M. S. BURR.

Comparison between dialysis and ultrafiltration, electrodialysis and electroultrafiltration. E. HEYMANN (Kolloid-Z., 1926, **38**, 58—59).—See this vol., 31.

Mechanism of ultrafiltration. J. DUCLAUX and J. ERRERA (Kolloid-Z., 1926, **38**, 54—57).—See A., 1925, ii, 530.

Dialysis and ultrafiltration. H. REINBOLDT (Kolloid-Z., 1925, **37**, 387—397).—A comprehensive treatment of the uses and technique of, and the apparatus employed for, dialysis and ultrafiltration. N. H. HARTSHORNE.

Electric phenomena and ionic permeability of membranes. VI. Membranes of paraffin, wax, mastic, and rubber. L. MICHAELIS and S. DOKAN (Biochem. Z., 1925, **162**, 258—265).—Paraffin, wax, mastic, and rubber membranes generally cause the more dilute solution of a diffusion cell to become positively charged. A smaller effect is obtained with multivalent than with univalent ions, especially when the cations are multivalent. If the cation is the hydrogen ion or a ter- or quadri-valent cation, the influence of the membrane almost disappears. An inversion of the effect is observed in the case of the mastic cell in presence of thorium when the more dilute solution became negatively charged. P. W. CLUTTERBUCK.

Electrical properties and ionic permeability of membranes. IV. Potential differences and permeability of collodion membranes. L. MICHAELIS and A. FUJITA (Biochem. Z., 1925, **161**, 47—60).—A completely dried collodion membrane is practically impermeable, but a slight permeability still exists for cations. Two methods are available for the detection of permeability: measurements of potential difference and diffusion experiments of long duration. Such a membrane is to be found in the skin of an apple. The theory involving the contact potential between two phases is scarcely applicable here, however, and a theory based on capillarity is preferred. C. RIMINGTON.

Osmotic pressure of solutions. M. LEVALT-EZERSKI (J. Russ. Phys. Chem. Soc., 1925, **56**, 249—264; cf. *ibid.*, 1924, **55**, 160).—The osmotic pressure of aqueous sucrose solutions at 0° is directly proportional to the depression of the f. p. and amounts to $12{\cdot}04\Delta t$ atm.; this rule is applicable to all values of Δt not exceeding 10°, and holds for electrolytes as

well as non-electrolytes and for mixed as well as single solutes. The osmotic pressures of solutions at 100° are given by the expression $58{\cdot}89\Delta t$, where Δt represents the elevation of b. p. and should not exceed 2·8°. As regards their change with temperature, osmotic pressures follow Gay-Lussac's law, the limitations as to range of temperature being as above.

The concentration of the solution, expressed in molecular quantities of solute taken, is a characteristic magnitude only for highly dilute solutions of non-electrolytes and in no way characterises the properties of solutions of high concentrations. For the latter solutions, a very useful characteristic is the magnitude Δt, expressing either the depression of the f. p. or the elevation of the b. p.

For different solutions of all concentrations, the results available are in conformity with the modification of Raoult's equation, $(p-p')/p=in/(N+in)$ or $(p-p')/p=1/[1+EN/\Delta t(\text{obs.})]$; this equation agrees completely with the figures for both 0° and 100° given in the published tables. The equation $(p-p')/p=in/(N+in)$ furnishes a new and convincing proof of the hydrate theory, and in the case of solutions of non-electrolytes permits of the calculation of the fraction of the total quantity of water which takes part in the formation of hydrates. T. H. POPE.

Osmotic pressure of aqueous solutions of cerous chloride. A. CHISTONI (Arch. Farm. sperim. Sci. aff., 1925, **40**, 161—163).—Cryoscopic measurements with solutions containing between 0·5% and 4·0% of cerous chloride indicate that a solution containing 2·57% of this salt is isotonic with one containing 0·75% of sodium chloride. The ionisation of the cerous chloride is considerably less than that of sodium chloride in these isotonic solutions, the ionisation coefficients being 0·487 and 0·991, respectively. F. G. TRYHORN.

Electrolyte-free, water-soluble proteins. V. Acid proteins. II. Donnan equilibrium and colloidal behaviour of proteins. J. FRISCH, W. PAULI, and E. VALKÓ (Biochem. Z., 1925, **164**, 401—436; cf. A., 1925, ii, 518).—The authors have investigated the alterations in conductivity, anion activity, and viscosity of solutions of pure electrolyte-free ovalbumin and serum-albumin after the addition of increasing amounts of hydrochloric, sulphuric, and phosphoric acids. The conductivity coefficient, f_u, and activity coefficient, f_a, differ considerably in the presence of excess of hydrochloric acid. On the assumption that the protein salt behaves as a completely ionised electrolyte, and taking Sørensen's value for the mol. wt., the value 40 has been obtained for the maximum acidity of ovalbumin. This corresponds closely with the value 39 for the free amino-groups of the diamino-acids in the protein molecule, deduced from the results of Osborne and Harris and of Hausmann (A., 1899, i, 653). The curves of conductivity, activity, and viscosity of the protein solution with increasing concentration of acid follow one another closely, each rising to a maximum. Since there can be no question of Donnan equilibria in a system of freely diffusible ions, these results support the Pauli theory of the imbibition of gelatin rather than that advocated by Loeb. E. C. SMITH.

Quantitative studies in dispersoid synthesis by von Weimarn's mechanical method. S. UTZINO (Japanese J. Chem., 1925, **2**, 21—26).—Von Weimarn's method has been applied to the following substances, all of which have thereby been obtained in the dispersoid condition: "metallic" selenium, "metallic" tellurium, rhombic sulphur, microcrystalline aluminium hydroxide, microcrystalline barium sulphate, crystalline antimony trisulphide, silver (thin foil), mercury, gold, and denatured egg-albumin. The substances were triturated with anhydrous dextrose at the ordinary temperature, except in the case of mercury and gold, where satisfactory results could only be obtained by trituration at the temperature of liquid air, and denatured albumin, which was triturated with ice at a low temperature. The dispersive medium was distilled water, except for barium sulphate, where 55% of alcohol was used. The average size of the dispersoid particles was about 52 μμ, and in some cases (*e.g.*, selenium and tellurium), the colloidal solutions remained stable for more than a year. A table is given to show that the stability of colloidal selenium solutions decreases with increasing degree of dispersion of the particles. Possible explanations for this are suggested.

L. L. BIRCUMSHAW.

Colloidal bismuth. A. GUTBIER, T. KAUTTER, and R. GENTNER (Z. anorg. Chem., 1925, **149**, 167—180; cf. Gutbier and Hofmeier, A., 1905, ii, 327; Gutbier and Huber, A., 1916, ii, 556).—A warm glycerol solution of bismuth nitrate made alkaline with sodium hydroxide is reduced by formaldehyde. The resulting sol oxidises very readily unless dialysed and neutral. By carrying out the reduction in presence of a protective colloid such as gum arabic, completely reversible sols can be obtained. The colloid particles are negatively charged. R. CUTHILL.

Colloidal rhodium. A. GUTBIER and E. LEUTHEUSSER (Z. anorg. Chem., 1925, **149**, 181—190; cf. Gutbier and Hofmeier, A., 1905, ii, 533).—A solution, which must not be too dilute, of sodium hexachlororhodate containing 1% of gum arabic (in absence of which the resulting sol is very unstable) is reduced at 90° with hydrazine hydrate. The product shows considerable resistance to coagulation by electrolytes, and, if dialysed, is not immediately coagulated by boiling. Chloride ion is always present, apparently being adsorbed by the gum. The colloid particles are negatively charged. A new method of preparing pure rhodium is described. R. CUTHILL.

Colloidal tellurium. A. GUTBIER and B. OTTENSTEIN (Z. anorg. Chem., 1925, **149**, 223—229).—Telluric acid is reduced with dextrose in presence of ammonia. The sol formed contains, even after dialysis, adsorbed dextrose (and often tellurous acid), and to this it probably owes its remarkable stability. A method of determining the adsorbed substances is described. The colloid particles are negatively charged. R. CUTHILL.

Colloidal sugar. P. P. VON WEIMARN (Japanese J. Chem., 1925, **2**, 63—72).—The author's theory of the colloidal stage of crystallisation is summarised, and it is shown that the method previously used for

the synthesis of colloidal solutions of potassium hydroxide (cf. "Kolloides und kristalloides Lösen und Niederschlagen," 153, 410) can be applied to the preparation of colloidal sugar solutions. The sugar must be dissolved in one organic liquid, which is miscible with another organic liquid in which the sugar is practically insoluble. Results are given of preliminary experiments with solutions of dextrose in acetone and ethyl alcohol, precipitated by pouring into ethyl ether at 20—21°. By this means, the colloidal stage of crystallisation of dextrose can be observed over a period of several hours. Microscopical measurement of the crystals formed 48 hrs. after pouring into ethyl ether showed that larger crystals were formed from the more dilute solutions than from the less dilute.

Acetone solutions of dextrose, sucrose, and lactose, poured into aromatic hydrocarbons (xylene, toluene, or benzene), gave dispersoid sugar solutions, characterised by various well-defined colours.

L. L. Bircumshaw.

Colloid chemistry of humic acid and peat. Wo. Ostwald and A. Steiner.—See B., 1926, 34.

Determination of size of colloidal particles by means of alternating electric fields. E. F. Burton and (Miss) B. M. Reid (Phil. Mag., 1925, [vi], **50**, 1221—1226).—The limiting velocity of settling under gravity of colloidal particles of such a size that the gravitational settling is ordinarily masked by the Brownian movement has been measured. The U-tube used was only slightly modified from that ordinarily used in cataphoresis measurements. An electric field was applied for a short time in one direction, then for an equal time in the reverse direction. The total movement was thus due only to gravitational settling and was measured after a suitable time. An 80-volt storage battery supplied the *E.M.F.*, and a mechanical device reversed the potential every 1½ min. The method was applied to a series of copper sols prepared by forming the arc under water containing increasingly larger traces of potassium hydroxide. The rate of settling increased from $0{\cdot}89\times10^{-5}$ cm./sec. for the copper sol in water alone to $1{\cdot}29\times10^{-5}$ cm./sec. with 24 drops of 0·01*N*-potassium hydroxide in 200 c.c. of water. The corresponding radii of the particles, calculated by assuming Stokes' law, are $7{\cdot}14\times10^{-6}$ cm. and $8{\cdot}60\times10^{-6}$ cm., respectively. A. B. Manning.

Diffusion analysis. R. Auerbach (Kolloid-Z., 1925, **37**, 379—387).—A description of the determination of the degree of dispersion from diffusion measurements. The theory, practice, and range of applicability of the method are discussed.

N. H. Hartshorne.

Measurement of particle size. A. Kuhn (Kolloid-Z., 1925, **37**, 365—377).—A review is given of methods for determining the size of colloid particles, based on measurements of velocity of movement under gravity or centrifugal force, diffusion constants, sedimentation equilibria, Brownian movement, osmotic pressure, ultrafiltration, dialysis, and viscosity, and of optical methods involving the counting under the microscope of the chemically enlarged particles or direct counting under the ultramicroscope, measurement of the mean distance between particles, the application of Rayleigh's theory, and *X*-ray interference. N. H. Hartshorne.

Mechanical analysis of sediments. J. R. H. Coutts and E. M. Crowther.—See B., 1926, 31.

Size distribution of particles. D. Werner.—See B., 1926, 31.

Measurement of the charge on colloidal particles. H. R. Kruyt (Kolloid-Z., 1925, **37**, 358—365).—A review of the methods for the measurement of the charge on colloid particles. The paper embraces the cataphoresis of coloured and colourless sols, and transport measurements.

N. H. Hartshorne.

Application of Röntgenspectrography to the study of colloidal systems. R. O. Herzog (Kolloid-Z., 1925, **37**, 355—358).—The author summarises the results obtained by the application of Röntgenspectrography to colloidal systems, under the headings: (i) transition from the liquid (amorphous) state and *vice versa*; (ii) determination of the crystal type; (iii) determination of crystal size and form, and (iv) the crystallite arrangement in gels.

N. H. Hartshorne.

Röntgenoscopy of colloidal systems. H. Mark (Kolloid-Z., 1925, **37**, 351—355).—A treatment of the theory and practice of the Röntgenographic investigation of colloids. In particular, the production of a suitable source of *X*-rays, and the interpretation of the results are dealt with.

N. H. Hartshorne.

Optical methods for the investigation of anisotropy in colloids. H. Zocher (Kolloid-Z., 1925, **37**, 336—351).—The methods available for the detection and measurement of anisotropy in colloids are described and discussed. N. H. Hartshorne.

Viscosity of soap solutions. B. L. Clarke (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 1, 1—9).—Soap solutions undergo change in viscosity with age, the change proceeding faster the lower the temperature and the more dilute the solution. Solutions may be brought to reproducible viscosities by merely boiling them for a short time and taking precautions to prevent the absorption of carbon dioxide. Determinations of the viscosities of sodium oleate solutions at 18° over the concentration range 0·04—0·10*N* and of sodium stearate solutions at 98·3° over the range 0·015—0·12*N* show that the viscosities conform to the requirements of the formula $\log \eta/\eta_0=0c$, where η_0 and η are the viscosities of pure water and of a soap solution of concentration c, 0 being a constant. The data of Farrow (J.C.S., 1912, **101**, 347) on the viscosities of solutions of sodium palmitate at 70° are also in accordance with this equation. J. S. Carter.

Stability of colloidal solutions. IV. Antagonistic effect of electrolytes on concentrated and dilute sols and a general theory of ion antagonism. K. C. Sen (Z. anorg. Chem., 1925, **149**, 139—149; cf. A., 1925, ii, 664).—The antagonistic effect of the chlorides of sodium and calcium,

potassium and calcium, sodium and barium, and potassium and barium in the coagulation of suspensions of arsenious sulphide (cf. Mukherjee and Ghosh, A., 1925, ii, 394; Weiser, A., 1924, ii, 309) is more pronounced with dilute sols than with more concentrated sols. It is suggested that, in general, if any ion with the same sign of charge as the colloid particle is more strongly adsorbed or concentrated at the interface, then it will oppose the action of the oppositely charged coagulating ion. If the concentration of the latter increases sufficiently, coagulation, or change in sign of the charge, or (in emulsions) inversion of the phases may occur. R. CUTHILL.

Constitution of the system sodium stearate-water. A. VON BUZAGH (Chem. Rundschau Mittel-europa Balk., 1925, **2**, 52—54, 72—73; from Chem. Zentr., 1925, II, 271—272).—The author has studied the conductivity and hydroxyl-ion concentrations of sodium stearate gels below 60°. With falling temperature, the conductivity approaches a limiting value which is reached more slowly with more concentrated solutions. The water in soap gels is apparently mechanically bound, since the composition of the liquid phase expressed from gels several weeks old is inconstant, the amount of stearate in solution decreasing with increase of the solid phase. The conductivity of the ultrafiltrate is less than that of the original system. This is attributed to adsorption of stearate molecules by stearic acid liberated by hydrolysis, in agreement with the fact that the system becomes more basic as the quantity of solid phase increases. G. W. ROBINSON.

Viscosity of colloids in presence of electrolytes. N. R. DHAR (J. Physical Chem., 1925, **29**, 1556—1567).—A theoretical paper, in which it is shown that previous experimental results on the viscosity of colloids, especially of the hydrophobe type, support the assumptions that (1) other things being equal, the uncharged substance is more hydrated than the sol; (2) the greater the hydration of a substance, the greater is its viscosity; (3) when a sol adsorbs an ion carrying the same charge as the sol, the charge on the sol is increased and the viscosity decreases, and (4) when a sol adsorbs more of the ion carrying the opposite charge than the ion carrying the same charge, the charge on the sol is decreased, further hydration takes place, and the viscosity increases (cf. Sen, Ganguly, and Dhar, A., 1924, ii, 394; Sen and Dhar, *ibid.*, 733; Ghosh and Dhar, A., 1925, ii, 386, 778). Support is also afforded for the view that sols which behave abnormally on dilution and towards mixtures of electrolytes of different valencies, and further which show positive acclimatisation, should also show a greater decrease of viscosity when small quantities of a coagulating electrolyte are added to them, than sols which behave normally on dilution and towards mixtures of electrolytes, and which show negative acclimatisation. The behaviour of hydrophile colloids as regards viscosity is discussed, and the results obtained by Pauli, Loeb, and others with substances like gelatin, albumin, etc., are explained qualitatively on the basis of the views expressed above. An alternative, and more satisfactory, explanation is based on the assumption that particles of gelatin or albumin have a natural tendency to disintegrate. In the case of isoelectric gelatin, the suspended particles disintegrate, these smaller particles adsorb more water, and consequently the viscosity of the system increases. When acids or alkalis are added, the charge on the sol is increased by preferential adsorption of hydrogen or hydroxyl ions, and hence the tendency to disintegrate, the degree of hydration, and the viscosity will also increase. L. L. BIRCUMSHAW.

Coagulation of complex negative sols by electrolytes. N. A. YAJNIK and S. L. BHATIA (J. Chim. phys., 1925, **22**, 589—594).—The coagulating effect of many electrolytes on Turnbull's-blue and Prussian-blue sols has been studied. The electrolytes included halides, nitrates, sulphates, etc. of the alkali metals; chlorides of barium, mercury, nickel, cobalt, and aluminium; nitrates of lead and cadmium; and sulphates of zinc, nickel, cobalt, aluminium, and chromium. The concentrations of electrolyte which completely coagulated, but did not precipitate, the sol in 2 hrs. at 17—18° were compared. With Turnbull's-blue, the order is chromium > aluminium > nickel > cobalt > zinc > barium > lead > mercury > rubidium > potassium > sodium > lithium. The Schultze-Hardy law holds for complete coagulation, but not when sedimentation is involved (cf. Ganguli and Dhar, A., 1923, ii, 58; Burton and MacInnes, A., 1922, ii, 130). The coagulating power of rubidium bromide is less than that of potassium chloride in the case of Prussian-blue sols. L. S. THEOBALD.

Influence of hydrogen-ion concentration on the speed of flocculation of negative colloids. A. BOUTARIC and (MME.) Y. MANIÈRE (Compt. rend., 1925, **181**, 913—915).—Observations on the flocculation of some negative colloids (*e.g.*, arsenic sulphide) with various acids indicate that the most important factor is the actual hydrogen-ion concentration and not the normality of the acid. The speed of flocculation is not always independent of the nature of the acid; this may be because the speed of adsorption of hydrogen ions varies for the different acid media, or because the acid radical itself undergoes adsorption. The latter explanation would also account for the protection phenomena previously observed (cf. A., 1925, ii, 526, 778). S. K. TWEEDY.

Supposed influence of lævulose and the action of magnesium salts on the coagulation of citrate- and phosphate-blood. (MISS) E. SLUITER (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 636—639).—Blood or plasma, which has been rendered non-coagulable by the addition of sodium citrate or metaphosphate, is coagulated by 1 c.c. of a 10% solution of commercial lævulose, but not by a specimen of pure lævulose prepared from inulin. The coagulating action of the former is due to the presence of a quantity of magnesium chloride (0·62 g. $MgCl_2$ per 100 g. sugar) sufficient in itself to produce the observed effects. J. W. BAKER.

Action of electrolytes on clays. S. KONDO.—See B., 1926, 14.

Theory of peptisation. K. C. SEN (J. Physical Chem., 1925, **29**, 1533—1547; cf. A., 1925, ii, 666).—By means of examples, it is shown that a high degree of adsorption and a suitable concentration of the electrolyte are necessary for peptisation, and that with the same electrolyte and the same peptisable substance, peptisation depends to a certain extent on the amount of adsorption. When different peptisable substances are used, peptisation is specific and depends on the nature of the adsorbent and on that of the peptising agent. The agglomeration of a precipitate decreases its power of adsorption, and hence its peptisability. With different acids and the same adsorbent, the amount of adsorption and ease of peptisation are not necessarily proportional. Peptisation is markedly retarded by the presence of bi- and ter-valent negative ions, although the corresponding acids are usually the most highly adsorbed. Univalent acids in general follow the rule that the greater the adsorption, the greater is the peptising power. The stability relations of peptised substances are considered at some length. L. L. BIRCUMSHAW.

Velocities of chemical reactions in presence of organic colloids. N. A. IZGARYSCHEV and M. I. BOGOMOLOVA.—See this vol., 132.

Structure of gelatin gels. E. O. KRAEMER (J. Physical Chem., 1925, **29**, 1523—1527).—A rough calculation shows that the gelatin sol unit (considered as a compact impenetrable cube) must measure about 5 μμ, and if the gelatin gel consists of chains of sol units loosely knit together, then the average interval between such chains will be about 100 μμ. With such a loose structure, the water phase in the interstices would be expected to exhibit the properties of water in mass. In an attempt to demonstrate the heterogeneity of gelatin gels, mercury particles, about 200—250 μμ in radius, were mixed with dilute gelatin systems before gelation, and cinematographic records of the Brownian motion of these particles were made with an apparatus previously described ("Colloid Symposium Monograph," 1924, **2**, 57). In gels of 0·5% and above, the Brownian movement was practically prevented, but gradually appeared on warming, whilst in gels of about 0·3% a measurable Brownian motion persisted. The distribution of the displacement magnitudes was normal, indicating that the structure of such weak gels is still considerably finer than the indicating mercury particles and their displacements. These experiments, whilst giving no evidence as to the heterogeneity of gelatin gels, must not be taken to support the view that the structure is molecular in magnitude. L. L. BIRCUMSHAW.

Hydrates of antimony trioxide. A. SIMON and H. POEHLMANN (Z. anorg. Chem., 1925, **149**, 101—124; cf. Lea and Wood, J.C.S., 1923, **123**, 259; Jander and Simon, A., 1923, ii, 772).—Hydrated antimony trioxide prepared by the decomposition of tartar emetic with hydrochloric acid cannot be freed from all traces of electrolytes without becoming crystalline and anhydrous. The amount of water in the product varies with the temperature of precipitation, and desiccation curves give no indication of the presence of definite hydrates, but rather suggest that the hydrated oxides are merely colloidal modifications of antimony trioxide differing primarily in fineness of division. This view is supported by experiments on their adsorptive power for potassium hydroxide (cf. Jander and Simon, *loc. cit.*). The water in the gels can be replaced by alcohol, and the vapour-pressure isotherms of both hydrogels and alcogels show that the liquids in them are contained in a system of capillary cavities, the gels being constant in volume. The colloid particles are negatively charged. No hydrates can be isolated by Willstätter's acetone method (A., 1924, ii, 615). R. CUTHILL.

Kinetics of the swelling and shrinking of gels. S. LIEPATOV (Biochem. Z., 1925, **166**, 220—233).—See A., 1925, ii, 685, 968.

Measurement of swelling. P. A. THIESSEN (Kolloid-Z., 1925, **37**, 406—411).—A description of the methods and apparatus used for the measurement of swelling. N. H. HARTSHORNE.

Diffusion. Free path of water molecules. Influence of a field of force. Statistical equilibrium. N. V. KARPEN (Bull. Acad. Sci. Roumaine, 1925, **9**, [9—10], 2—7).—Theoretical and mathematical. Formulæ for the diffusion of dissolved substances are derived. The diffusion coefficient K is related to the free path λ_0 of the molecules between two consecutive collisions with molecules of the solvent, the mol. wt., M, and the temperature, T, by the equation $K=\lambda_0/\sqrt{12}\,.\,\sqrt{RT/M}$. Assuming λ_0 to have approximately the same value, the values of $K\sqrt{M}$ at constant temperature for certain non-electrolytes have been calculated, the mean value being 8·2. From this, the value of λ_0 is $2{\cdot}12\times10^{-9}$ cm. at 17°. This is also the free path of the water molecules. The influence of a field of force and the conditions for equilibrium are considered. J. S. CARTER.

Kinetic activation as a factor in gas reactions. W. TAYLOR (Trans. Faraday Soc., Jan., 1926, advance proof).—Theoretical, in which it is shown that the expression deduced by Franck and also by Rice (cf. A., 1925, ii, 1076) for the velocity coefficient of a unimolecular reaction in a single gas can be generalised for the case of a mixture of gases with any number of components. L. S. THEOBALD.

Thermal formation of ozone. E. H. RIESENFELD and M. BEJA (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 8, 1—20).—The ozone–oxygen equilibrium has been investigated by exploding different mixtures of ozone and oxygen and determining the concentration of ozone in the residual gas by means of starch–iodide paper. Using mixtures containing up to 37% by volume of ozone, no ozone could be detected by this method after explosion, and hence the amount of ozone present is less than corresponds with a partial pressure of 2×10^{-8} atm. The maximum temperature attained by explosion of a 37% ozone mixture is 2130° Abs. Using mixtures containing 45—94% ozone by volume, the partial pressure of ozone in the gas after explosion lies between 2 and 4×10^{-8} atm., independent of the initial composition of the gas mixture. By these explosions, maximum temperatures of 2300° to 2850° Abs. are

obtained. According to the Nernst theorem, the maximum pressure of the ozone formed from pure oxygen at atmospheric pressure is $1{\cdot}3\times10^{-7}$ atm., this pressure being obtained at 3500° Abs. Within the limits of error, which are very wide, the experimentally determined ozone concentrations are in fairly good agreement with those calculated. J. S. CARTER.

Ionisation of weak electrolytes in water–alcohol solutions. III. Relations between the chemical constitution and alcohol-sensitivity of dibasic acids in ethyl alcohol. M. MIZUTANI (Z. physikal. Chem., 1925, **118**, 318—326; cf. A., 1925, ii, 793, 867).—The ionisation of oxalic, malonic, succinic, glutaric, malic, fumaric, maleic, and phthalic acids dissolved in ethyl alcohol has been investigated. The sensitivities to alcohol of the two ionisation constants when the carboxyl groups in a dibasic acid are far apart are about the same, but this rule does not hold when these groups are near to each other. The ionisation of solutions of glycollic and monochloroacetic acids, phenol, *p*-chlorophenol, and resorcinol in ethyl alcohol was also studied.

L. F. GILBERT.

Ionisation of weak electrolytes in water–alcohol solutions. IV. Ionisation in methyl alcohol solutions. M. MIZUTANI (Z. physikal. Chem., 1925, **118**, 327—341; cf. preceding abstract).—The same experimental (potentiometric) method was used as with the ethyl alcohol solutions. Results are given of measurements with solutions of formic, acetic, propionic, butyric, *iso*valeric, lactic, glycollic, salicylic, benzoic, and monochloroacetic acids, phenol, resorcinol, and *p*-chlorophenol, malonic, succinic, phthalic, malic, fumaric, and maleic acids, ammonia, methylamine, dimethylamine, trimethylamine, ethylamine, aniline, methylaniline, dimethylaniline, pyridine, and *o*-toluidine. The observed effects are correlated with differences between the solubilities of the substances in water and the alcohols. L. F. GILBERT.

Hydrogen-ion concentration and "electropy." M. BÁLINT (Biochem. Z., 1925, **165**, 465—472).—The p_H range of "electropic" dyes is determined. Electropic colour changes are due to change of the p_H of the dye solution, and not of electrostatic charge (cf. A., 1924, i, 688). The action of the usual decolorising substances is prevented if the solution be suitably buffered. Regeneration of colour is only effected either by acids or acid buffers and decolorisation by bases, basic buffers, and substances which adsorb hydrogen ions. P. W. CLUTTERBUCK.

Expression for the true reaction of solutions. D. GIRIBALDO (Biochem. Z., 1925, **163**, 8—12).—An expression $lr=\log[H^{\cdot}]/[OH']$ is proposed as an alternative to p_H. It has zero value at neutrality, becomes positive on the acid side, and negative on the alkaline side of neutrality. E. C. SMITH.

Dissociation constants, solubility products, and the titratability of alkaloids. I. M. KOLTHOFF (Biochem. Z., 1925, **162**, 289—353).—Those alkaloids which are monacid bases and have a dissociation constant greater than 5×10^{-7} give a sharp end-point with methyl-red. When the constant is smaller, dimethyl-yellow, methyl-orange, or bromophenol-blue must be used, and the titration carried to the correct p_H by comparison with a standard of p_H calculable from the dissociation constant. In presence of 50% alcohol, the end-point with methyl-red is not sharp and bromophenol-blue should be used. A table is given showing the dissociation constants, solubilities, and solubility products of 49 alkaloids and related substances. P. W. CLUTTERBUCK.

Solubility product of dicalcium phosphate. M. K. DOMONTOVITSCH and O. V. SARUBINA (Biochem. Z., 1925, **163**, 464—469).—From direct determinations, in saturated solutions, of the concentrations of calcium, phosphate, and hydrogen ions, the solubility product, $(\overset{++}{Ca})(\overset{--}{HPO_4})$, was found to be $10^{-6{\cdot}25}$ at 19—22° in distilled water. In various electrolyte solutions of total ion concentration equal to $M/10$, the value was $10^{-5{\cdot}75}$. R. K. CANNAN.

Neutral salt effect in the acetochloroanilide → *p*-chloroacetanilide rearrangement as a function of hydrogen-ion activity. G. ÅKERLÖF (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 2, 1—15).—The velocity measurements of Rivett (A., 1913, ii, 202, 1041) have been extended so as to include the effect of addition of aluminium chloride and the influence of lithium, sodium, potassium, magnesium, calcium, barium, zinc, and aluminium chlorides at concentrations up to about $3N$ on the activity of the hydrogen ion from $0{\cdot}2485N$-hydrochloric acid, as determined by *E.M.F.* measurements on the cell, Pt H_2|$0{\cdot}2485N$-HCl+salt|Sat.KCl|Sat.KCl Hg_2Cl_2|Hg, at 20° have been investigated. Addition of neutral salt results in an increased activity of the hydrogen ion, *e.g.*, in presence of $2{\cdot}75N$-potassium chloride, $2{\cdot}81N$-lithium chloride, and $2{\cdot}70N$-calcium chloride the hydrogen-ion activities are 0·446, 0·981, and 0·838, respectively, as compared with the value 0·208 for the salt-free solution. The values of $K-K_0/C$ for the various salts, where K_0 and K are the velocity constants in the absence of and in presence of neutral salt and C is the salt concentration expressed as a normality, are all of the same order of magnitude and increase somewhat with increasing salt concentration. The experimental numbers are in fair agreement with the equation $K/K_0=(\alpha/\alpha_0)^{D/\sqrt[3]{C}}$, where α_0 and α are the hydrogen-ion activities in the salt-free solution and in a salt solution of concentration C, and D is a constant the mean value of which is 0·65. The equation is in fair agreement with the data of Harned (A., 1918, ii, 436) and the author (A., 1922, ii, 134) on the influence of neutral salts on the rate of ester hydrolysis in acid media.

J. S. CARTER.

Water of hydration of crystalline compounds. Tensimetric analysis of the system anhydride–water. I. A. G. BERGMAN (J. Russ. Phys. Chem. Soc., 1925, **56**, 177—232).—The theory of the vapour pressure of hydrated compounds, the various methods proposed for its measurement, and the results obtained by previous investigators are discussed.

Observations on the efflorescence of hydrated salts lead to the conclusion that crystallohydrates exhibit two vapour pressures: the one for damaged crystals,

this being what is usually observed and measured, and the other for undamaged crystals, this being of considerably lower magnitude. For cadmium sulphate, the former vapour pressure is seventy times the latter. By means of van Bemmelen's method, measurements have been made of the hydration and dehydration isotherms for a series of sixteen solid systems of the type, anhydride–water. These vapour-pressure isotherms are of all possible types, ranging from the ideal stepped form to the continuous zeolite form. The water of hydration of bi-complex salts of the type $[X3en][X(C_2O_4)_3]$, in which X=Co or Cr, exhibits certain peculiar characteristics not observed in other hydrated compounds. T. H. POPE.

Influence of pressure on equilibria in binary systems. I. N. A. PUSHIN and J. V. GREBENSHCHIKOV (Z. physikal. Chem., 1925, **118**, 276—294).—The influence of pressure on conditions of equilibrium on the systems urethane and diphenylamine, urethane and *p*-nitroanisole, and sodium and mercury has been investigated. The results are in accordance with theoretical considerations (cf. A., 1912, ii, 331). L. F. GILBERT.

The system water and the nitrates and sulphates of ammonium and potassium at 25°. Y. OSAKA and R. INOUYE (Japanese J. Chem., 1925, **2**, 87—98).—The system has been studied by analysis of the solid and liquid phases existing in equilibrium at 25°. The following five series of solid solutions appear as solid phases: $(NH_4,K)_2SO_4$, a complete series with no gap; $(NH_4,K)_2(NO_3)_2\alpha$ and $(NH_4,K)_2(NO_3)_2\beta$, two series with a gap from 15·6 to 65 molal % of ammonium nitrate; $(NH_4K)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$, which extends from the double salt $(NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$ to the solid solution of the approximate formula $(0{\cdot}6NH_4,0{\cdot}4K)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2$; and $(NH_4,K)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$, which extends from the double salt $(NH_4)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$, to the solid solution of the approximate formula $(0{\cdot}865NH_4,0{\cdot}135K)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$. The relations are represented by a space model, and by its projection on the plane of the four radicals. The compositions of the solutions characteristic of the ternary and quaternary systems represented in terms of the formula $100mH_2O,xK_2,(100-x)(NH_4)_2,ySO_4,(100-y)(NO_3)_2$, are as follows: solid phases $K_2SO_4+K_2(NO_3)_2$, x=100, y=14·89, m=26·49; $0{\cdot}844K_2,0{\cdot}156(NH_4)_2,(NO_3)_2+0{\cdot}35K_2,0{\cdot}65(NH_4)_2(NO_3)_2$, x=20·52, y=0, m=4·15; $(NH_4)_2SO_4,(NH_4)_2(NO_3)_2+(NH_4)_2SO_4$, x=0, y=27·28, m=5·26; $(NH_4)_2SO_4,(NH_4)_2(NO_3)_2+2(NH_4)_2SO_4,3(NH_4)_2(NO_3)_2$, x=0, y=16·68, m=4·90; $(NH_4)_2(NO_3)_2+2(NH_4)_2SO_4,3(NH_4)_2(NO_3)_2$, x=0, y=6·99, m=3·96; $(K,NH_4)_2SO_4+(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\beta$, x=23·51, y=18·53, m=6·03; $(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\beta+(K,NH_4)_2(NO_3)_2\alpha$, x=18·4, y=5·9, m=3·5; $(K,NH_4)_2,0{\cdot}5SO_4,0{\cdot}5(NO_3)_2+(K,NH_4)_2(NO_3)_2\alpha+(K,NH_4)_2,0{\cdot}4SO_4,0{\cdot}6(NO_3)_2$, x=10, y=8, m=4. L. L. BIRCUMSHAW.

Complex formation in lead nitrate solutions. II. Quaternary system potassium nitrate–lead nitrate–barium nitrate–water. S. GLASSTONE and E. J. RIGGS (J.C.S., 1925, **127**, 2846—2854; cf. Glasstone and Saunders, *ibid.*, 1923, **123**, 2134).—The measurements of Foote (A., 1904, ii, 658) on the system KNO_3–$Ba(NO_3)_2$–H_2O at 25° have been extended, and the isotherms determined both for this system and for the system $Pb(NO_3)_2$–$Ba(NO_3)_2$–H_2O at 50°. The quaternary system was investigated both at 25° and at 50°. It appears that lead nitrate can exist in some form isomorphous with either potassium nitrate or the double salt $2KNO_3,Ba(NO_3)_2$, but the experimental results permit of no definite conclusion being reached. R. CUTHILL.

New mass action law. I. Treatment of the new formula. R. LORENZ (Z. anorg. Chem., 1925, **150**, 99—104; cf. A., 1924, ii, 761; 1925, ii, 536, 537, 866, 870).—In a reversible reaction in a condensed system of the type $Cd+PbCl_2 \rightleftharpoons Pb+CdCl_2$ at equilibrium $\mu_{Cd}+\mu_{PbCl_2}-\mu_{Pb}-\mu_{CdCl_2}=0$, in which μ is the molar thermodynamic potential. The values of the thermodynamic potentials of the reacting substances are given by equations of the type $\mu=K+\alpha x^2/(1+rx)^2+RT\log_e(1-x)$, from which is derived the new equation for the law of mass action in condensed systems $x(1-y)/y(1-x)=Ke^u$, in which x, y, $(1-x)$, and $(1-y)$ are molar fractions. u has the value

$$u=(\alpha/RT)\,.\,\{x^2-(1-x)^2/(1+r)\}/(1+rx)^2-(\alpha'/RT)\,.\,\{y^2-(1-y)^2/(1+r')\}/(1+r'y).$$

α, α', r, and r' are constants which are related to the values a and b in van der Waals' equation: $\alpha=(b_2^2a_1-2b_1b_2a_{12}+b_1^2a_2)/b_1^3$; $\alpha'=(b_4^2a_3-2b_3b_4a_{34}+b_3^2a_4)/b_3^3$; $r=(b_2-b_1)/b_1$, and $r'=(b_4-b_3)/b_3$, in which 1, 2, 3, and 4 refer to the four reacting substances. When the reacting substances are in corresponding states, $r'=(b_4-b_3)/b_3=(v_4-v_3)/v_3$, in which v is the molar volume. In condensed molten systems, this is usually sufficiently nearly true, and a table of corrections is given for reduced temperatures of 0·4—0·7°. If more than 1 mol. of a reactant takes part in the reaction, the thermodynamic potential becomes $\nu\mu=\nu k+\alpha\nu x^2/(1+rx)^2+RT\log_e(1-x)^\nu$, where ν is the number of molecules, and in general at equilibrium $\Sigma(\nu\mu)=0$ (cf. van Laar, "Sechs Vorträge ü. d. thermodynamische Potential," Braunschweig, 1906). A. GEAKE.

Fractional precipitation. II. Topochemical influence, and the separation of manganese and zinc with sodium sulphide. O. RUFF and B. HIRSCH (Z. anorg. Chem., 1925, **150**, 84—98; cf. A., 1925, ii, 992).—The solubility product of manganese sulphide ($1{\cdot}4\times10^{-15}$) is much greater than that of zinc sulphide ($1{\cdot}2\times10^{-23}$), but, if sodium sulphide is added to a solution containing both metals, the zinc sulphide is not precipitated in pure condition owing to the mechanical inclusion of manganese sulphide. The two sulphides have similar crystal forms and lattice parameters, and it is probable that, on this account, zinc sulphide forms such a compact layer round manganese sulphide that zinc ions from the solution cannot penetrate it to the manganese sulphide nuclei. When a solution of a zinc salt is added to precipitated manganese sulphide,

completion of the reaction is favoured by freshness of precipitation, low temperature, and fine division, but is independent of the concentration of zinc; it is concluded that zinc sulphide skins of similar thickness are always formed. When mixtures of zinc and manganese are fractionally precipitated with sodium sulphide, separation is improved by increasing the ratio $Zn^{\cdot\cdot} : Mn^{\cdot\cdot}$, by diluting the sodium sulphide, by rapid stirring, and by low temperature; under suitable conditions, the precipitate contains less than 0·2% of manganese. The addition of neutral salts has little effect, but increasing hydrogen-ion concentration improves the separation, and manganese sulphide cannot be precipitated from a normal solution when this is greater than 89×10^{-6}.

A. GEAKE.

Determination of transition points in non-aqueous solutions by the electromotive force method. R. B. MASON and J. H. MATHEWS (J. Physical Chem., 1925, **29**, 1507—1516).—The *E.M.F.* method has been used for the determination of transition points in anhydrous pyridine solutions. There is a sharp break in the temperature–*E.M.F.* curve at 55° for the half cell Cu-Hg|$CuCl_2,2C_5H_5N$ when connected to either the half cell $HgCl_2,2C_5H_5N$|Hg or $CdCl_2,2C_5H_5N$|Cd-Hg. This break is evidently due to the transition of $CuCl_2,2C_5H_5N$ to $2CuCl_2,3C_5H_5N$. On account of several secondary chemical reactions, the *E.M.F.* of the cupric chloride cell gradually changes. The temperature–conductance curve shows a break at approximately 56°. The Cd-Hg|$CdCl_2,2C_5H_5N$|sat. solution of $ZnCl_2$|$ZnCl_2,2C_5H_5N$|Zn-Hg cells were the most satisfactory of all the cells tried as regards conductance, stability, and reproducibility. The temperature–*E.M.F.* curve shows a sharp break at 9·3°, at which the compounds $CdCl_2,6C_5H_5N$ and $CdCl_2,2C_5H_5N$ are in equilibrium. This value is in good agreement with the temperature obtained by the solubility method (9°). On heating the cell Pb-Hg|$PbCl_2,2C_5H_5N$|sat. solution of $PbCl_2$|$CdCl_2,2C_5H_5N$|Cd-Hg, the cadmium and zinc amalgams change polarity. This reversal is apparently an irreversible change, although there is some indication of a transition point at 53°.

L. L. BIRCUMSHAW.

Decomposition of metallic sulphates by heat. (MLLE.) G. MARCHAL (J. Chim. phys., 1925, **22**, 559—582; cf. Hofman and Wanjulow, Trans. Amer. Inst. Min. Eng., 1913, **43**, 563).—Results in greater detail are given for the sulphates already mentioned (A., 1925, ii, 1162). The anhydrous sulphates of gallium, beryllium, nickel, cobalt (violet form), manganese, cadmium, silver (yellow form), and magnesium, respectively, afford evidence of decomposition at 500°, 565°, 690°, 690°, 720°, 780°, 850°, and 880°. The total equilibrium pressures become equal to atmospheric at 690°, 788°, 883°, 958°, 1028°, 1060°, 1108°, and 1150°, respectively. Curves showing the logarithm of the total pressure and the total pressure itself, each against temperature, as well as the data for the measured total pressure, and for the calculated partial pressures of the resulting sulphur oxides and oxygen, are given. Equilibrium is quickly established once a given suitable temperature is reached. The mean value of the calculated heat of reaction for nickel sulphate between 800° and 900° is 62·8 cal.; for cobalt sulphate between 820° and 950°, 50·6 cal.; and for gallium sulphate between 600° and 650°, 52·6 cal. With the cadmium salt, the results were confined to the dissociation represented by $5CdSO_4 \rightleftharpoons CdSO_4,4CdO + 4SO_3$. At the same temperature, the total equilibrium pressure for nickel sulphate is greater than that for cobalt sulphate, for zinc sulphate much greater than for the cadmium salt, and for gallium sulphate greater than for aluminium sulphate, and hence the separation of the metals from their respective pairs by selective decomposition is possible.

The order found above agrees with that predicted from a knowledge of the heats of reaction at the ordinary temperature. L. S. THEOBALD.

Suggestion for a second thermochemical standard. P. E. VERKADE and J. COOPS, jun. (Bull. Soc. chim., 1925, [iv], **37**, 1536—1540).—Polemical, in reply to Swientoslawski (A., 1925, ii, 540). Since it is admitted that salicylic acid is suitable as an auxiliary substance to benzoic acid, it is urged that salicylic acid should be recognised as a second standard, as previously suggested by the authors (A., 1925, ii, 39). C. H. D. CLARK.

Thermal properties of viscous sulphur. P. MONDAIN-MONVAL (Compt. rend., 1926, **182**, 58—60).—Calorimetric experiments with sulphur are described. The transition S(liq.) ⟶ S(viscous), which occurs above 160°, absorbs 2·8 cal./g., and the transition $S_\alpha \longrightarrow S_\beta$ absorbs 2·7 cal./g. The mean specific heat of S_α is 0·176, of liquid sulphur, 0·220, and of viscous sulphur, 0·290 (cf. Lewis and Randall, A., 1911, ii, 371). S. K. TWEEDY.

Heat of adsorption and surface tension. H. CASSEL (Physikal. Z., 1925, **26**, 862—864).—Theoretical. Iljin's method of treatment (A., 1925, ii, 958) is extended and the connexion between various expressions for heat of adsorption is explained.

R. A. MORTON.

Vapour pressure and heat of dilution of aqueous solutions [of carbamide]. E. P. PERMAN and T. LOVETT (Trans. Faraday Soc., Jan., 1926, advance proof; cf. Perman and Price, A., 1913, ii, 20).—The vapour pressures of aqueous solutions of carbamide have been determined by a statical method (Trans. Faraday Soc., 1923, **19**, 112—116) over a wide range of concentrations at 40·02°, 49·99°, 60·28°, 70·39°, and 80·10°. The smooth curves obtained by plotting the lowering of vapour pressure against the weight of carbamide per 100 c.c. of solution meet, on extrapolation, in a point representing a vanishingly small vapour pressure and a concentration of 132 g./100 c.c. of solution. The proportionality between $\log p_0/p$ and n/N holds fairly well for all concentrations and temperatures, but the agreement is improved by adding to N a small fraction of n. Since the introduction of a hydration factor, as in Callendar's formula, lessens agreement, it is concluded that there is no hydration of the carbamide, and that the mol. wt. is normal. The vapour pressure–temperature curves for solutions of the same concentration

are shown and are named "isosthens." Van Babo's law does not hold for aqueous solutions of carbamide. The densities for solutions up to a concentration nearly approaching saturation are given for the above temperatures. The curves form a regular series. The derived density–temperature curves for equal concentrations appear to be linear, their slopes decreasing slightly with increasing concentration.

For determining the heats of dilution of concentrated solutions of carbamide in water, a new method, involving the measurement, by electrical means, of the heat change occurring, was employed. The heat lost by radiation was compensated by the use of a heating coil, whilst a second coil exactly counterbalanced the heat absorbed on dilution. The amounts of heat absorbed by the saturated solutions when 1 mol. of water is added are small compared with the values for metallic salt solutions. The curves heat absorbed–concentration are for the most part almost linear, but alter sharply at the ends. They overlap at the lower concentrations and their slope becomes less at higher temperatures. Data at temperatures 40·02°, 49·99°, 60·28°, 70·39°, and 80·1° are given. At the lower temperatures, the calculated affinity of water for various solutions is roughly proportional to the heat of dilution, but at the higher temperatures it increases more rapidly with increasing concentration, and finally becomes greater. The observed values of H, the heat of dilution defined by Kirchhoff's equation, agree well with those calculated from the equation $H=RT^2\partial(\log_e p_0/p)_c/\partial T$. In general, the heat of dilution was observed to fall as the temperature increased.

The results of Tucker (A., 1915, ii, 674) are discussed, and a new method for determining solubility is suggested. L. S. THEOBALD.

Conductivity of mixtures of strong electrolytes. H. EGNÉR (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 5, 1—8; cf. Bray and Hunt, A., 1911, ii, 688; Kraus, A., 1922, ii, 269).—Measurements have been made of the electrical conductivities at 25° of solutions of hydrogen, lithium, sodium, potassium, magnesium, and calcium chlorides and of mixtures of hydrogen chloride with lithium, sodium, and calcium chlorides, of magnesium chloride with sodium and calcium chlorides, and of potassium chloride with lithium chloride in the concentration range 0·002—0·1N. The conductivities of the mixed solutions as calculated by the aid of the isohydric principle from the data for the single salts are always slightly greater than those experimentally determined. For the mixtures which contain hydrogen chloride the differences (2·2—0·3%) are decidedly in excess of the errors of experiment, but even in this case the difference tends to disappear with dilution. The viscosity correction changes the calculated values only slightly and in a favourable direction. A small difference in the value of λ_0 has very little influence on the value of the computed conductivity.
J. S. CARTER.

Influence of iodine on the conductivity of aqueous solutions of cadmium iodide and potassium iodide. H. BRUNS (Z. Physik, 1925, **34**, 751—765).—The solubility of cadmium iodide in water has been determined between 21° and 87°. Little change in the conductivity of 5% cadmium iodide solution is caused by addition of iodine; the conductivity of more concentrated cadmium iodide solutions is, however, definitely increased. Addition of iodine decreases the conductivity of potassium iodide solutions, owing to the formation of the comparatively slow I_3 ions. These ions are also formed in the cadmium iodide solutions, but their effect is said to be more than compensated by the splitting up of $(CdI_2)_n$ aggregates. The results of f. p. determinations agree with the above theory. The effect of iodine on the emission of ions from the heated salts is correlated with conductivity observations (cf. Schmidt, A., 1925, ii, 251). L. F. GILBERT.

Mobility of ions in solid cuprous and silver sulphides. H. BRAUNE (Z. Elektrochem., 1925, **31**, 576—581).—The rate of migration of the anions in solid cuprous and silver sulphides is known to be very much less than that of the cations. Approximate data for the mobility of both ions have been obtained by measuring the diffusion which takes place between a cast cylinder of pure sulphide and one of a dilute solid solution of the one sulphide in the other, or of selenides in sulphides. The temperature of the experiments ranged from 100° to more than 800°. For the silver ion, the diffusion coefficient is given by $D_T=113e^{-2285/T}$, for the cuprous ion by $D_T=40{\cdot}3e^{-1893/T}$, and for the sulphide ion by $D_T=89{\cdot}3e^{-10120/T}$, confirming the great difference in the temperature coefficients of cations and anions. The transport numbers of sulphide ion in silver sulphide have been calculated: they range from $0{\cdot}9\times10^{-8}$ at 177° to $0{\cdot}7\times10^{-3}$ at 836°. W. A. CASPARI.

The hydrate problem. III. Electroendosmose and the electrolytic transport of water. H. REMY (Z. physikal. Chem., 1925, **118**, 161—192; cf. A., 1915, ii, 310).—The movement of liquids under the action of applied potential differences has been studied with pure water and solutions of electrolytes of concentration 0·001N to N and with diaphragms of powdered sulphur, animal charcoal, clay, the Zsigmondy–Bachmann membrane, gelatin, and parchment paper. With parchment and gelatin diaphragms, the effect of increasing the concentration of electrolyte is to accelerate the shift of liquid. At the concentrations used, this effect is not truly endosmotic, *i.e.*, is not due to increase of anion adsorption on the diaphragm, and must be ascribed to transport of water attached to the ions.
L. F. GILBERT.

Oxidation potentials and equilibria in the system: chlorine–iodine–hydrochloric acid–water. G. S. FORBES, S. W. GLASS, and R. M. FUOSS (J. Amer. Chem. Soc., 1925, **47**, 2892—2903).—The oxidation potentials of chlorine and of chlorine plus iodine in 4, 5, and 6N-hydrochloric acid have been measured at 25°. For iodine trichloride, the results are given by $E=E_0+0{\cdot}0124\log[ICl_3]$, and for the monochloride by $E=E_0+0{\cdot}0154\log[ICl]$, where E_0 is the extrapolated $E.M.F.$ for solutions containing 1 g.-equiv. of iodine and 3 or 1 g.-equiv. of chlorine, respectively, per litre. These equations

indicate a valency change twice as great as that actually occurring; this may be explained by the assumption that the electrochemical change is $Cl_2+2e \rightleftharpoons 2Cl'$, and not $ICl \rightleftharpoons I'+Cl'$.

The above solutions may be accurately titrated electrometrically, providing escape of chlorine is avoided and platinum–iridium electrodes are used. The following equilibrium constants, which are independent of the acid concentrations, are calculated: $[ICl][Cl_2]/[ICl_3]=7{\cdot}2\times10^{-4}$; $[I_2][Cl_2]/[ICl]^2=7{\cdot}8\times10^{-15}$; $[I_2][ICl_3]/[ICl]^3=1{\cdot}1\times10^{-11}$. Oxidation-potential measurements form a sensitive test for the presence in iodine of impurities of higher oxidation potential. S. K. TWEEDY.

Effect of electrode material on oxidation potentials. J. A. V. BUTLER, W. E. HUGH, and D. H. HEY (Trans. Faraday Soc., Jan., 1926, advance proof).—A comparison of the oxidation potentials of various metals has been made. At 25°, in the cells $Hg|Hg_2Cl_2|N/200|K_3Fe(CN)_6$ or $K_4Fe(CN)_6|$metal and $Hg|N$-KCl$|N$-KCl|metal, platinum (platinised and plain), palladium, iridium, osmium, gold, rhodium, and ruthenium gave a constant potential (0·1905± 0·0001 volt) within an hour. Molybdenum, tungsten, nickel, silver, and mercury did not give constant potentials. The system, cuprous–cupric chlorides in aqueous ammonia allowed a wider range of metals to be compared directly with two platinised platinum electrodes as standards. Palladium, iridium, gold, osmium, rhodium, ruthenium, silver, nickel, and mercury as electrodes quickly reached the potential of the standards (to within ±0·0001 volt). Metallic selenium and graphite gave constant values differing from that of platinum by 0·3 and 0·6 millivolt, respectively. Electrodes of molybdenum, tungsten, tantalum, arsenic, and antimony did not give constant potentials. The independence of oxidation potentials of the electrode material, when this takes no appreciable part in the cell reaction, is thus confirmed. L. S. THEOBALD.

Oxidation–reduction potentials of organic substances. H. VON EULER and A. ÖLANDER (Z. anorg. Chem., 1925, **149**, 1—17).—By means of the oxygen and hydrogen electrodes, *E.M.F.* measurements have been made with buffered solutions of quinol, quinone, acetaldehyde, ethyl alcohol+acetic acid (or acetate), ethyl alcohol+acetaldehyde+acetic acid, lactic acid, sodium lactate, dextrose, lævulose, sodium benzoate, and potassium cinnamate. R. CUTHILL.

Does radium exert an influence on the potential of the hydrogen electrode? M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1925, **118**, 240—250).—Calculations of the degree of dissociation of molecular hydrogen at 20° and 760 mm. give values ranging from $2{\cdot}3\times10^{-32}$ to $2{\cdot}01\times10^{-34}$. Experiments in which the degree of dissociation of the hydrogen was changed by subjecting it to the action of radium bromide showed no measurable change in the potential of the hydrogen electrode. L. F. GILBERT.

Mixed electrodes of the second type. P. GROSS and O. HALPERN (Z. physikal. Chem., 1925, **118**, 255—256; cf. A., 1925, ii, 405).—A reply to Horovitz's criticism (A., 1925, ii, 673). L. F. GILBERT.

Thermodynamic potential difference at the boundary of two liquid phases. III. S. VOSNESSENSKI and K. ASTACHOV (Z. physikal. Chem., 1925, **118**, 295—300; cf. A., 1925, ii, 673; this vol., 30).—The cells N-calomel electrode|HCl in water|HCl in phenol|N-calomel electrode; Hg|HgCl,N-KCl in water|HCl in water|HCl in phenol|KCl in phenol, HgCl|Hg; N-calomel electrode|H_2SO_4 in water|H_2SO_4 in phenol|N-calomel electrode; and N-calomel electrode|H_3PO_4 in water|H_3PO_4 in phenol|N-calomel electrode were studied. Measurements were also made of the distribution of hydrogen chloride and sulphuric acid between water and phenol. The results are discussed theoretically. L. F. GILBERT.

Potential difference and equilibrium across a semipermeable collodion membrane in the case of sodium chloride and Congo-red. R. AZUMA and N. KAMEYAMA (Phil. Mag., 1925, [vi], **50**, 1264—1276).—The potential differences and ionic equilibria across a collodion membrane separating solutions of sodium chloride and sodium chloride plus Congo-red have been measured. If the Congo-red be assumed to ionise as a uni-univalent electrolyte ($Na_2R=Na^++NaR^-$) in the range of concentrations measured (2·0—6·0 millimol. per litre), and if the ionic-strength principle of G. N. Lewis be assumed to hold good for the mixtures of sodium chloride and Congo-red used (sodium chloride from 6 to 50 millimol. per litre), the experimental results are in general agreement with the thermodynamical requirement of the equality of the activities of sodium chloride on either side of the membrane. The potentials of the following cells were measured: $N.E.|N$-KCl$|B|$C.R.$+NaCl(c_1)||NaCl(c_2)|B|N$-KCl$|N.E.$, and $N.E.|N$-KCl$|B|NaCl(c_1)||NaCl(c_2)|B|N$-KCl$|N.E.$, where $N.E.$ is a normal calomel electrode, B is a gelatin-salt bridge (0·05—0·1N-sodium chloride in 10% gelatin), || is the membrane, and C.R. is Congo-red. It was hoped thus to obtain the potential difference across the membrane, but owing to the difficulty of eliminating liquid–liquid potentials in solutions containing Congo-red, it was not possible to prove that this potential difference agreed with that predicted thermodynamically. A. B. MANNING.

Potential of fluorine from measurements of the decomposition voltages of fused fluorides. O. RUFF and W. BUSCH (Z. Elektrochem., 1925, **31**, 614—615).—Investigations on the electrodeposition of magnesium from fused mixtures of magnesium fluoride with the fluorides of the alkali and alkaline-earth metals (A., 1925, ii, 569) led the authors to arrange these metals in a deposition series. Neumann and Richter (A., 1925, ii, 1164) are wrong in identifying this with a potential series. Neumann and Richter's data are criticised on the grounds that there is not sufficient proof that the measured potentials correspond with decomposition voltages and that the values differ considerably from those of Arndt and Willner (A., 1908, ii, 457) for the fused alkaline-earth chlorides. The identification of the potentials with normal potentials is open to criticism and the linear extrapolation from 800° to the ordinary temperature is thermodynamically unsound. J. S. CARTER.

Electromotive behaviour of cupric oxide. R. E. W. MADDISON (Trans. Faraday Soc., Jan., 1926, advance proof; cf. Allmand, J.C.S., 1910, **97**, 603).—The behaviour of the electrode

$$Pt|CuO,Cu_2O,N\text{-}NaOH$$

has been re-examined at 25°±0·1°. Smooth platinum foil with mercury contacts, and a standard element $Hg|HgO,N$-NaOH as auxiliary electrode, were used. Initially, the electrodes gave a relatively high value, which became more negative in the course of a few weeks, and the final values were not the same in every case. The fall in *P.D.* varied up to 40 millivolts. In the final stages, many electrodes seemed to show a certain periodicity with regard to values of *P.D.* In order to examine the effect of temperature, copper oxide was prepared by heating the carbonate for 30 min. at temperatures from 245° to 760°, in air and in a vacuum. Both the initial and final *P.D.* of the electrode vary with the temperature of preparation of the oxide and the duration of heating. Higher initial values were obtained after vacuum treatment, but the final *P.D.* was scarcely affected. Storage of the oxide during a year produced no change in its electromotive behaviour; the effect of chilling the oxide gave contradictory results. The polymerisation hypothesis of Allmand (*loc. cit.*) was tested, but without definite results.

The appearance and specific gravity of the cupric oxide specimens varied considerably.

L. S. THEOBALD.

Improved salt bridge. H. S. STERN (J. Physical Chem., 1925, **29**, 1583—1584).—A modification of Müller's salt bridge is described, in which the rubber tube is replaced by a stop-cock, one of the paper stoppers being omitted. The advantages of the apparatus and the method of using it are discussed.

L. L. BIRCUMSHAW.

Theory of static and dynamic displacement. D. REICHINSTEIN (Z. Elektrochem., 1925, **31**, 593—613).—Largely retrospective. The author's hypothesis relative to the constant sum of equilibrium concentrations is applied to passivity, to adsorption, and to processes taking place at electrodes. In the last-mentioned case the summation constancy refers, not to concentrations, but to thicknesses of layers.

W. A. CASPARI.

Method of measuring the relative surface charges of electrolytes. A. GARRISON (J. Physical Chem., 1925, **29**, 1517—1522).—The principle of the electric condenser has been used to measure the potentials of the surfaces of a number of electrolytes relative to the surface of water. The apparatus consists essentially of the electrolyte contained in a shallow glass dish, connected to a 0·1*N*-calomel electrode, the mercury of which is connected to a quadrant electrometer and a horizontal metal plate which can be raised or lowered and charged to a definite potential. The surface of the electrolyte and the metal plate form the two plates of a condenser. The metal plate is given different potentials until no charge is induced in the electrometer when the plate is moved. By comparing the potentiometer readings for no deflection of the electrometer needle, using different electrolytes, the surface charges of the electrolytes relative to water may be measured to 0·005 volt. Measurements with a number of salts and acids showed that the first traces of a substance added to water have the largest effect on its surface charge, whilst subsequent additions as a general rule have a small effect, often decreasing the charge and sometimes reversing the sign.

The general relations between concentration and surface charge are similar to the relations between concentration and adsorption. L. L. BIRCUMSHAW.

Overvoltage. F. MEUNIER (J. Chim. phys., 1925, **22**, 595—632).—A review, with bibliography, of the whole subject, in which definitions of overvoltage and methods of measurement are discussed. The influence of time, current density, nature, and concentration of the electrolyte, added substances, and other factors is described in detail.

L. S. THEOBALD.

Electrolysis of acid solution of copper sulphate. L. V. REDMAN (J. Physical Chem., 1925, **29**, 1548—1555).—The relative merits of Siegrist's "kinetic theory" (Z. anorg. Chem., 1901, **26**, 273) and the "mathematical theory" of Rosebrugh and Miller (cf. A., 1911, ii, 181) are discussed, and experiments with solutions of copper sulphate in sulphuric acid are described which were made with the object of deciding between the two theories. If the liberation of hydrogen first occurs when the rate of deposition of copper called for by Faraday's law exceeds the maximum rate at which copper can be chemically reduced from a given solution, then periodic interruptions of the current will be without effect, and a current which when uninterrupted will liberate hydrogen, will also liberate it if periodically interrupted. If, on the other hand, the liberation of hydrogen is due to the exhaustion of copper salt in the solution at the cathode, then with an interrupted current nothing but copper may be deposited, although the same current uninterrupted would bring about liberation of hydrogen. Measurements with interrupted current showed that the limiting current rises continuously with the number of interruptions per second, and when the interruptions are frequent enough, the limiting current is about double that with uninterrupted current. This result disposes of Siegrist's kinetic theory, and shows that the assumptions made by the mathematical theory are applicable to the case in question.

The voltage–time curve during the first few seconds of electrolysis was studied in more detail by means of an oscillograph. L. L. BIRCUMSHAW.

Amphoteric ionisation of polonium and bismuth. F. PANETH (Z. Elektrochem., 1925, **31**, 572—576).—The electrolytic dissolution of thin deposits on gold electrodes in dilute solutions of potassium hydroxide has been examined by the method of Le Blanc (A., 1906, ii, 67). Polonium goes into solution both at the cathode and the anode; the ratio of the rates is 1 : 1·4 in 0·1*N*-electrolyte and 1 : 10 in 0·005*N*-electrolyte. Bismuth (thorium-*C*)

behaves similarly, the ratio of the rates of cathodic to anodic dissolution being 1 : 1·2 and 1 : 3·0 for 0·004*N*- and 0·001*N*-electrolytes, respectively.

W. A. CASPARI.

Catalytic phenomena when zinc is dissolved in acids. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1925, **118**, 415—437).—The addition of salts of iron, silver, antimony, bismuth, copper, arsenic, cobalt, gold, nickel, and the consequent precipitation of these metals accelerates the dissolution of zinc by acids, the effect increasing from left to right of the series. Retardation is produced by salts of thallium, cadmium, tin, and lead. Highly oxygenated compounds, *e.g.*, ammonium molybdate and potassium permanganate, accelerate the process. The velocity of dissolution increases in proportion to the concentration of the catalyst when the concentration is small, but at higher concentrations a limiting value is approached. An induction period is ascribed to the time occupied in the separation of the catalysing metal. Theoretical considerations suggest that the induction period should be inversely proportional to the zinc surface and should diminish as the concentration of catalyst is increased; actual observations are in qualitative agreement with this prediction. The addition of colloidal substances retards the precipitation of the catalyst, thus causing an increase of the induction period and a decrease in the rate of dissolution. L. F. GILBERT.

Overpotential of hydrogen on finely divided metals and its connexion with the catalytic influence of metals on the solution of zinc. M. CENTNERSZWER and M. STRAUMANIS (Z. physikal. Chem., 1925, **118**, 438—446; cf. preceding abstract).—Measurements have been made of the potential difference which must be applied to effect the dissolution of metals nobler than zinc, usually in *N*/2-hydrochloric and sulphuric acids. The overpotential of hydrogen is much greater on smooth crystalline surfaces than on finely divided metallic precipitates; this behaviour is correlated with the observation that large bubbles of hydrogen are evolved from smooth surfaces and much smaller bubbles when the overpotential is low. At a given current density, hydrogen has a definite overpotential which depends on the chemical nature of the metal. The velocity of dissolution of zinc in the presence of other metals cannot yet be interpreted in the light of a quantitative theory. L. F. GILBERT.

Theory of the velocity of chemical reactions. II. N. BJERRUM (Z. physikal. Chem., 1925, **118**, 251—254; cf. A., 1924, ii, 240; 1925, ii, 681).—The author maintains the correctness of his deduction of Brönsted's formula (A., 1922, ii, 699). The hypotheses underlying this deduction are more fully explained. L. F. GILBERT.

Molecular attraction and velocity of reactions. O. MAASS and C. SIVERTZ (J. Amer. Chem. Soc., 1925, **47**, 2883—2891).—The reaction between dry propylene and liquid hydrogen chloride, yielding *iso*propyl chloride, and a chlorohexane as side product, was examined at 0° and 20° by the method described previously (A., 1925, ii, 214). With equimolar quantities, 75% of the acid reacts with all the propylene at 20°; when 2 mols. of acid to 1 mol. of propylene are used, the reaction velocity is increased fourteen-fold. Mercury has no influence on the reaction in the liquid state; 1—2% of water has only a slight effect, but large quantities cause the formation of two distinct liquid phases and the reaction velocity is greatly increased. The rate with hydrogen bromide is 200 times as great as that with hydrogen chloride. The acid acts as a catalyst probably because of regional orientation in the liquid phase caused by its polar nature. No perceptible reaction occurs in the gaseous phase, even at 100°. It is considered that the translational and rotational energies of molecules hinder chemical combination, whereas vibrational energy promotes it; on this basis, the effects of pressure and temperature may be qualitatively explained, increased pressure causing closer proximity of the molecules and so aiding regional orientation and consequently affecting the reaction velocity.

S. K. TWEEDY.

Behaviour of cyanamide in acid and alkaline solution. G. GRUBE and G. MOTZ (Z. physikal. Chem., 1925, **118**, 145—160; cf. A., 1914, i, 152).—The reaction $2CN{\cdot}NH_2 \rightleftharpoons (CN{\cdot}NH_2)_2$ goes practically completely from left to right at low temperatures and in weakly alkaline solutions; rise of temperature and increase in alkalinity shift the equilibrium point towards the left. The hydrolysis of cyanamide to carbamide is a first order reaction when cyanamide and acid concentrations are low, the velocity being approximately proportional to the concentration of the acid when this is less than 0·1*N*. With higher acid and smaller cyanamide concentrations, constants corresponding with a unimolecular reaction are still obtained, but increase more rapidly with rising acid concentration than is demanded by proportionality. The reaction is of a higher order with concentrated cyanamide solutions containing low concentrations of acid; this is due to salt formation between part of the acid and the carbamide. L. F. GILBERT.

Chemical reactions in powdered mixtures of two kinds of crystals. G. TAMMANN [with F. WESTERHOLD, B. GARRE, E. KORDES, and H. KALSING] (Z. anorg. Chem., 1925, **149**, 21—98; cf. Hedvall and Heuberger, A., 1923, ii, 860; 1924, ii, 484).—If in the plane of contact of compressed pastilles of two powdered crystalline substances a layer of a third substance be formed on heating, the rate of isothermal growth of the layer is given by $l = b \log_e t +$ constant, where l is the thickness of the layer after heating for a time t, and b is a constant depending on the temperature. A similar law holds for the rate of reaction in powdered mixtures, which is in every case increased by stirring, so that in many cases the reaction goes almost to completion. The rate of interpenetration of the different crystals is determined more by the movement of the molecules within the crystal, *i.e.*, recrystallisation, than by the movement of the lattices themselves. At the temperature at which this effect becomes appreciable, the powdered mass commences to cake, and it is found empirically that the ratio of this temperature (Abs.) to the temperature (Abs.) at which reaction becomes appreciable

is about 0·57, unless one of the reactants has a transition point above the former temperature. The actual temperature range over which reaction occurs and also the approximate heat of reaction are determined from heating curves. Where neither reactants nor resultants conduct metallically, conductivity measurements will detect traces of liquid formed in the reaction. In many reactions no liquid could be detected in this way, but adsorbed films of liquid may have played a part in bringing about reaction.

Investigation of the reaction between tungsten trioxide or molybdenum trioxide and basic oxides and carbonates has shown that if the radius of the particles of the reactants exceeds the thickness of the layer of resultant formed on their surface, the rate of transformation decreases with increasing size of grain. The temperature at which reaction commences between basic oxides and sulphates and nitrates is much affected by the salt having a transition point. With this proviso, it is the same for a given basic oxide reacting with any sulphate. Experiments on the reaction between carbonates and sulphates have failed to confirm many of Spring's results (cf. A., 1888, 1243), *e.g.*, no reaction occurs between sodium carbonate and barium sulphate below 500° (cf. Balareff, A., 1924, ii, 483). The reaction of silver carbonate with sodium halides has been examined. Silica is more reactive as glass than as quartz. In the reaction between oxides and sulphides, the rate of heating and compression of the reactants have a varying effect on the rate of the reaction and the temperature of its commencement. The reactivity of silicon, titanium, and zirconium dioxides with basic oxides decreases in this order. Experiments have also been made on the reaction between vanadium pentoxide, antimony trioxide, and arsenic trioxide, and a series of basic oxides. Of the latter, calcium and lead oxides were the most reactive, whilst ferric oxide and alumina did not react at all. Some new vapour-pressure determinations have been made for arsenic trioxide, and the influence of foreign substances on the vapour pressure has been examined.

The reaction between powdered mixtures of crystals has been investigated thermodynamically.

R. CUTHILL.

Corrosion of cast iron in sulphuric acid of varying concentration. G. DELBART.—See B., 1926, 56.

Action of silica on electrolytes. A. F. JOSEPH (Nature, 1926, **117**, 17).—Taking into consideration the retention of water by silica prepared as described by Mukherjee (A., 1925, ii, 962), the author still fails to detect the slightest adsorbing power for hydrochloric acid.

A. A. ELDRIDGE.

Action of silica on electrolytes. II. A. F. JOSEPH and H. B. OAKLEY (J.C.S., 1925, **127**, 2813—2818).—The investigation of Joseph and Hancock (J.C.S., 1923, **123**, 2022) has been extended to the action of silica on bases. The titration curve of silica with sodium hydroxide is typical of the combination of a strong base with a weak dibasic acid. In the action of sodium or potassium hydroxide on silica, the main factor determining the extent of reaction is an equilibrium between the solid silica, the layer of solid silicate formed on its surface, and the liquid phase. With bases forming no readily soluble silicate, the main factor is an ordinary solubility relationship between solid and soluble silicates. Addition of a neutral salt increases the amount of solid silicate formed.

R. CUTHILL.

Velocities of chemical reactions in presence of organic colloids. N. A. IZGARYSCHEV and M. I. BOGOMOLOVA (J. Russ. Phys. Chem. Soc., 1925, **56**, 61—66).—The authors have investigated (1) the influence of egg-albumin and globulin on the hydrolysis of ethyl acetate in 0·2*N*-concentration by 0·1*N*-sulphuric acid, (2) that of egg-albumin and edestin on the hydrolysis of this ester by 0·1*N*-hydrochloric acid, and (3) that of gelatin, egg-albumin, and globulin on the inversion of sucrose by 0·1*N*-hydrochloric acid. Increase in the concentration of egg-albumin, globulin, or edestin causes increasing retardation of both reactions, and determination of the hydrogen-ion concentration of the solutions shows that the retardation is the result of the formation of compounds between the acid and the proteins. Increasing proportions of gelatin cause increase to a maximum and then progressive diminution in the velocity of inversion of sucrose; possibly the colloidal–capillary properties of the gelatin molecules play a part in this case.

T. H. POPE.

Kinetics of ester hydrolysis by liver lipase. E. KNAFFL-LENZ (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 3, 1—18).—The rate of hydrolysis of ethyl butyrate by the glycerol extract from liver is proportional to the concentration of enzyme and inversely proportional to that of the substrate. In alkaline solution at constant p_H, the velocity coefficient calculated on the assumption of a unimolecular process increases as the reaction proceeds, but in more acid media (p_H 5·45) remains constant. In alkaline solution, the quotient x/t, where x is the amount of ester hydrolysed in time t, has a constant value. The rate of reaction diminishes continuously if the acid formed as a result of hydrolysis is not neutralised. It is suggested that the ester itself has an arresting action on the activity of lipase, the magnitude of which is proportional to the substrate concentration. Although sodium butyrate has very little influence on the rate of hydrolysis in alkaline solution, in more acid media (p_H 5·7) it has a considerable retarding effect, the rate of reaction decreasing as the reaction proceeds. Under the experimental conditions, a synthesis of ester from alcohol and acid by lipase is not possible. The equilibrium point reached depends on the initial concentration of ester, the enzyme completely losing its activity at p_H 5·2; hence by increasing the substrate concentration the equilibrium is displaced towards the ester side. The rate of hydrolysis of mono- and tri-butyrin even in alkaline media continually diminishes. The optimum for hydrolysis of ethyl butyrate by lipase is in the p_H region 7·8—8·8 and that for butyrin about p_H 9·7.

J. S. CARTER.

Kinetics of lipase reactions. S. ARRHENIUS (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 4, 1—33).—The data of Knaffl-Lenz (A., 1923, i, 621, and preceding abstract) are discussed. Under the conditions where the rate of hydrolysis of ethyl butyrate conforms to the requirements of the unimolecular law (p_H 5·45) there is a progressive destruction of enzyme. In alkaline solution where the rate of destruction of enzyme is extremely slow, the deviations from constancy of the value of x/t are due to errors in the determination of the initial time t_0. The continual decrease in the value of x/t for propyl propionate and butyrin is due to a relatively rapid destruction of lipase. Lipase is held to be a mixture of enzymes which are inactivated at varying rates, the more active varieties being most rapidly destroyed. The inversion of sucrose by invertase (Michaelis and Menten, A., 1913, i, 540) is discussed and the equation put forward by the above authors is shown to hold only over a limited range of sucrose concentration. Constant rate of hydrolysis is probably the normal course of lipase reactions, gradual inactivation of enzyme and the influence of reaction products being responsible for the observed deviations.

J. S. CARTER.

Precipitation of calcium sulphite. R. G. W. FARNELL.—See B., 1926, 72.

Passivity, catalytic action, and other phenomena. A. S. RUSSELL (Nature, 1925, **117**, 47—48).—An extension of the author's view of passivity (A., 1925, ii, 406) and its correlation with the recent work of Taylor, Armstrong and Hilditch, Heyrovský, and Lowry; in chromium, manganese, iron, cobalt, and nickel, the number of electrons in the outermost orbit is "ideally" between 1 and 2, and the state is regarded as passive or active, respectively, when one or two electrons are in the outer orbit. When passive, chromium and iron lie between copper and bismuth in their susceptibility to attack by acids, although when active they are more reactive than cadmium. Probably both iron and chromium when in true solution in a second metal become passive; in solution in each other, the passive "stainless" steel is produced. If metallic atoms may conduct an electron from one reacting molecule to another, adsorption and catalytic action may be related with passivity. Such metals, which may exist normally in either the active or the passive form, are, it is considered, best able to adsorb gases and to act as catalysts when in the passive form, passing in so doing into the active form. The theory explains why the metals which exhibit passivity alone have very low overvoltages, and suggests an explanation of the fact that gases adsorbed on nickel, platinum, palladium, etc. are sometimes in the atomic condition.

A. A. ELDRIDGE.

Case of mutarotation, and its application to the study of the hydrolysis of ethyl oxalate by water and dilute acids. E. DARMOIS (Compt. rend., 1925, **181**, 1137—1138).—Whilst the depression in rotatory power of ammonium dimolybdomalate produced by the addition of oxalic acid is immediate, addition of ethyl oxalate brings about a depression which increases with the time, finally reaching the value obtained directly by addition of oxalic acid. This effect is ascribed to the hydrolysis of the ester, which may thus be followed in neutral and acid solution. The hydrolysis is catalysed by hydrogen ions, and is thus autocatalytic when no foreign acid is present. Ethyl hydrogen oxalate acts very much more rapidly on the complex salt than the neutral ester.

S. I. LEVY.

Autocatalysis with varying catalyst. Biperiodic febrile reactions. A. QUARTAROLI (Gazzetta, 1925, **55**, 619—638).—The results of further experiments (cf. A., 1925, ii, 53) show that, under the influence of hydrogen peroxide in alkaline solution, iron, cobalt, and nickel undergo only an oxidising action, which results in products capable of decomposing hydrogen peroxide. In the case of copper, however, there exists for any definite degree of alkalinity a critical zone of hydrogen peroxide concentration, the action being either oxidising or reducing, according as this concentration is exceeded or the reverse. Hence, if a relatively concentrated hydrogen peroxide solution is used, its decomposition exhibits two successive and distinct febrile periods, the first and weaker one being due to copper peroxides, and the second, violent one to suboxides; these periods are separated by a period of minimum activity due to the normal oxide.

With silver, and especially with gold and mercury, the action of alkaline hydrogen peroxide solution is solely a reducing action which increases in intensity with the alkalinity. An excessive reducing action here leads to formation of the free metal in a pulverulent, non-colloidal form of only slight activity. Thus, when the concentration of the alkali is at least 1·66%, intense but ephemeral febrile periods occur, diminution of the ratio of the concentration of the hydrogen peroxide to that of the alkali below a certain limit resulting in reduction to the free metal and consequently to rapid fall in the velocity of the reaction. If the concentration of the alkali is continuously lowered, the intense febrile period undergoes amplification until it comprises almost the whole reaction. With lead, there arises an analogous phenomenon due, however, to different causes. When the alkalinity and hence the reducing action is low, a highly active lead peroxide is formed, whilst a greater alkalinity and a sufficient concentration of hydrogen peroxide lead to a brief febrile period, followed, when the ratio between hydrogen peroxide and alkali falls below a certain limiting value, by a sudden slackening of the reaction owing to the formation of ordinary lead oxide. The behaviour of thallium in this respect is similar to that of lead.

T. H. POPE.

Relation of homogeneous to catalysed reactions. Catalytic decomposition of hydrogen iodide on the surface of platinum. C. N. HINSHELWOOD and R. E. BURK (J.C.S., 1925, **127**, 2896—2900; cf. Hinshelwood and Prichard, A., 1925, ii, 310, 981, 983).—This reaction occurs in a unimolecular manner in accordance with the equation $HI=H+I$. Hydrogen has a slight retarding influence.

R. CUTHILL.

Catalytic activity of contact substances. III. Catalysis of detonating gas at high temperatures by metals inactive at the ordinary temperature and binary alloys from group 8 of the periodic system. H. REMY and H. GÖNNINGEN (Z. anorg. Chem., 1925, **149**, 283—296; cf. A., 1925, ii, 1176).—The metals of the iron group, ruthenium, and the alloys of these metals with the platinum metals were used as catalysts. The temperature at which catalytic action commences can be accurately determined from the temperature–volume curve. If the catalysts are first charged with hydrogen, the alloys rhodium–iron and iridium–iron are the most active, nickel alloys except that with iron are rather less active, and iron and the alloys osmium–iron and nickel–iron are the least active. Previously charging with oxygen reduces the activities of most of the pure metals, but has a varying effect on the alloys. The effect of the rate of heating and of diluting the detonating gas with hydrogen has been studied. Contact masses prepared by reduction of the oxides are more active than those obtained by reduction of the chlorides. R. CUTHILL.

Mechanism of catalysis by aluminium oxide. M. C. BOSWELL and H. M. DILWORTH (J. Physical Chem., 1925, **29**, 1489—1506; cf. A., 1923, ii, 231; 1925, ii, 215, 805).—It is suggested that the catalytic power of aluminium oxide is due to a very stable surface film of hydrogen ions and hydroxyl ions in a state of great tension, surrounding the particles of oxide. In support of this theory, it is found that aluminium oxide catalyses the following reactions, involving, simultaneously, hydrogen and oxygen: (1) the dehydration of ethyl alcohol to ethylene; (2) the combination of acetylene and water to form acetaldehyde; (3) the combination of ethylene and water to form ethyl alcohol; (4) the union of hydrogen and oxygen to form water. The dehydrogenation of ethyl alcohol at 350° has been studied quantitatively. In addition to the formation of ethylene, the following reactions occur: (1) $2C_2H_4 \longrightarrow C_2H_6+C_2H_2$ and (2) $C_2H_4 \longrightarrow 2C+2H_2$. The acetylene from (1) is polymerised and adsorbed by the aluminium oxide along with the carbon from (2). The combination of free hydrogen and ethylene to form ethane does not occur, since the dissociation is a much faster reaction. Further support for the theory is obtained by measurements of the adsorption of ethylene and acetylene on aluminium oxide for several partial pressures, and of the variation of adsorption of ethylene on aluminium oxide with variation of temperature and variation of water content. A mechanism is suggested for the adsorption of electrolytes from aqueous solution on aluminium oxide. L. L. BIRCUMSHAW.

Catalytic hydrogenation of organic substances. O. SCHMIDT (Z. physikal. Chem., 1925, **118**, 193—239).—Elements suitable for hydrogenation catalysis have small ionic radii and a large number of electrons in the outer shell; they take up hydrogen, which is converted into an active dissociated form. It is known that electrically neutral atomic hydrogen is capable, in many cases, of effecting reduction, but the dissociated hydrogen here formed probably consists of ions. Quantitative theoretical considerations show that the ease of ionisation depends on the effective sphere of action of the metallic ions formed in the solid catalyst, *i.e.*, with constant valency those ions with the smallest radii are the most effective catalysts. Rise of temperature increases catalytic activity. These conclusions are borne out by a study of the reduction of ethylene to ethane using finely divided iron, cobalt, nickel, copper, silver, gold, zinc, and lead as catalysts. It is considered that the catalytic hydrogenation of carbon compounds is an ionic reaction (cf. Thomas, A., 1923, ii, 64). Measurements were made of the surfaces of various nickel catalysts. Methods of determining the hydrogen taken up by catalysts are described: systematic measurements were made in the case of nickel. The hydrogen taken up by finely divided nickel at constant temperature and pressure is proportional to the surface, but is affected by the presence of impurities. At low temperatures, part of the hydrogen is present in the form of loose compounds with the catalyst. The reactivity is proportional to the surface and sorbed hydrogen, but is modified by the solubility of the other reactants in the catalyst. L. F. GILBERT.

Formation and growth of silver nuclei in the decomposition of silver oxalate. J. Y. MACDONALD and C. N. HINSHELWOOD (J.C.S., 1925, **127**, 2764—2771).—A new method of following chemical changes in which gas is evolved has been applied to the study of the thermal decomposition of silver oxalate, which is found to occur in accordance with the equation $Ag_2C_2O_4=2Ag+2CO_2$. The reaction appears to be autocatalytic, this being shown to be due to the formation of silver nuclei on the surface of the oxalate crystals at a rate which governs the rate of reaction, so that the simple equation for homogeneous autocatalysis does not apply. Oxygen retards the reaction. R. CUTHILL.

Catalytic oxidation of ammonia. W. J. MALIAREVSKI and N. A. MALIAREVSKAJA.—See B., 1926, 50.

[Catalytic] oxidation of ammonia. C. ELLIS.—See B., 1926, 51.

Catalytic effect of lead and manganese on the drying of China-wood (tung) oil. G. E. LUDWIG.—See B., 1926, 67.

Toxicity of thiophen for nickel catalyst: action of the copper catalyst. B. KUBOTA and K. YOSHIKAWA (Japanese J. Chem., 1925, **2**, 45—62).—See A., 1925, ii, 805.

Composition of reduced nickel as catalyst. B. KUBOTA and K. YOSHIKAWA (Japanese J. Chem., 1925, **2**, 99—107).—See A., 1925, ii, 1174.

Production of sulphuric acid by electrolysis. R. SAXON (Chem. News, 1925, 385).—Electrolysis of a solution of an equimolar mixture of copper sulphate and ammonium aluminium sulphate yields a solution of sulphuric acid which may reach a concentration of 17% in 7 hrs. Simultaneously copper is deposited on the cathode and aluminium hydroxide in the catholyte. A. R. POWELL.

Electrometric study of the reactions between alkalis and silver nitrate solutions. H. T. S. Britton (J.C.S., 1925, **127**, 2956—2970).—The precipitation of silver oxide by sodium hydroxide has been followed electrometrically, and the values of the solubility product $[Ag^{\cdot}][OH']$ have been calculated. From the results, the *E.M.F.* of the cell $Ag|Ag_2O,NaOH|H_2$ and of the oxygen–hydrogen cell have been deduced. The average value of the former lies between the extreme values obtained by Rørdam (A., 1922, i, 338), thus making it appear likely that the variability of the silver electrode in presence of silver oxide in alkaline solutions is due to reduction, rather than to the existence of two forms of the oxide (cf. Luther and Pokorný, A., 1908, ii, 277). Lewis' value for the *E.M.F.* of the oxygen–hydrogen cell (A., 1906, ii, 262) seems to be too low, because a low value was taken for $[Ag^{\cdot}][OH']$.

The titration of silver nitrate with ammonia has been examined by means of both the silver and oxygen electrodes. Precipitation is incomplete even when the amount of ammonia required by the equation $AgNO_3+NH_4OH=AgOH+NH_4NO_3$ has been added, apparently owing to complex formation: $AgNO_3+2NH_3 \rightleftharpoons Ag(NH_3)_2NO_3$ proceeding at the same time as this reaction, and to the dissolution of some of the silver oxide in the ammonium nitrate formed. Calculation of the equilibrium constant for complex formation, assuming the above equation, leads to a fairly constant value, which agrees with the value deduced from the *E.M.F.* data of Bruni and Levi (A., 1917, ii, 470). Very nearly the same figure is obtained from the measurements of these authors for ammoniacal solutions of silver nitrite, indicating that the dissociation constant of the diammino-silver complex is independent of the anion. R. Cuthill.

Electrolytic deposition of nickel. R. Saxon (Chem. News, 1926, **132**, 4).—Electrolysis of a mixture of equal volumes of saturated solutions of nickel and potassium sulphates yields first a precipitate of nickel hydroxide, then a deposit of metallic nickel on the cathode, whilst sulphuric acid concentrates round the anode. The yield of nickel is increased if a sheet of zinc is placed between the electrodes, the zinc dissolving with evolution of hydrogen.

A. R. Powell.

Photochemical kinetics. R. Wegscheider (Rec. trav. chim., 1925, **44**, 1118—1120).—Polemical against Plotnikov (cf. A., 1925, ii, 838; Langedijk, *ibid.*, 1116). L. L. Bircumshaw.

Reactions caused by light-excited bromine. J. Eggert [with F. Wachholtz and R. Schmidt] (Physikal. Z., 1925, **26**, 865—868).—Ethyl maleate is converted into the corresponding fumarate by illumination of the liquid (or a solution in carbon tetrachloride) provided bromine is present. The reaction is exothermic and the bromine acts as a sensitiser. A second photochemical reaction also occurs simultaneously in the bromination of ethyl maleate to ethyl dibromosuccinate. The first change has been followed thermally and the second by titration. The absorption of a single quantum $h\nu$ at 436 μμ by a 0·1*N*-solution of bromine in liquid ethyl maleate results in the stereochemical change of 295 mols. and the addition of 8 mols. of bromine. These values are independent within fairly wide limits of (*a*) light intensity, (*b*) dilution up to 1 : 70 with carbon tetrachloride. The quantum equivalents vary with temperature; for the first reaction, the efficiency is doubled in going from 19·5° to 23°, and for the second from 17° to 25°. Between the limits 0·03—0·3*N*-solutions of bromine, the quantum efficiency of the stereochemical change does not vary, whilst that of the additive process varies directly as the halogen concentration. When mixtures of ethyl maleate and fumarate undergo similar treatment, the quantum equivalent of the first change depends on the ratio of the two esters, whilst that of the second reaction is unaltered. Both changes depend on the size of the quantum employed, the quantum efficiency at 436 μμ being about twice that observed at 546 μμ.

Excited bromine molecules appear to have a relatively long life-period. Collisions of activated bromine molecules with ethyl maleate molecules are inelastic; collisions with inactive bromine molecules or carbon tetrachloride molecules are elastic. After collision, the ester molecules are activated. Those which collide during the activation period with inactive bromine molecules react by addition, those which collide only with the solvent suffer stereoisomeric change. These views are supported by the fact that ethyl fumarate brominates with the same quantum efficiency as ethyl maleate. The interpretation involves the assumptions of a life period of 10^{-5}—10^{-6} sec. for activated bromine, and of a capacity to hand on its activation energy in small amounts to 300 mols.

The first assumption is supported by the demonstration that when bromine is activated in the vapour phase it retains its energy long enough to hand it on after penetrating the liquid surface. For the second assumption, no evidence is adduced.

R. A. Morton.

Selective action of polarised light on starch grains. (Lord) Rayleigh (Nature, 1926, **117**, 15).—*A priori* reasoning indicates that polarisation of light should diminish chemical action in the case of starch grains, if these are oriented at random (cf. this vol., 34). A. A. Eldridge.

[Selective action of polarised light on starch grains]. W. N. Jones (Nature, 1926, **117**, 15—16; cf. preceding abstract).—Polemical.

A. A. Eldridge.

Measurement of radiation intensities by photographic methods. F. C. Toy (Nature, 1926, **117**, 83—84).—In the method preferred, the intensity of the stronger beam is reduced by means of a "neutral" absorbing screen, so that the intensities are equal; the function of the plate is then solely to detect equal intensities of the same kind of radiation, and the accuracy is dependent only on the constancy of emulsion characteristics over a small portion of any single plate. A. A. Eldridge.

Ozone formation through electronic impact. F. KRÜGER and O. UTESCH (Ann. Physik, 1925, [iv], **78**, 113—156).—An extensive investigation has been made of the conditions and extent of ozone formation by the action of cathode rays on oxygen and air. The cathode rays emerged from a hot cathode tube through a window of thin aluminium foil into a small vessel, which was fitted with charged plates in order that the ionisation current, due to the rays, might be measured. The effects of varying the current strength in the cathode tube, the primary voltage, the thickness of the aluminium foil, and the rate of passage of the oxygen or air current were investigated. An estimation and comparison of the number of ions and of ozone molecules formed per unit of time showed that the latter were from 20 to 40 times as numerous as the former. Although the ratio of these quantities was not constant for different experimental conditions, they are to be regarded as approximately proportional, the discrepancies being attributed to fluctuations in the strength of the cathode ray stream. The equivalence found by Moeller (Diss., Danzig, 1912) between the number of ions formed in nitrogen and the number of ozone molecules formed in oxygen by cathode rays of equal intensity is thus not confirmed. A comparison of the action of cathode rays on air, oxygen, and nitrogen indicated that the secondary radiation produced is, in accordance with Lenard's rule, proportional to their densities, and that it is therefore unnecessary to postulate any influence of a chemical reaction on the production of the secondary radiation. As a result of these experiments, it is concluded that the formation of ozone is unconnected with the ionisation process, but is the result of collision of normal oxygen molecules with oxygen molecules excited by electronic impacts. Such a mechanism is to be anticipated from the photochemical formation of ozone. The yield of ozone was determined under various conditions, the maximum value being 150 g. per amp.-hr. expended in the cathode tube. This is very much smaller than the yield from technical ozonisers. The low yield is due to the absorption of energy in the passage of the cathode rays through the foil window, the energy of the emergent rays being computed as 3—5% of the electrical energy expended in the tube. The distribution of the cathode-ray energy in the process of ozone formation was determined by measuring the secondary ionisation, the yield of ozone, and the increase of pressure in the irradiated gas. From the latter, the heat generated in the process was calculated. The results show that of the total energy of the cathode rays incident on the gas, 2—4% is used in the ionisation process, 5—11% for ozonisation, and the residue dissipated as heat.

F. G. TRYHORN.

Action of silica on barium and magnesium sulphates. G. MARCHAL.—See B., 1926, 51.

Decomposition of the alkaline-earth phosphates by alkali carbonates. D. RAQUET (Bull. Soc. chim., 1925, [iv], **37**, 1548—1549; cf. Colani, A., 1925, ii, 1001).—The decomposition of calcium, barium, or strontium phosphate by potassium carbonate solution (incomplete in the first case) is impeded by the presence of sodium hydroxide; with sodium carbonate, it is incomplete and also so impeded. The decomposition of magnesium ammonium phosphate is accelerated by sodium hydroxide.

C. H. D. CLARK.

Reduction of heavy metal sulphides by barium oxide. W. BILTZ and E. VON MÜHLENDAHL (Z. anorg. Chem., 1925, **150**, 1—9).—When heated with barium oxide, cupric sulphide is partly reduced to the metal, according to the equations: $CuS+BaO=CuO+BaS$, $4CuO+BaS=4Cu+BaSO_4$. Lead sulphide is similarly reduced, but neither cupric nor lead sulphide is reduced by calcium oxide, as these reactions would be endothermic. The reaction between cupric sulphide and barium oxide was followed thermally, and the product was examined chemically and microscopically. Reaction begins between 200° and 400° and the largest yield of metal is obtained when double the theoretical amount of barium oxide is taken; after 1 hr. at 1150°, the reaction had gone completely to the first stage and 72% to the second, and varying the conditions did not further increase the yield. The reaction with lead sulphide also begins between 200° and 400°, but some sulphide remains unreduced at 1150°, the highest temperature used.

A. GEAKE.

Fluoro-salts of aluminium and of tervalent iron and chromium. R. WEINLAND, I. LANG, and H. FIKENTSCHER (Z. anorg. Chem., 1925, **150**, 47—67).—Except in the case of prosopite, aluminium has the co-ordination number 6 in all its known fluoro-salts, both natural and artificial; these compounds contain either a hexafluoro- or an aquopentafluoro-anion. Prosopite has the formula $[Al(F,OH)_4]_2Ca$, and in it aluminium has the co-ordination number 4. The following organic *fluoroaluminates* have been prepared and analysed: $AlF_3,N_2H_4,2HF$; $AlF_3,2C_5H_5N,2HF,H_2O$; $AlF_3,C_2H_4(NH_2)_2,2HF,H_2O$; AlF_3,CH_5N_3,HF,H_2O; $AlF_3,2CH_5N_3,2HF$; $AlF_3,3CH_5N_3,3HF$. Only one of these contains the hexafluoro-anion and two the aquofluoro-anion; the other three can be represented with a co-ordination number of 6 if the nucleus is doubled, *e.g.*, $[F_4Al<^{F}_{F}>AlF_4](N_2H_4)_2$. A *potassium aluminium fluoride*, $AlF_3,2KF,2H_2O$, obtained by the addition of acid potassium fluoride to aluminium chloride, is similarly formulated. Tervalent iron also forms hexafluoro- and aquopentafluoro-anions with the co-ordination number 6; the following organic *fluoro*-compounds were prepared: $[Fe,F_5,H_2O]H_2,2CH_5N_3$; $[Fe,F_5,H_2O]H_2,C_2H_4(NH_2)_2$; $[Fe,F_5,H_2O]H_2,2C_5H_5N,2H_2O$; $[FeF_4]H,C_5H_5N,H_2O$. In the last compound, it is probable that the water is not in the anion and that the co-ordination number is 4; this is also the case for the *alkali* salts, $[FeF_4]K$ and $[FeF_4]NH_4$, which contain no water. The heavy metals, on the other hand, form *salts* in which the iron has the co-ordination number 6: $[Fe,F_5,H_2O]Ag_2,2H_2O$; $[Fe,F_5,H_2O]Tl_2,2H_2O$; $[Fe,F_5,H_2O][Cd(H_2O)_6]$; $[FeF_6]_2[Cu(H_2O)_6]_3$. No fluoro-salts of chromium could be obtained having a co-ordination number other than 6; the only organic salt that could be

prepared was the *guanidine* salt, $[CrF_6]H_3,3CH_5N_3$. The compound formulated $2FeF_3,FeF_2,10H_2O$ (A., 1907, ii, 265) contains no ferrous iron and no fluorine ions. Its conductivity is low and it is therefore formulated as the non-electrolyte

$$[Fe,F_3,(H_2O)_3],1{\cdot}5H_2O.$$

A. GEAKE.

Double sulphates of the rare-earth and alkali metals. III. Double sulphates of lanthanum and sodium. F. ZAMBONINI and G. CAROBBI (Atti R. Accad. Lincei, 1925, [vi], **2**, 300—302; cf. A., 1925, ii, 222, 579).—A determination of a portion of the 25° isotherm of the system $La_2(SO_4)_3$–Na_2SO_4–H_2O confirms the existence of the compound $La_2(SO_4)_3,Na_2SO_4,2H_2O$. It is obtained as minute white crystals by the slow evaporation of very dilute solutions of the two simple sulphates, and is stable in contact with solutions containing from 0·13% to 16·28% of sodium sulphate, and up to 0·19% of lanthanum sulphate. The water of crystallisation is not lost below 150°. F. G. TRYHORN.

Black oxides of praseodymium. W. PRANDTL and K. HUTTNER (Z. anorg. Chem., 1925, **149**, 235—262).—The formula of the brownish-black powder obtained by heating praseodymium hydroxide or its salts with volatile acids in air is Pr_6O_{11}, the conflicting results of other authors being due to the presence of impurities. This oxide does not dissociate below 900°, forms no definite hydrates with water, and has d^{20} 6·61. It is to be regarded as a salt-like compound of Pr_2O_3 with some higher oxide.

The substances claimed by Meyer (A., 1904, ii, 734) and Brauner (Proc. C. S., 1898, 70) to be PrO_2 appear to be hydrated Pr_6O_{11}. The oxide PrO_2 has, however, been prepared by oxidation of Pr_2O_3, or from Pr_6O_{11} by fusion with sodium chlorate or treatment with acetic acid. Admixture of various metallic oxides with the oxide Pr_2O_3 prevents its complete oxidation (cf. Meyer and Koss, A., 1903, ii, 45), some lanthanum praseodymate being formed in the presence of lanthanum oxide (cf. Marc, A., 1902, ii, 503). The oxide PrO_2 is a black powder, d^{20} 6·82, which above 350° loses oxygen and forms Pr_6O_{11}, It has neither acidic nor basic properties. Both oxides have similar chemical properties, which are those of higher oxides rather than of peroxides. No corresponding salts have been obtained.

R. CUTHILL.

Colour imparted to glass by fluorine, sulphur, and selenium compounds. K. FUWA.—See B., 1926, 13, 14.

Colouring glass with phosphates, arsenious oxide, and carbon. K. FUWA.—See B., 1926, 53, 54.

Separation of hafnium and zirconium. N. V. PHILIPS GLOEILAMPENFABR.—See B., 1926, 12.

Lead dihydride and lead tetrahydride. E. J. WEEKS (J.C.S., 1925, **127**, 2845—2846).—Lead dihydride, Pb_2H_2, is formed as a grey deposit when aluminium foil is added to a solution of an alkali plumbite. It appears to form the tetrahydride when heated in hydrogen. R. CUTHILL.

Reaction between gaseous ammonia and the chlorides of phosphorus.—H. PERPÉROT (Bull. Soc. chim., 1925, [iv], **37**, 1540—1548; cf. A., 1925, ii, 1186).—Further investigation of the reaction between ammonia and the chlorides of phosphorus in carbon tetrachloride solution suggests that the primary products of reaction are the compounds $PCl_5,10NH_3$, $PCl_3,6NH_3$, and $POCl_3,6NH_3$. The decomposition curve of the compound $PCl_5,10NH_3$ with time shows a sharp break at about 310°. Since ammonium chloride mixed with sand shows a similar break at about the same temperature, it is concluded that the substance is partly a mixture of the amine $P(NH_2)_5$ and ammonium chloride, this result being confirmed by the action of liquid ammonia. The intermediate tervalent compound, $PCl_3,6NH_3$, is found to be somewhat more stable than the quinquevalent compounds, and has a break in the time–decomposition curve at about 200°.

C. H. D. CLARK.

Pyrophoric bismuth. L. VANINO and A. MENZEL (Z. anorg. Chem., 1925, **149**, 18—20; cf. Thibault, A., 1904, i, 247).—A co-precipitated mixture of bismuth and aluminium hydroxides is reduced by hydrogen at 170—210°. The product is spontaneously inflammable at the ordinary temperature, its activity being dependent on the presence of the aluminium hydroxide and to some extent on its amount. R. CUTHILL.

Reaction between bismuth trisulphide and hydrochloric acid. S. RAMACHANDRAN (Chem. News, 1925, **131**, 386).—Bismuth trisulphide is slightly soluble even in 1 : 16-hydrochloric acid at 29°; its solubility increases rapidly with the temperature, and hydrogen sulphide begins to be evolved at 70° (cf. A., 1925, ii, 1208). A. R. POWELL.

Tellurium nitride. W. STRECKER and W. EBERT (Ber., 1925, **58**, [*B*], 2527—2539; cf. Strecker and Claus, A., 1923, **11**, 152).—The action of ammonia, dried over potassium hydroxide, on a solution of tellurium tetrachloride or tetrabromide in ether gives mixtures of tellurium dioxide or trioxide with ammonium salt. An explosive product is not obtained when the ammonia is condensed over sodium and the gas from the evaporating liquid is led into the ethereal solution. If dry ammonia is passed over tellurium tetrachloride at 0°, the *compound* (?) $TeCl_4,6NH_3$ is obtained, which becomes white and absorbs moisture when exposed to air. If the halide is cooled to −80° and ammonia condensed thereon, a mixture is produced which detonates when heated; it cannot, however, be freed from admixed ammonium salts by treatment with water, which causes it to become white and lose its explosive properties. The action of ammonia on tellurium halides is therefore investigated in an apparatus which allows the dry halide to be treated with liquid ammonia with exclusion of water and the pasty product of the reaction to be washed with liquid ammonia and thus to achieve as complete as possible an extraction of the ammonium salts produced in the reaction. A highly explosive compound is thereby obtained which contains tellurium, halogen, and nitrogen. It

appears unlikely that this is the nitride, TeN, described by Metzner and by Damiens (A., 1923, ii, 316) contaminated with ammonium salts. Action probably occurs in accordance with the scheme $3TeBr_4+16NH_3=Te_3N_4+12NH_4Br$. This conception is in harmony with the quantitative observation that the explosive compound and ammonium salt are the sole products of the change. The reaction is therefore to be regarded as ammonolysis in accordance with the equations $3TeBr_4+4NH_3=Te_3Br_9N+3NH_4Br$, $3TeBr_4+8NH_3=Te_3Br_6N_2+6NH_4Br$, $TeBr_4+4NH_3=TeBrN+3NH_4Br$, thus explaining the presence of halogen in the product. The primary action consists in the addition of ammonia to the tetrahalide, and this is followed by gradual replacement of the halogen atom by the amino-group and then by loss of ammonia into imino-compounds and ultimately nitride and ammine salts which do not contain eliminable ammonia.

H. WREN.

[Hypochlorous acid and the alkali perchlorides.] O. VON DEINES (Z. anorg. Chem., 1925, **149**, 99—100).—The conclusions of Dietzel and Schlemmer (A., 1925, ii, 892) on the course of the reaction between chlorine and sodium hydroxide are shown to be vitiated by numerical errors. The reaction in the cold occurs according to the equation: $2NaOH+Cl_2=NaOCl+NaCl+H_2O$. R. CUTHILL.

Potentiometric indication in the action of halogens on ferrocyanides. C. DEL FRESNO (Z. Elektrochem., 1925, **31**, 617—621).—See A., 1925, ii, 1192.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. J. HEYROVSKÝ (Nature, 1926, **117**, 16).—A reply to Campbell's criticisms (this vol., 37) and a more detailed explanation of the nature of the author's polarographic electro-analytical method with the dropping mercury cathode. Besides showing good agreement with the deposition potentials at the dropping mercury cathode expected for the triad 25, 43, and 75, the "75" hump in the curve, when specially prominent, is accompanied by appearance of the *L*-lines of the element 75 in the *X*-ray spectra. A. A. ELDRIDGE.

Occurrence of dvi-manganese (atomic number 75) in manganese salts. G. DRUCE (Nature, 1926, **117**, 16; cf. Campbell, this vol., 37, and preceding abstract).—Explanatory. A. A. ELDRIDGE.

Reducing action of ferrous hydroxide. S. MIYAMOTO (Sci. Papers Inst. Phys. Chem. Res., 1922, **1**, 31—56).—See A., 1922, ii, 648; 1923, ii, 76. B. FULLMAN.

Ruthenium. VIII. Isomeric chlorides. J. L. HOWE and L. P. HAYNES (J. Amer. Chem. Soc., 1925, **47**, 2920—2925).—α-Potassium pentachlororuthenite crystallises from hot acid solution largely as anhydrous, dark brownish-red, tetragonal octahedra; from cold solutions reddish-buff, feather-like crystals, apparently the hydrated form, are obtained. Dechlorination of potassium hexachlororuthenate yields a pentachlororuthenite having properties similar to those of dehydrated β-salt, which is Aoyama's γ-salt, since recrystallisation of both the latter and dehydrated β-salt from acidulated water yields β-salt (cf. Aoyama, A., 1924, ii, 771; Howe, A., 1902, ii, 86). Dehydrated β-salt only hydrates in solution after some hours; when first made, the solution becomes blue with sodium hydroxide and gives a black precipitate with bromine. Briggs' salt, K_2RuCl_5,K_2RuCl_5OH, is considered to be a mixture of anhydrous and monohydrated ordinary α-salts (cf. A., 1925, ii, 703). Hexachlororuthenates are precipitated from concentrated, strongly acid solutions of β-salts by leading in chlorine; concentration of the mother-liquor after precipitation yields chiefly α-pentachlororuthenite. Evaporation of solutions of hexa-salts seems to yield α-penta-salts. α-Salts are converted into β-salts by the action of reducing agents (*e.g.*, stannous chloride) and organic compounds (*e.g.*, phenol, but not acetic acid).

S. K. TWEEDY.

Ruthenium. IX. Solubility of ruthenium in hypochlorite solutions; attempted determination of the metal. J. L. HOWE and F. N. MERCER (J. Amer. Chem. Soc., 1925, **47**, 2926—2932).—Finely divided ruthenium is readily soluble in concentrated alkaline solutions of hypochlorites, sodium hypochlorite being more effective than the potassium salt. Ruthenium may be separated from the other platinum metals, except osmium, by this means. The hypochlorite oxidises the ruthenium to tetroxide; free alkali hydroxide converts the latter into ruthenate. Even in the absence of alkali much ruthenium may be retained as ruthenate. Ruthenium may be completely distilled as tetroxide from a potassium ruthenate solution after treatment with chlorine; no evidence for the intermediate formation of perruthenate during the latter process was obtained. No satisfactory way of quantitatively precipitating ruthenium from the tetroxide in a weighable form was discovered. S. K. TWEEDY.

Rhodium chlorides and oxides. L. WÖHLER and W. MÜLLER (Z. anorg. Chem., 1925, **149**, 125—138).—Rhodium reacts with chlorine only between 300° and 968°, the product being the trichloride below 948°, and a mixture of two new reddish-brown *chlorides*, RhCl and $RhCl_2$, at 948—968°. The dissociation tensions of all three chlorides, measured at a series of temperatures, agree with a formula of the type proposed by Wöhler and Günther (A., 1923, ii, 471). Attempts to prepare a tetrachloride have been unsuccessful. By dissociation of rhodium trioxide, prepared by heating the trichloride to above 750° in oxygen, two new *oxides*, RhO and Rh_2O, have been obtained. These are insoluble in acids, but readily reduced by hydrogen. The dissociation tensions of all the oxides have been determined at various temperatures. Rhodium is not volatile in air even at 1150°. R. CUTHILL.

Compounds of metallic salts and carbon monoxide. XII. Behaviour of carbon monoxide towards salts of palladium and platinum and separation of palladium and platinum depending thereon. W. MANCHOT (Ber., 1925, **58**, [*B*], 2518—2521).—Re-examination of the action of carbon

monoxide on platinum chloride has confirmed the existence of the three compounds, $PtCl_2,CO$, $PtCl_2,2CO$, and $2PtCl_2,3CO$, described by Schützenberger. The analogous compounds of palladium, described by Fink, do not, however, exist; the compounds actually isolated were the platinum salts due to the presence of platinum in the palladium employed. Dry palladous chloride does not give a sublimate when heated in carbon monoxide at any temperature below red heat, whereas at a higher temperature palladous chloride sublimes; this behaviour is also exhibited when chlorine is substituted for carbon monoxide. Moist palladous chloride is reduced by carbon monoxide at about 250° and reduction becomes complete at a higher temperature. Small quantities of platinum in palladium may be determined by heating the dry mixture of the chlorides in a dry current of carbon monoxide at 250° until increase in the amount of sublimate is not observed; platinum, ruthenium, rhodium, and osmium sublime as their compounds with carbon monoxide. The sublimate is removed from the tube by water and aqua regia; the solution is evaporated to dryness and the residue ignited, leaving the platinum present in the palladium.

Palladium appears to occupy a unique position in the platinum family, since it yields no compound with carbon monoxide; the reducibility of palladous chloride in aqueous solution by carbon monoxide points to the existence of such a compound, but the conditions necessary for the production of the primary additive compound appear to lie very close to those of its decomposition. In the absence of water, palladous chloride is not reduced by carbon monoxide and addition of carbon monoxide does not occur.

Reaction of carbon monoxide with platinous chloride commences at about 120°; at 150°, the compound, $PtCl_2,2CO$, is directly obtained; this substance was isolated by Schützenberger from the product of the action at 250°. H. WREN.

Simple preparation of fluorine. P. LEBEAU and A. DAMIENS (Compt. rend., 1925, **181**, 917—919).—Fluorine is prepared by the electrolysis of acid fluorides of the alkali metals which are richer in hydrogen fluoride than the compounds MF,HF (*e.g.*, KF,3HF). These compounds are readily made and fuse below 150°. Carbon-free iron or nickel anodes are used, the nickel or copper containing-vessel acting as cathode (cf. A., 1924, ii, 847).
S. K. TWEEDY.

Ashing of small amounts of material. O. DAFERT (Biochem. Z., 1925, **164**, 444—445).—A method of ashing small quantities of substance and a new form of fume-trap for Kjeldahl determinations are described. E. C. SMITH.

Determining hydrogen and methane in gas mixtures. W. STEUER.—See B., 1926, 3.

Determination of hydrogen-ion concentration in liquids and suspensions. Application of Biilmann's quinhydrone method. C. W. G. HETTERSCHIJ and J. HUDIG (Chem. Weekblad, 1926, **23**, 2—3).—A method and apparatus for carrying out large numbers of determinations, by unskilled persons, very rapidly and with great accuracy, are described. The quinhydrone electrode gives more rapid and accurate results in determinations of hydrogen-ion concentration in soils than any alternative method, and is very cheap. Compensating resistances are employed to obviate the necessity for much calculation in obtaining results.
S. I. LEVY.

Reaction of neutral and distilled water. I. M. KOLTHOFF (Chem. Weekblad, 1925, **22**, 590—594).—The employment of methyl-red may involve great errors, which may amount with neutral water to as much as 100 times the real hydrogen-ion concentration. For distilled water, the sodium salt of methyl-red is recommended; this gives a value of p_H 5·9—6·0 for distilled water in equilibrium with air. The sodium salt of chlorophenol-red is also suitable, but the most accurate indicator is 2 : 4 : 6 : 2′ : 4′ : 2″ : 4″-heptamethoxytriphenylcarbinol. After rapid boiling for 1 min. and subsequent cooling, the p_H for distilled water, using the sodium salt of methyl-red, is found to be 6·7—6·6, but falls very rapidly after shaking with air; this indicator is proposed for the determination of carbon dioxide in air. The sources of error in the determination of the reaction of a very dilute solution of a weak acid are considered theoretically. S. I. LEVY.

Reliability of vacuum analysis for solid metallic hydrides. E. J. WEEKS (Chem. News, 1926, **132**, 17—18).—A mathematical paper based on results obtained in the analysis of metallic hydrides by heating them in a vacuum, showing that more accurate results are obtained from weighing the residual metal than from measuring the volume of hydrogen evolved. A. R. POWELL.

Determination of hydrochloric acid by means of potassium iodate, as compared with the results obtained with sodium carbonate and borax. I. M. KOLTHOFF (Pharm. Weekblad, 1925, **63**, 37—48).—A solution of potassium iodate, potassium iodide, and a slight excess of sodium thiosulphate can be employed for the titration of hydrochloric acid. The mixture must be shaken continuously to avoid decomposition of the thiosulphate. With dimethyl-yellow as indicator, a correction must be made for the slight excess of acid necessary to effect the colour change; with methyl-red, no correction is necessary, but the titration is slower, since time is required for the colour to become stable. The titration is extremely accurate. Anhydrous sodium carbonate is less suitable, on account of its hygroscopic nature and the necessity of boiling off carbon dioxide. Borax is very suitable; the results indicate that the accepted atomic weight of boron, 10·82, is correct. The decahydrate is easily obtained pure by recrystallisation and drying over fused sodium bromide. S. I. LEVY.

Micro-titration of iodide. I. M. KOLTHOFF (Mikrochem., 1925, **3**, 75—79).—The method is based on the reaction $IO_3' + 2I' + 3HCN + 3H^{\cdot} \rightleftharpoons 3ICN + 3H_2O$. Ten c.c. of the iodide solution are mixed with 80 c.c. of water, 20 c.c. of 25% hydrochloric acid, and 5 c.c. of a 10% solution of potassium

cyanide in a stoppered conical flask. After addition of a few c.c. of carbon tetrachloride or chloroform the solution is titrated with potassium iodate until the violet colour in the lower layer disappears. Starch is not a suitable indicator, owing to the slowness with which the blue colour disappears towards the end of the titration. For very small amounts of iodide a 5-c.c. micro-burette graduated in 0·01 c.c. is used with 0·00016*M*-potassium iodate solution. Even very large amounts of bromide do not interfere. In the presence of other substances which are oxidised by iodate, the solution is acidified with acetic or succinic acid and boiled with hypochlorite to convert the iodide into iodate. The converse of the above method is then used for the determination of the iodate. A. R. Powell.

Micro-determination of the oxygen content of water. C. Risch (Biochem. Z., 1925, **161**, 465—467).—A method is described exactly similar in principle to that of Winkler, the apparatus being adapted so that only small quantities of the water are required. H. I. Coombs.

Determination of molecular oxygen in aqueous solution in the presence of nitrous acid. H. Noll (Biochem. Z., 1925, **165**, 497—499).—A reply to Alsterberg's criticisms (cf. A., 1925, ii, 1198). P. W. Clutterbuck.

Measurement of the amount of ozone in the earth's atmosphere. G. M. B. Dobson and D. N. Harrison (Proc. Physical Soc., 1925, **38**, 74—76).—The quantity of ozone present in the atmosphere was determined by measuring the intensity of a number of Fraunhofer transmission lines in the region of the ultra-violet absorption band of ozone (3000—3300 Å.). Observations made over a period of 4 months show that the amount of ozone is low during an anticyclone and high during a cyclone, with a variation of 50%. The average quantity of ozone in the atmosphere would form a layer on the earth's surface 3 mm. thick if reduced to *N.T.P.* C. J. Smithells.

Apparatus for the determination of helium in natural gas mixtures and minerals. W. Chlopin and A. Lukašuk.—See B., 1926, 51.

Determination of free calcium ions by Brinkmann and van Dam's method. H. Schulten (Biochem. Z., 1925, **164**, 47—52).—In this method, supersaturated solutions arise, the solubility product cannot be obtained, and the method is therefore subject to an unknown and varying error. P. W. Clutterbuck.

Electrolytic determination of zinc in ores. R. E. Sullivan and H. S. Lukens.—See B., 1926, 16.

Determination of copper by Feigl's method. E. Azzalin (Annali Chim. Appl., 1925, **15**, 373—377; cf. Feigl, A., 1923, ii, 880).—With copper alone, the method is unsatisfactory, since the excess of benzoinmonoxime is difficult to eliminate and washing is tedious because of the bulk and compactness of the precipitate, and it is difficult to secure constant weight. The method is rendered more exact and expeditious by igniting the precipitate and weighing the copper as oxide. Benzoinmonoxime is not a specific reagent for copper; it does not separate the latter completely from iron, aluminium, zinc, etc., and so is incapable of affording a rapid technical means of determining copper. W. E. Ellis.

Simple acidimetric determination of mercuric chloride. E. Rupp and P. Maiss (Apoth.-Ztg., 1925, **40**, 474; from Chem. Zentr., 1925, II, 332).—Mercuric chloride may be titrated with 0·5*N*-potassium cyanide solution, using phenolphthalein as indicator. Since hydrocyanic acid is without effect on dimethylaminoazobenzene, methyl-orange, or methyl-red, mercuric chloride may also be determined, using these indicators and titrating with sodium hydroxide as follows. Potassium cyanide solution (0·2 g. in 30 c.c.) is neutralised with 0·1*N*-hydrochloric acid, using one of the above indicators. Mercuric chloride solution is added and titration carried out with 0·1*N*-sodium hydroxide. When mercuric chloride is to be determined in pastilles, eosin must first be removed by animal charcoal if either methyl-orange or dimethylaminoazobenzene is to be used as indicator. G. W. Robinson.

Sensitive differential reaction of cerium. L. Fernandes (Gazzetta, 1925, **55**, 616—618).—As little as 1 part of cerium per 400,000 parts of solution is detectable by the coloration given with pyrocatechol. If rare elements only are present, the solution is made neutral or but slightly acid by addition of ammonia solution, a crystal of sodium thiosulphate and about 1 g. of pyrocatechol being then dissolved in a small portion of the liquid, which may require dilution. Treatment with excess of ammonia solution then gives a more or less intense violet coloration if the solution contains cerium. A control test is desirable when very small traces of cerium are present. If the total proportion of rare-earth metals is relatively high, a white precipitate is formed on addition of the excess of ammonia solution, but the colour of the liquid is readily seen after settling. When the rare-earth elements have been separated in the form of oxalate, direct treatment of this with pyrocatechol and ammonia is permissible. Other elements yielding highly coloured complexes with pyrocatechol must be removed before the test is applied; the elements of the first two analytical groups are eliminated by precipitation with their usual reagents, and any iron by agitation of the liquid with ether in presence of ammonium thiocyanate and hydrochloric acid until the red coloration vanishes. T. H. Pope.

Detection and separation of indium. I. Wada and S. Ato (Sci. Papers Inst. Phys. Chem. Res., 1922, **1**, 57—77).—See A., 1923, ii, 657.

Electrometric determination of iron with bromate. O. Collenberg and K. Sandved (Z. anorg. Chem., 1925, **149**, 191—202; cf. Kolthoff, A., 1919, ii, 352).—The ferric salt is reduced with excess of stannous chloride, and the mixture, to which are added 10—20 c.c. of concentrated hydrochloric acid for each 100 c.c., and 5 c.c. of a 6% solution of cobalt chloride, is titrated at 50° with standard potassium bromate solution. From the positions of the two turning points (stannous to stannic and

ferrous to ferric) on the titration curve the amount of bromate used in the latter oxidation can be determined. In the absence of such a catalyst as cobalt chloride, the rate of establishment of a steady potential at the end-point is too slow. Ferrous salts act similarly in the oxidation of stannous salts. In the oxidation of ferrous salts the potential set up at the end-point is independent of the experimental conditions, but in the oxidation of stannous salts it depends on the amount of hydrochloric acid present. R. CUTHILL.

Determination of foreign elements in scheelite, tungstic acid, and metallic tungsten. K. AGTE, H. BECKER-ROSE, and G. HEYNE.—See B., 1926, 60.

Separation and determination of bismuth. A. GIRARD and E. FOURNEAU (Bull. Soc. chim., 1925, [iv], **37**, 1669—1673).—See A., 1925, ii, 1207.

Benzoylmethylglyoxime as a precipitant of palladous salts. J. HANUŠ, A. JILEK, and J. LUKAS (Chem. News, 1925, **131**, 401—402; 1926, **132**, 1—4).—Palladium may be separated from the other platinum metals and from the common base metals by addition of a 2% alcoholic solution of benzoylmethylglyoxime to the solution of the chlorides of the metals in dilute hydrochloric acid (6 c.c. of the concentrated acid per 100 c.c. of solution). After boiling for a few minutes, the solution is kept over-night and the yellow, flocculent precipitate is then collected on a Gooch crucible, washed first with dilute hydrochloric acid, then with water, dried at 100—105°, and weighed as $C_{20}H_{18}O_6N_4Pd$ (20·64% Pd). If the solution contains antimony, tartaric acid must be added before precipitation of the palladium, and if molybdenum, vanadium, or tungsten is present a soluble phosphate must be added. *Palladium benzoylmethylglyoxime* is a yellow substance, m. p. 254—256°, insoluble in dilute acids but soluble in ammonia. A. R. POWELL.

Separation of iridium from rhodium and platinum, and the separation of platinum and rhodium. I. WADA and T. NAKAZONO (Sci. Papers Inst. Phys. Chem. Res., 1923, **1**, 139—154).—Titanous sulphate, in the cold, immediately reduces salts of bismuth, copper, gold, palladium, and platinum to metals or lower oxides; mercury as nitrate is reduced to metal, as mercuric chloride to a mixture of mercurous chloride and metal; complete reduction of rhodium salts takes some minutes; tellurites are reduced to tellurium. In hot solution, ruthenium salts are partly reduced to metal. Most of the elements of the sulphide group may be separated from the iridium, rhodium, and platinum by treatment with hydrogen sulphide in 0·3*N*-acid solution, ruthenium and molybdenum, which remain in solution, being then removed. The mixed chlorides of platinum, iridium, and rhodium are treated with titanous sulphate in the absence of nitric acid. The precipitated rhodium and platinum are heated with a mixture of 1 vol. of 6*N*-nitric acid and 3 vols. of 6*N*-hydrochloric acid, which dissolves the platinum and only a small part of the rhodium, a black residue indicating the presence of the latter. The platinum and rhodium in the aqua regia are converted into the chlorides, the metals precipitated from the latter by treatment with aluminium in hydrochloric acid, and fused with potassium hydrogen sulphate. The rhodium and only a small part of the platinum are removed, and on treatment of the fusion product with water a black residue shows the presence of platinum. If 1 c.c. of a solution containing 1 mg. of platinum and not more than 1 mg. of rhodium as chlorides be treated with 1 c.c. of 95% alcohol and then with solid ammonium chloride almost to saturation, nearly all the platinum separates out as ammonium chloroplatinate if the liquid is kept, whilst the remaining red solution contains all the rhodium.

The iridium in the filtrate from the titanous sulphate reaction may be precipitated as sulphide by treating the solution with an equal volume of glycerol or 30 g. of tartaric acid per 100 c.c., saturating with hydrogen sulphide, and heating in a closed vessel at 100°. B. FULLMAN.

Calorimetric bomb. P. LANDRIEU.—See B., 1926, 34.

Steel bomb calorimeter. W. KOHEN.—See B., 1926, 3.

Thermoregulator. H. J. WING and T. J. THOMPSON (Ind. Eng. Chem., 1925, **17**, 1242).—The inner tube (25 mm. diameter with a wall 1·5 mm. thick) is sealed inside the expansion bulb, and the stopcock and overflow cup are sealed to the upper end of the tube, whilst another tube is sealed to the bulb (for filling) and a second to the inner tube between the stopcock and the point where it enters the bulb. This latter carries the electrodes. The bulb is filled with mercury well above the end of the inner tube, and for a 100° range of the regulator 10 c.c. of mercury are added for each 100 c.c. volume of the bulb, which is then filled with toluene, heated to drive off air, cooled, completely filled, and sealed off. Dry hydrogen is drawn through into the side tube after filling with mercury, and the tube sealed off so that the contact points are left in an atmosphere of hydrogen. The regulator is set by drawing the mercury surface below the level of the upper contact point and the temperature of the bath adjusted by use of the stopcock. D. G. HEWER.

Establishment of the temperature scale to −193° by means of platinum-resistance thermometers. A. G. LOOMIS and J. E. WALTERS (J. Amer. Chem. Soc., 1925, **47**, 2851—2856).—It is shown that suitably constructed thermometers of the flat-coil calorimetric type enable the thermometric scale to be reproduced precisely at low temperatures by calibration at one low-temperature point only. The deviations found by Keyes, Townshend, and Young (J. Math. Phys. Massachusetts Inst. Tech., 1922, **1**, 243) are attributed to strains. The experimental results, together with those of Van Dusen (A., 1925, ii, 590), establish the reproducibility of pure platinum as a thermometric resistance wire when used under strain-free conditions at low temperatures, so that Henning's proposed method of establishing the thermodynamic temperature scale is valid and reproducible. S. K. TWEEDY.

Small resistance thermometer. G. F. TAYLOR (Physical Rev., 1925, [ii], **26**, 841—850).—The method of making the thermometer is described; a lead filament 1·5 cm. by 2×10^{-3} mm. in a glass tube embedded in a type metal for contact is employed. A sensitivity of 0·005° is readily obtained. The type metal employed (lead 85%, antimony 12%, tin 3%) has a coefficient of thermal expansion $25{\cdot}23\times10^{-6}$ per 1° between 0° and 100°.

A. A. ELDRIDGE.

Pressure-temperature charts; extended ranges. G. CALINGAERT and D. S. DAVIS (Ind. Eng. Chem., 1925, **17**, 1287—1289; cf. B., 1925, 690; 1923, 699A).—Cox's method of laying off the non-uniform temperature scale from a straight line, taken as the vapour-pressure curve for water and along which the temperature ordinates may be marked by means of a steam table, drawn at any convenient angle with the logarithmic pressure abscissæ, is extended for temperatures above the critical (370°) by making use of the equation $1/y=a+b/t$, where y is the distance from 0° to t°, the constants depending on the scale and units chosen. The non-uniform scale of temperature ordinates as given by Cox's method is shown to be the equivalent of a reciprocal temperature scale, the reciprocal being $1/(t+230)$. The graphical representations are fairly straight lines, and the lines of a given family of substances intersect at a common point, so that only a single experimental point is required once the point of convergence is known. Graphs are shown for halogen-substituted benzene and alcohol series, silicon hydrides, certain metals (silver, lead, cadmium, and mercury show a point of convergence), etc. and vapour-pressure data for a large number of compounds have been plotted.

D. G. HEWER.

Photographic spectro-polarimeter for the ultra-violet region. A. COTTON and R. DESCAMPS (Compt. rend., 1926, **182**, 22—26).—The instrument is constructed so that rotation of the analyser, which is replaced by the prisms of the spectrograph, produces automatically and continuously a corresponding movement in the image on the photographic plate, the angle of rotation being measured from the photograph.

S. K. TWEEDY.

Spectrograph with a non-inclined plate. P. SÈVE (Compt. rend., 1926, **182**, 57—58).—A simple spectrograph for use in the ultra-violet region is described in which, by the aid of quartz lenses and a reflector of small aperture, the spectrum is obtained normal to the photographic plate.

S. K. TWEEDY.

Light-filter for polarimetry. N. SCHOORL (Pharm. Weekblad, 1926, **63**, 21—23).—Coebergh's filter No. 5, a solution of 8·8 g. of hydrated copper sulphate and 9·4 g. of potassium dichromate in 200 c.c. of water, employed with a 50 c.p. metal-filament lamp with matte surface, may be used to replace the sodium flame with very good results.

S. I. LEVY.

Dark field illumination. H. SIEDENTOPF (Kolloid-Z., 1925, **37**, 327—335).—The theory of dark field illumination is discussed and two new dark field condensers by Zeiss and some of their applications are described.

N. H. HARTSHORNE.

Ebullition device for low-temperature and vacuum distillation. A. F. O. GERMANN and D. M. BIROSEL (J. Physical Chem., 1925, **29**, 1528—1532).—An ebullition tube is described which can be used for all types of distillation, but is particularly designed for vacuum distillation. The essential feature of the device is a tube, closed at its upper end and drawn out into a capillary at its lower, which is sealed into the neck of the distilling bulb. A series of parallel fractional distillations made with the new and the old types of bulb, using technical carbonyl chloride or a solution of sulphur dioxide in pure carbonyl chloride, showed that the vacuum ebullition tube is considerably more efficient than the ordinary type of distilling tube. The action of the tube is explained, and it is claimed that it is quite as efficient in the fractional distillation of liquefied gases as is the use of an inert gas as recommended by Ramsay and Travers (Phil. Trans., 1901, **A**, **197**, 58).

L. L. BIRCUMSHAW.

Viscosimetry. W. STAUF (Kolloid-Z., 1925, **37**, 397—405).—An account of the theory of viscosimetry and a description of capillary, torsion, and technical viscosimeters.

N. H. HARTSHORNE.

Micro-determination of melting and transition temperatures. D. VORLÄNDER and U. HABERLAND (Ber., 1925, **58**, [*B*], 2652—2656).—The microscope hot plate consists of a nickel disc in the centre of which is a quartz plate pierced with a hole in the edges of which platinum foil is inset. The foil is heated electrically. A small watch glass is fixed below the quartz plate and, during the measurements, covered by a second watch glass in such a manner that the substance under investigation and the quartz plate are in a very small, lens-shaped, hot-air bath. The instrument is calibrated by noting the current strength and potential at the platinum foil necessary to melt standard compounds.

H. WREN.

Laboratory pure culture apparatus. F. M. HILDEBRANDT (Ind. Eng. Chem., 1925, **17**, 1279).—In order to deal with relatively large quantities of active pure culture, an apparatus has been evolved consisting essentially of a culture tube connected by a side tube to the side tube of a Pasteur flask which holds sterile nutrient solution. Both are mounted on a wooden frame, and the culture tube is drawn down to a small diameter at the bottom, and is furnished at the top with a small bent-over tube with a cotton plug. A T-piece is interposed in the connexion of the flask, with glass beads in rubber for stopcocks, and the Pasteur flask is furnished with a guard at the top. After filling the Pasteur flask two-thirds full of nutrient solution, the whole apparatus is sterilised, and tubes of antiseptic are hung under the lower openings of the culture tube and the connecting T-piece. A suspension of organisms is blown into the culture flask through the bottom opening with due precautions, and nutrient solution run in by raising the Pasteur flask. The culture can easily be withdrawn when required. The apparatus

may readily be adapted for anaërobic work, and may be used in acclimatising organisms to various types of solution. D. G. HEWER.

History of investigation of internal pressures. T. W. RICHARDS (Chem. Reviews, 1925, **2**, 315—348).

Mineralogical Chemistry.

Sources of carbon in the pre-Cambrian formations. E. S. MOORE (Trans. Roy. Soc. Canada, 1925, [iii], **19**, IV, 21—26).—Carbon occurs in pre-Cambrian rocks as carbonates, graphite, and solid bitumen (anthraxolite). These may have been derived from the primary hydrocarbons and carbon dioxide of igneous rocks; but in recent years much evidence has been forthcoming of the presence of algal plant remains in these ancient rocks, and it is therefore likely that the carbon may be of organic origin. A limestone from Belcher Islands, Hudson Bay, containing algal concretions, showed specks of graphite, and an analysis gave 0·21%.

L. J. SPENCER.

Equilibrium between carbon dioxide and carbonates in the air, water, and earth of the globe. R. LEGENDRE (La Nature, 1925, **53**, ii, 138—142).—A discussion of the causes tending to increase or decrease the carbon dioxide content of the terrestrial atmosphere. The existing content is an equilibrium quantity, the resultant of reservoirs of atmospheric carbon dioxide and of carbonates in the earth, both dissolving and reacting in an intervening stratum of water. Chlorophyll at the atmosphere–water interface acts as a biological membrane, diminishing the partial pressure of the carbon dioxide at the surface of contact.

CHEMICAL ABSTRACTS.

Origin of terrestrial helium and its association with other gases. S. C. LIND (Proc. Nat. Acad. Sci., 1925, **11**, 772—779).—The inert gases cannot have been produced or retained in the earth's crust by chemical action; in the case of helium, its origin may be either primordial or due to radioactive decomposition. The gas will have been migrating slowly to the surface, be swept along at times by other gases, and be retained where a bed of shale capped by clay forms a favourable geological structure. It is generally, but not always, found in hydrocarbon gases, but in some cases with nitrogen which may possibly have been produced by the action of α-particles on nitrogenous organic matter or nitrides; it is almost universally associated with some nitrogen. The various hypotheses are discussed and analyses are given of gases collected recently from Dakota and Belgian Congo. E. B. LUDLAM.

Colour and composition of thunderbolts. E. MATHIAS (Compt. rend., 1925, **181**, 1111—1114).—The colours most frequently observed are those of black bodies cooling, *i.e.*, yellow, orange, or red. In many cases, however, blue, or a colour produced by superposition of blue on one of the preceding, is observed; these are attributed to burning sulphur, possibly arising from sulphur-containing organic matter in the atmosphere. The blackening of gilded objects, and the nature of odours observed in some cases, support this conclusion. S. I. LEVY.

Epidote of Monte Rosso di Verra (Monte Rosa group). T. CARPANESE (Atti R. Accad. Lincei, 1925, [vi], **2**, 349—355).—The epidote has a composition agreeing with the formula $HCa_2(Al,Fe)_3Si_3O_{13}$, and d 3·343. A comparison of its optical properties with its chemical composition indicates that it is to be regarded as a normal member of the clinozoizite–epidote series of mixed crystals. F. G. TRYHORN.

Identity of composition of planchéite and shattuckite. A. SCHOEP (Bull. Soc. chim. Belg., 1925, **6**, 315—321).—A well-crystallised sample of planchéite from Tantara was found to have the percentage composition: SiO_2, 39·23; CuO, 44·99; CaO, 6·93; H_2O, 5·74; Co_3O_4, 0·49; CO_2, 2·75, total 100·22. After deducting Co_3O_4 and $CaCO_3$ the molecular formula indicated is $2SiO_2,2(Cu,Ca)O,H_2O$, identical with that of shattuckite, but for the partial molecular replacement of copper oxide by calcium oxide. Indices of refraction were $\alpha=1·665$, $\gamma=1·720$, whilst all water was eliminated at 600—620°.

A. COUSEN.

Autunite from Lurisia. C. PORLEZZA and A. DONATI (Annali Chim. Appl., 1925, **15**, 518—534).—The results are given of chemical and spectrometrical analyses of autunite from the mines of Lurisia.

T. H. POPE.

Beidellite, a new mineral name. E. S. LARSEN and E. T. WHERRY (J. Washington Acad. Sci., 1925, **15**, 465—466).—A gouge-clay from Beidell, Colorado, previously described as leverrierite (A., 1917, ii, 324), is now named beidellite. It is a metasilicate with the formula $Al_2O_3,3SiO_2,nH_2O$, where n is about 4, coming between kaolinite and pyrophyllite. It is optically negative with small axial angle; $n(\alpha)$ 1·494, $n(\beta)$ and $n(\gamma)$ 1·536; and is probably orthorhombic.

L. J. SPENCER.

Composition and optical properties of beidellite. C. S. ROSS and E. V. SHANNON (J. Washington Acad. Sci., 1925, **15**, 467—468).—New analyses are given of: I, the finer separation from bentonite from Nashville, Arkansas; II, the coarser separation of the same; III, iron-beidellite from Spokane, Washington. These, and earlier analyses of material previously referred to leverrierite, suggest the formula $Al_2O_3,3SiO_2,4H_2O$. In the green iron-beidellite, with rather higher refractive indices, there is a passage to $Fe_2O_3,3SiO_2,4H_2O$.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.
I.	45·52	—	27·52	2·80	—	0·52	3·00	19·60	98·96
II.	45·12	—	28·24	4·12	—	0·88	2·32	18·72	99·40
III.	46·06	0·84	12·22	18·54	0·28	1·66	1·62	17·26	98·48

L. J. SPENCER.

Japanese minerals containing rarer elements. I—III. Y. SHIBATA, K. KIMURA, and T. UEMURA (Japanese J. Chem., 1923, **2**, 1—20).—English translations, with some rearrangement, of papers previously published in Japanese (A., 1921, ii, 269; 1922, ii, 220, 305, 516, 861). L. J. SPENCER.

Japanese minerals containing rarer elements. IV. Analyses of zircon, xenotime, and allanite. K. KIMURA (Japanese J. Chem., 1925, **2**, 73—79).—Crystals of reddish-brown zircon (*d* 4·3—4·4) and brownish-grey xenotime (*d* 4·4) were washed from a stream in the pegmatite region of Ishikawa, prov. Iwaki. The two are intimately intermixed and sometimes show parallel intergrowths. Zircon separated as far as possible from xenotime gave analysis I (also MgO, CaO, MnO traces). The rare-earths in excess of the phosphoric acid presumably belong to the zircon rather than to the xenotime. Analysis II (also CaO 0·35) of radial aggregates of xenotime shows the material to be a mixture of xenotime and zircon.

	SiO_2.	ZrO_2.	UO_2.	$(Nb,Ta)_2O_5$.	P_2O_5.	Al_2O_3.	Fe_2O_3.	Rare earths.	Ign.	Total.
I.	32·40	58·71	1·06	trace	1·31	0·25	0·95	3·79	2·10	100·57
II.	12·49	19·84	1·92	0·44	23·87	0·48	0·23	37·37	2·35	99·34

Allanite from the pegmatite of Ishikawa is black and radioactive with *d* 3·60. Analysis gave SiO_2 32·93, ThO_2 1·64, Al_2O_3 14·51, Ce_2O_3 4·87, La_2O_3 etc. 8·19, FeO 15·23, MnO 4·32, CaO 12·61, MgO 0·74, CO_2 0·11, H_2O 4·58, UO_2, SnO_2 traces, total 99·73. Spectrum analysis of the rare-earth fraction (free from ceria) shows a predominance of lanthanum and neodymium, and presence of yttrium, gadolinium, etc. L. J. SPENCER.

Japanese minerals containing rarer elements. V. Analyses of fergusonite, hagatalite, and oyamalite. K. KIMURA (Japanese J. Chem., 1925, **2**, 81—85).—Crystals of fergusonite, *d* 5·30, from the pegmatite of Hagata, province Iyo, gave on analysis: $(Nb,Ta)_2O_5$ 44·97, SiO_2 0·79, TiO_2 1·15, UO_2 3·18, SnO_2 0·35, Al_2O_3 1·35, Fe_2O_3 0·66, Y_2O_3 etc. 40·39, Nd_2O_3 etc. 0·89, CaO 1·40, MgO 0·58, CO_2 0·35, H_2O 3·92, total 99·98. Spectrum analysis showed the presence of predominant yttrium, together with scandium, neodymium, prascodymium, europium, dysprosium, holmium, erbium, and thulium; and, in the tin precipitate, of lead, copper, and germanium. Hagatalite is the name given to a variety of zircon, which occurs as small crystals embedded in biotite from the pegmatite of Hagata. The crystalline form is that of zircon, *d* 4·4. Analysis I [also $(Nb,Ta)_2O_5$ 2·7, UO_2 trace] shows the presence of more rare-earths (mainly yttria) and less zirconia than in naegite (A., 1921, ii, 269). Another variety of zircon, named oyamalite, occurs in the pegmatite of Oyama, province Iyo, as green to brown radial aggregates resembling naegite; analysis II (also P_2O_5 7·6) shows that in addition to rare-earths it contains a considerable amount of phosphoric acid.

	SiO_2.	ZrO_2.	ThO_2.	Al_2O_3.	Fe_2O_3.	Rare earths.	CaO.	MgO.	Ign.	Total.
I.	29·7	42·0	1·5	2·8	2·3	13·1	0·3	0·2	5·5	100·1
II.	25·7	40·9	0·6	2·0	0·6	17·7	0·6	0·8	3·5	100·0

L. J. SPENCER.

Buttgenbachite, a new mineral. A. SCHOEP (Bull. Soc. chim. Belg., 1925, **34**, 313—314).—See A., 1925, ii, 1196.

Organic Chemistry.

Identification of primary alkyl bromides and iodides. C. S. MARVEL, C. G. GAUERKE, and E. L. HILL (J. Amer. Chem. Soc., 1925, **47**, 3009—3011).—The alkyl halide (1 c.c.) is treated with magnesium (0·3 g.) in dry ether (15 c.c.), the solution filtered into a test-tube containing 4·5—5·0 g. of mercuric bromide or iodide, the mixture warmed and shaken for a few min., and then evaporated to dryness. The residue is boiled with 95% alcohol (20 c.c.), the extract filtered, diluted with water (10 c.c.), and cooled, when the corresponding mercuric alkyl halide separates. These derivatives are well crystallised, have well-defined m. p., and are well adapted to the identification of alkyl halides. The following new mercuric alkyl halides are described: *mercuric ethyl*, m. p. 193·5°; n-*propyl*, m. p. 138°; iso*butyl*, m. p. 55·5°; n-*amyl*, m. p. 122°; n-*hexyl*, m. p. 118·5°; n-*heptyl*, m. p. 114·5°; and n-*octyl bromide*, m. p. 109°; *mercuric* n-*propyl*, m. p. 112·5°; n-*butyl*, m. p. 117°; and iso*butyl iodide*, m. p. 72°. F. G. WILLSON.

Catalytic hydrogenation of organic substances. O. SCHMIDT.—See this vol. 134.

Narcotic and toxic effects of halogen derivatives of hydrocarbons. J. MÜLLER.—See B., 1926, 75.

Oxonium compounds. D. MCINTOSH (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 71—72; cf. J.C.S., 1905, **87**, 784; A., 1912, i, 825).—*n*-Propyl alcohol adds 1 atom of chlorine or bromine, methyl ethyl ketone 2 atoms, methyl acetate, *n*-propyl acetate, and *iso*amyl acetate (bromine only) 3 atoms. The additive compounds melt at a low temperature, are formed with slight heat evolution, and when substitution is prevented are not electrically conductive. The above substances, together with *iso*propyl alcohol, methyl propionate, ethyl butyrate, and acetic anhydride, give compounds with hydrogen bromide which in solution are electrically conducting. Ethylene glycol gives compounds containing 1 and 2 mols. of hydrogen bromide, but forms no additive compounds with hydrogen chloride or iodide or with the halogens. J. S. CARTER.

Condensations of the sodium derivatives of trimethylene glycol and glycerol. A. FAIRBOURNE and G. E. FOSTER (J.C.S., 1925, **127**, 2759—2764; cf. *ibid.*, 1921, **119**, 1035, 2077).—1-Chloro-2 : 4-dinitrobenzene reacts at 100° with a solution of sodium in trimethylene glycol, and treatment with acetic acid leads to the separation of *trimethylene glycol mono-2 : 4-dinitrophenyl ether*, m. p. 52° (*acetyl* deriv-

ative, m. p. 85°, *benzoyl* derivative, m. p. 95°), and *trimethylene glycol bis*-2 : 4-*dinitrophenyl ether*, m. p. 180°, the relative yields of which vary with the concentration of the sodium derivative. Benzoyl chloride with monosodium glyceroxide yields α-benzoylglycerol, but with disodium glyceroxide it yields tribenzoylglycerol, m. p. 71—72° (from light petroleum), 76° (from alcohol). Mono- or di-sodium glyceroxide reacts with one equivalent of *p*-toluenesulphonyl chloride in ether or benzene solution to give *glyceryl tri*-p-*toluenesulphonate*, m. p. 103°, whilst *glyceryl tribenzenesulphonate*, m. p. 80°, is similarly prepared. In spite of this, and of the fact of the formation of the bisdinitrophenyl ether, it is concluded that in the above condensation of 1-chloro-2 : 4-dinitrobenzene, direct interaction between halogen and hydroxyl groups does not occur, since no ionisable halogen is detected when 1-chloro-2 : 4-dinitrobenzene, in presence of calcium carbonate, is heated with glycerol, ethylene glycol, or trimethylene glycol, or with trimethylene glycol mono-2 : 4-dinitrophenyl ether in a solvent. Treatment of the mono-ether with a solution of sodium in trimethylene glycol does not give rise to the bis-ether.

iso*Propylideneglycerol* 3 : 5-*dinitrobenzoate*, m. p. 85° (prepared by interaction of 3 : 5-dinitrobenzoyl chloride and *iso*propylideneglycerol in presence of quinoline and chloroform), is converted by dilute hydrochloric acid at 70—80° into *glycerol* α-3 : 5-*dinitrobenzoate*, m. p. 118°; since this is also prepared by condensation of monosodium glyceroxide and 3 : 5-dinitrobenzoyl chloride in ethereal solution, and since monosodium glyceroxide and *p*-nitrobenzoyl chloride similarly yield α-*p*-nitrobenzoylglycerol, the α-structure of monosodium glyceroxide is confirmed.

F. M. HAMER.

Oxidation of ethyl ether to oxalic acid in presence of uranyl nitrate. S. W. ROWELL and A. S. RUSSELL (J.C.S., 1925, **127**, 2900—2902).—When an ethereal solution of uranyl nitrate is exposed to sunlight in presence of water, after removal of the ether and of unchanged uranyl nitrate there remains the normal hydrated uranium oxalate, $UO_2C_2O_4,2H_2O$; sometimes a basic oxalate is formed, probably $U(OH)_4,UO_2C_2O_4,2H_2O$ or $UO_2(OH)_2,UO_2C_2O_4,2H_2O$. Exposure to sunlight of a neutralised ethereal solution of uranyl nitrate yields uranous hydroxide. Even carefully purified ether with uranyl nitrate gives the oxalate, but none results when ether is replaced by alcohol, although the latter favours the formation of uranium hydroxide in neutral solution. It is suggested that sunlight reduces the uranyl to the uranous ion and oxidises ether to diglycol, of which part is oxidised to diglycollic acid and part hydrolysed to glycol, which is further oxidised to oxalic acid.

F. M. HAMER.

Formation of ethyl mercaptan by the action of phosphorus pentasulphide on alcohol. P. S. PISCHTSCHIMUKA (J. Russ. Phys. Chem. Soc., 1925, **56**, 11—14).—The interaction of ethyl alcohol and phosphorus pentasulphide is expressed, according to Kekulé, by the equation $5EtOH+P_2S_5=P_2O_5+5EtSH$ and, according to Carius (Diss., Heidelberg, 1861), by the equation $5EtOH+P_2S_5=H_2O+H_2S+Et_3PO_2S_2+Et_2HPO_2S_2$. The author finds that the reaction between anhydrous alcohol and phosphorus pentasulphide under various conditions always yields diethyl dithiophosphate, $SH\cdot SP(OEt)_2$. At a high temperature, this acid decomposes with evolution of ethyl mercaptan in small proportions. Treatment of the lead salt of the acid with ethyl iodide yields its *ethyl* derivative, $SEt\cdot SP(OEt)_2$, which may be obtained also by heating in a sealed tube a mixture of sulphur with the compound $PCl_2\cdot SEt$ (cf. Michaelis, A., 1872, 283) and treating with dry sodium ethoxide the resulting *ethyldithiophosphoryl chloride*, $SEt\cdot SPCl_2$, b. p. 92°/10 mm., d_0^0 1·4453. The ethyl derivative of diethyl dithiophosphate, but not the acid itself, readily gives ethyl mercaptan when heated with water.

T. H. POPE.

Hydroxy- and ethoxy-mercaptans and their condensation products. C. A. ROJAHN and G. LEMME (Arch. Pharm., 1925, **263**, 612—624).—The following compounds have been prepared in an effort to obtain alkyloxy- or hydroxy-derivatives of the sulphonal or veronal series. The effort has up to the present proved abortive because the mercaptols resist oxidation. The compounds, unless otherwise specified, are oils without unpleasant odour. Those for which no b. p. is given decompose on heating.

γ-*Ethoxypropyl mercaptan*, b. p. 52—54°/20 mm., is prepared by treating γ-bromopropyl ethyl ether with potassium hydrogen sulphide; when treated with dilute alcoholic sodium hydroxide and benzyl chloride, it yields γ-*ethoxypropyl benzyl sulphide*, b. p. 161°/18 mm., which is oxidised by hydrogen peroxide to the corresponding *sulphone*, m. p. 45—46°. When γ-ethoxypropyl mercaptan is dissolved in acetone and the solution heated with zinc chloride, *acetone di-γ-ethoxypropylmercaptol* (iso*propylidene di-γ-ethoxypropyl disulphide*), $CMe_2[S\cdot[CH_2]_3\cdot OEt]_2$, is formed. An analogous product is formed when methyl ethyl ketone is used, or is prepared also by ethylating (with ethyl sulphate) the corresponding dihydroxymercaptol (see below). By treating γ-chloropropyl alcohol with sodium hydrogen sulphide γ-*hydroxypropyl mercaptan*, b. p. 85—90°/15 mm., is obtained. It yields a *dibenzoate*, and, when heated with fuming hydrochloric acid, γ-*thiolpropyl* γ-*chloropropyl sulphide*, the *benzoate* of which is described. γγ-*Dihydroxypropyl disulphide* is obtained by oxidising the mercaptan with sodium hydroxide and iodine. Its *dibenzoate* is described. γ-*Hydroxypropyl benzyl sulphide* has b. p. 185—188°/20 mm. (slight decomp.) and also affords a *benzoate*. iso*Propylidene di-γ-hydroxypropyl disulphide* and its *dibenzoate*, and the corresponding mercaptols from methyl ethyl ketone and benzaldehyde, and their *dibenzoates*, are also described. The *diacetate* of β-hydroxyethyl mercaptan (Bennett, J.C.S., 1921, **119**, 423) has b. p. 118—120°/25 mm. β-*Ethoxyethyl mercaptan*, which is obtained in poor yield owing to side reactions, diethylene disulphide and other products being formed, has b. p. 37—40°/15 mm. The corresponding *disulphide*, which also is a by-product, has b. p. 150—152°/15 mm. β-*Ethoxyethyl benzyl sulphide* has b. p. 146°/16 mm., and is oxidised to the corresponding sulphone, m. p. 53°

(Fromm and Jörg, A., 1925, i, 352). iso*Butylidene di-β-ethoxyethyl disulphide* is described.

When dichloroacetone interacts with mercaptans, the chlorine atoms, and not the ketonic group, take part. An alternative way of obtaining the sulphones referred to above is therefore not feasible. *αγ-Diethylthiolacetone*, from dichloroacetone and ethyl mercaptan, has b. p. 117—121°/15 mm. (*semicarbazone*, m. p. 98—99°, *dimethiodide*, m. p. 182°); it is accompanied by *αββγ-tetrathioethylpropane*, b. p. 51—53°/15 mm., which is the chief product when an excess of ethyl mercaptan is used.

W. A. SILVESTER.

Methyltrichloromethylsulphur chloride. CHEM. FABR. SCHERING.—See B., 1926, 38.

γγ'-Dichlorodipropyl sulphide. G. M. BENNETT and A. L. HOCK (J.C.S., 1925, **127**, 2671—2677).—The action of sodium sulphide on γ-chloropropyl alcohol yielded *γγ'-dihydroxydipropyl sulphide* (*bisphenylurethane*, m. p. 146—148°), and this on chlorination gave *γγ'-dichlorodipropyl sulphide*, b. p. 162°/43 mm., d_4^{20} (vac.) 1·175, n_a^{20} 1·5075, which formed a *compound* with platinic chloride, m. p. 83·5—85°, and an unstable *dibromide*. The chloro-sulphide gave on oxidation *γγ'-dichlorodipropylsulphone*, m. p. 66°, and with methyl iodide and mercuric iodide yielded *dichlorodipropylmethylsulphonium mercuri-iodide*, m. p. 84—88°. When heated with phenol and sodium ethoxide, the chloro-sulphide formed *γγ'-diphenoxydipropyl sulphide*, m. p. 45°, and similarly *γγ'-di-p-tolyloxydipropyl sulphide*, m. p. 50—52°, was obtained. With piperidine, *γγ'-dipiperidinodipropyl sulphide* (*picrate*, m. p. 200°) was formed. The rates of reaction of ββ'-dichlorodiethyl and γγ'-dichlorodipropyl sulphides with alcoholic alkali are approximately as 60 : 1.

B. W. ANDERSON.

Isomerism in compounds containing two similar asymmetric sulphur atoms. E. WEDEKIND (Ber., 1925, **58**, [*B*], 2510—2518).—Diethyl ethylene sulphide slowly unites with methyl iodide at the atmospheric temperature to yield ethylenedimethylethylsulphonium iodide, $C_2H_4(SMeEt\cdot I)_2$, which is separable by crystallisation from dilute alcohol into a sparingly soluble *α-salt*, decomp. 154°, and a more freely soluble *β-salt*, m. p. 123—124°. Measurable crystals have not been obtained, but the compounds are sharply differentiated from one another by crystalline form and solubility in 75% alcohol. It remains uncertain whether the isomerism persists in a series of salts; those of the two series do not appear to differ from one another markedly in appearance or temperature of decomposition, but complete identity cannot be assumed, since measurable crystals have not been obtained, and instances are on record in which isomeric salts decompose at the same temperature. The following salts have been obtained from the α- and β-iodides: mercuric chloride *compound*, $C_8H_{20}S_2Hg_2Cl_6$, m. p. 191°; cadmium iodide *compound*, $C_8H_{20}S_2CdI_4$, decomp. 147—148°; *chloroplatinate*, decomp. 236° after softening; *chloroaurate*, $C_8H_{20}S_2Au_2Cl_8$, decomp. 225°; *picrate*, decomp. 170°; *perchlorate*, decomp. 227°. The β-perchlorate appears to dissolve in water rather more freely than the α-perchlorate. Attempts to resolve the salts by means of *d*-camphorsulphonic acid or *d*-bromocamphor-π-sulphonic acid gave negative results on account of experimental difficulties. The d-*camphorsulphonate* from the α-iodide has m. p. 183°, whereas the corresponding *salt* from the β-iodide has m. p. 189—190°. The d-*bromocamphor-π-sulphonates* of the α- and β-series have m. p. 157—159° and 160° (indef.), respectively; the α-salt crystallises in long needles which, when preserved beneath the mother-liquor, become transformed into thick, coarse prisms. An actual interconversion of the salts of the two series could not be achieved.

Diethyl trimethylene disulphide, b. p. 228—231°, is converted by methyl iodide into the corresponding *sulphonium iodide*, $C_9H_{22}I_2S_2$, m. p. (indef.) 112°, which could not be separated into two possible isomerides.

H. WREN.

Acid and salts strongly absorbing ultra-violet rays. T. SUZUKI and S. SAKURAI.—See B., 1926, 76.

Acetato- and formato-cations of cadmium, manganese, lead, and the alkaline-earth metals. R. WEINLAND and H. SCHLAICH (Z. anorg. Chem., 1925, **150**, 35—46).—The following complex *salts* of cadmium acetate are described:

$[Cd_2(OAc)_2](OAc)(ClO_4),3H_2O$;
$[Cd_2(OAc)_2](NO_3)_2,3H_2O$; $[Cd_3(OAc)_4](ClO_4)_2,2H_2O$;
$[Cd_2(OAc)_2][O\cdot C_6H_2(NO_2)_3]_2,CH_3\cdot CO_2H,3H_2O$;
$[Cd_2(OAc)_2](O\cdot C_6H_4\cdot NO_2)_2,2OH\cdot C_6H_4\cdot NO_2,CH_3\cdot CO_2H,6H_2O$;
$[Cd_2(HCO_2)_2][O\cdot C_6H_2(NO_2)_3]_2,6H_2O$.

The first three are obtained by mixing cadmium acetate and the appropriate acid in aqueous solution, but the picrates and *p*-nitrophenoxides are obtained fron concentrated acetic or formic acid. A *picrate* of manganese acetate, $[Mn_2(OAc)_2][O\cdot C_6H_2(NO_2)_3]_2$, and the following p-*nitrophenoxides* are similarly obtained:

$[Mn_3(OAc)_4](O\cdot C_6H_4\cdot NO_2)_2,CH_3\cdot CO_2H,9H_2O$;
$[Pb_2(OAc)_2](O\cdot C_6H_4\cdot NO_2)_2,2CH_3\cdot CO_2H$,
$[Ba_2(OAc)_2](O\cdot C_6H_4\cdot NO_2)_2,2CH_3\cdot CO_2H,6H_2O$;
$[Sr_2(OAc)_2](O\cdot C_6H_4\cdot NO_2)_2,2CH_3\cdot CO_2H,6H_2O$;
$[Ca_2(OAc)_2](O\cdot C_6H_4\cdot NO_2)_2,2CH_3\cdot CO_2H,4H_2O$.

A. GEAKE.

α-Ethyloctoic acid and its esters. A. W. DOX (J. Amer. Chem. Soc., 1925, **47**, 3008—3009).—dl-α-*Ethyloctoic acid*, b. p. 252—255°, d^{25} 0·8905, is obtained in practically quantitative yield by distilling ethylhexylmalonic acid (cf. A., 1924, i, 1037). The following esters were prepared: *methyl*, b. p. 213—215°; *ethyl*, b. p. 221—223°, d^{25} 0·8580; *propyl*, b. p. 238—240°, d^{25} 0·8578; and n-*butyl*, b. p. 255—257°, d^{25} 0·8571. The first two esters do not react with cold, saturated, alcoholic ammonia.

F. G. WILLSON.

Evolution of hydrogen peroxide from oils on exposure to light. G. F. A. STUTZ, H. A. NELSON, and F. S. SCHMUTZ.—See B., 1926, 20.

Decomposition of oxalic acid by acetic anhydride. E. L. WHITFORD (J. Amer. Chem. Soc., 1925, **47**, 2934—2938).—The decomposition of oxalic acid in acetic anhydride solution is a reaction of the first order, k^{25}=0·0128, k^{35}=0·0375, and k^{45}=0·1105. The decomposition is not catalysed by carbamide,

pyrrole, aniline, phenylhydrazine, or aceto-, propio-, or butyro-nitriles. Impure picoline, lutidine, and collidine increase the rate of decomposition. The addition of pyridine also increases the rate of decomposition, but causes the temporary separation of pyridine hydrogen oxalate, which disappears as the reaction proceeds. The insolubility of this oxalate of pyridine in acetone, in comparison with those of pyridine derivatives, renders it suitable for the isolation of small quantities of pure pyridine from the commercial material. In pyridine solution, 1 mol. of acetic anhydride brings about the decomposition of 1 mol. of oxalic acid, indicating the probable formation of an intermediate compound between the two, the decomposition then being formulated $H_2C_2O_4 + Ac_2O \rightleftharpoons H_2C_2O_4,Ac_2O \longrightarrow CO + CO_2 + 2HO\cdot Ac$. The reaction-velocity constants, in pyridine solution, are independent of the amount of acetic anhydride added. F. G. WILLSON.

Uranyl oxalate. A. RAYNAUD (Bull. Soc. chim., 1925, [iv], **37**, 1375—1376).—The original work of the author (A., 1912, i, 535) was corrected by a later paper (Soc. Sci. Phys. Nat. Bordeaux, Meeting on March 26, 1914), which anticipates and confirms the results of Colani (A., 1925, i, 1235) on the hydration and dehydration of uranyl oxalate. W. HUME-ROTHERY.

Formation and growth of silver nuclei in the decomposition of silver oxalate. J. T. MACDONALD and C. N. HINSHELWOOD.—See this vol., 134.

Aluminioxalates of some optically active bases. T. B. CHILD, E. ROBERTS, and E. E. TURNER (J.C.S., 1925, **127**, 2971—2972).—By the action of barium aluminioxalate on the sulphate of the base, *strychnine aluminioxalate*, $[\alpha]_D^{20}$ $-24\cdot0°$ to $-21\cdot0°$, was prepared, and similarly *l-menthylamine aluminioxalate*, $[\alpha]_D^{20}$ $-28\cdot5°$, and *l-phenylethylamine aluminioxalate*, $[\alpha]_D^{20}$ $-3\cdot00°$, were obtained. Recrystallisation of these compounds gave no evidence of resolution. *Potassium distrychnine aluminioxalate* and *dipotassium* d-*phenylethylamine aluminioxalate* gave no better results. *Cinchonidine aluminioxalate* was obtained as a gummy solid. B. W. ANDERSON.

Ethyl γγ-diethoxyacetoacetate as a reagent for the synthesis of glyoxalines. E. W. RUGELEY and T. B. JOHNSON (J. Amer. Chem. Soc., 1925, **47**, 2995—3002).—For the preparation of ethyl γγ-diethoxyacetoacetate, moist silver diethoxyacetoacetate may be agitated for 12 hrs. with ethyl iodide in moist ether at the ordinary temperature (cf. Johnson and Cretcher, A., 1915, i, 1002; 1916, i, 756). Synthesis of this ester could not be accomplished by the method of Hamel (A., 1921, i, 537). When treated with nitrous acid (cf. Jovitschitsch, A., 1895, i, 447), the ester yields an iso*nitroso*-derivative, decomposing when heated, which could not be reduced to the corresponding amine. *Ethyl α-bromo-γγ-diethoxyacetoacetate*, decomposing when heated, appears to be formed by the action of bromine in carbon disulphide on the above ester. It does not react with carbamide, and the products of reaction with ammonia could not be purified. Treatment with hydrogen bromide affords *ethyl α-bromoglyoxalacetate*, m. p. 119°. Condensation of ethyl γγ-diethoxyacetate or ethyl formate with ethyl hydantoate, or of the first-named with ethylurethane acetate, in presence of sodium ethoxide, could not be accomplished. When treated with chlorodimethyl ether, ethyl sodio-γγ-diethoxyacetoacetate affords *ethyl α-methoxymethyl-γγ-diethoxyacetoacetate*, b. p. 130°/4 mm., n^{23} 1·4387. *Diethyl γγ-diethoxyacetosuccinate*, b. p. 156°/3 mm., n^{21} 1·4370, is obtained by alkylation of ethyl γγ-diethoxyacetoacetate with ethyl chloroacetate, or by application of the Claisen reaction to the former with diethyl succinate. It yields, on hydrolysis with barium hydroxide, succinic acid [identified as its *benzyl-ψ-thiocarbamide* salt ($+2H_2O$), m. p. 153°], and glyoxalpropionic acid, a small proportion of the latter being also obtained on hydrolysis with sulphuric acid or sodium hydroxide. The bearing of these results on the production of therapeutically valuable glyoxaline derivatives is discussed. F. G. WILLSON.

Formation of citric acid from gluconic acid by moulds. C. WEHMER (Ber., 1925, **58**, [*B*], 2616—2619).—Calcium gluconate is converted by a species of *Aspergillus niger* (strain 8 of A., 1924, i, 1282) into citric acid and smaller amounts of oxalic acid, whereas oxalic acid is almost exclusively produced by *A. niger cinnamomeus*. Additional confirmation is thus given to the hypothesis that the oxidative degradation of sugar follows the course dextrose → gluconic acid → citric acid → oxalic acid → carbon dioxide, but the mechanism of the formation of citric acid remains unexplained. H. WREN.

Formation of citric acid from gluconic acid by *Aspergillus*. R. SCHREYER (Ber., 1925, **58**, [*B*], 2647; cf. Falck and Kapur, A., 1924, i, 917).—Citric acid is formed by the action of *A. fumaricus* on 15%, but not on 10% solutions of calcium gluconate. H. WREN.

Constitution of α-ketogluconic acid. M. HÖNIG (Ber., 1925, **58**, [*B*], 2644—2646; cf. Hönig and Tempus, A., 1924, i, 712).—In reply to van Niel and Hooft (A., 1925, i, 1237), the author accepts the possibility of the non-homogeneity of the yeast used in the fermentation of α-ketogluconic acid, but maintains the identity of the *d*-arabinose produced thereby, which does not rest solely on the isolation of the osazone, but also on the oxidation of the carbohydrate to carbon dioxide and *d*-arabonic acid, isolated as the calcium and phenylhydrazine salts. The relationship of the α-ketogluconic acid to the product obtained by Bertrand (A., 1904, ii, 760) and by Kiliani (A., 1922, i, 1111) remains undecided.

The substance, $C_{18}H_{24}O_6N_4$, described (*loc. cit.*) as the osazone of α-ketoglutaric acid is identified as the *phenylhydrazone* of the *phenylhydrazide* of the *ketonic acid*. H. WREN.

Electrolytic reduction of aldehydes. I. Formaldehyde and acetaldehyde. G. SHIMA (Mem. Coll. Sci. Kyōtō, 1925, **9**, 183—196).—The electrolytic reduction of formaldehyde and acetaldehyde yields in each case 80—90% of the corresponding alcohol, but the current efficiency in the former case is 52% as against 80% in the latter. The concentration of the aldehyde must not be high, on account of possible polymerisation. Reduction of acetaldehyde to ethyl

alcohol is best carried out at 20°, using 10—15% sulphuric acid solution, a lead cathode, and a current density of 3·5—4 amp./cm.^{2} The aldehyde concentration should be kept at about 5%.

B. W. ANDERSON.

Assimilation hypothesis. D. VORLÄNDER (Ber., 1925, **58**, [*B*], 2656—2658).—Previous results on the production of formaldehyde and oxygen from carbon dioxide and water under the influence of light in the absence of protoplasm or organised matter are contradictory, possibly on account of reversibility of the reaction. Attempts are described to remove the formaldehyde as produced by precipitating it with 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione. Negative results are obtained when water saturated with 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione is treated with a current of carbon dioxide for months in sunlight or daylight or for weeks in the light from a mercury–quartz arc. Reaction is not induced by the presence of salts, alkalis, acids, uranyl sulphate, cerium carbonate or chloride, titanous sulphate, ferrous sulphate, or pyridine. H. WREN.

Aldehyde acetal of methylglyoxal. C. NEUBERG and O. DALMER (Biochem. Z., 1925, **162**, 488—489).—Commercial dichloroacetic acid can be used in the preparation of ethyl diethoxyacetate, since the mono- and di-ethoxy-esters are readily separable by fractionation. P. W. CLUTTERBUCK.

Reduction of ketones in presence of platinum-black. M. FAILLEBIN (Compt. rend., 1926, **182**, 138—140).—See this vol., 50.

Claisen reaction. G. T. MORGAN and E. HOLMES (J.C.S., 1925, **127**, 2891—2896).—The higher methyl monoketones, $C_nH_{2n+1}\cdot CO\cdot CH_3$, from $n=7$ to $n=19$, condense normally with ethyl acetate, giving a satisfactory yield of $\alpha\gamma$-diketone,

$$C_nH_{2n+1}\cdot CO\cdot CH_2\cdot CO\cdot CH_3.$$

The acids $C_nH_{2n+1}\cdot CO_2H$, where $n=10$, 12, 14, and 18, are obtained by oxidising the methyl ketone of the next higher acid and are isolated as barium salts. The method consists in condensing the ketone, prepared by distillation of the barium salt of the corresponding fatty acid with barium acetate, with sodium and ethyl acetate, acidifying with acetic acid, and isolating the co-ordinated copper derivative of the diketone, from which treatment with sulphuric acid in presence of ether liberates the diketone itself. The following are described: n-*octoylacetone*, b. p. 248°/755 mm., 118°/5 mm., *copper* salt, m. p. 118°; n-*nonoylacetone*, b. p. 150°/15 mm., *copper* salt, m. p. 115·5°; *n*-decoylacetone; n-*undecoylacetone*, m. p. 28°, *copper* salt, m. p. 112°; n-*dodecoylacetone*, m. p. 31—32°, *copper* salt, m. p. 112·5°; n-*tridecoylacetone*, m. p. 35°, *copper* salt, m. p. 111°; n-*tetradecoylacetone*, m. p. 39°, *copper* salt, m. p. 112°; n-*pentadecoylacetone*, m. p. 42°, *copper* salt, m. p. 111°; n-*hexadecoylacetone*, m. p. 49°, *copper* salt, m. p. 112°; n-*heptadecoylacetone*, m. p. 51°, *copper* salt, m. p. 112°; n-*octadecoylacetone*, m. p. 52·5°, *copper* salt, m. p. 113°; n-*nonadecoylacetone*, m. p. 55°, *copper* salt, m. p. 112·5°; n-*eicosanoylacetone*, m. p. 57°, *copper* salt, m. p. 114°. The influence of lengthening the carbon chain on the b. p. of the lower diketones, m. p. of the higher members, and fusibility of their copper salts, is shown in the form of graphs. The blue colour of the copper salts becomes less pronounced as the series is ascended. Probably the whole series of diketones would condense with tellurium tetrachloride (cf. this vol., 188). F. M. HAMER.

Dynamic isomerism. XX. Amphoteric solvents as catalysts for the mutarotation of the sugars. T. M. LOWRY and I. J. FAULKNER (J.C.S., 1925, **127**, 2883—2887; cf. A., 1925, i, 886).—A mixture of pyridine with twice its weight of water gives a maximum velocity of mutarotation for dextrose, or for tetramethylglucose, which is twenty times as great as the velocity for a solution of the sugar in pure water. Neither pyridine nor cresol has appreciable catalytic properties when water is not present, but a mixture of two parts of cresol to one part of pyridine is twenty times more active than is water in promoting the mutarotation of tetramethylglucose. The great activity of the mixed solvent is attributed to its amphoteric character. It is concluded that, for a proton within the sugar molecule to change its position, it is necessary to supply a medium into which a proton can escape and from which a proton can be provided. This theory is supported by the fact that the only substances known to act as catalysts for the mutarotation of the sugars possess either acidic or basic properties or both. Acetone and ethyl acetate, even in presence of water, do not accelerate mutarotation. F. M. HAMER.

Mechanism of carbohydrate oxidation. I. Dextrose, *d*-mannose, lævulose, *d*- and *l*-arabinose, and *dl*-glyceraldehyde. W. L. EVANS, C. A. BUEHLER, C. D. LOOKER, R. A. CRAWFORD, and C. W. HOLL (J. Amer. Chem. Soc., 1925, **47**, 3085—3098).—When the above compounds are oxidised by dilute aqueous potassium permanganate, the product, in neutral solution, is carbon dioxide in practically quantitative yield. In alkaline solution, oxalic acid and a volatile acid (probably acetic) are also formed. Elevation of temperature of oxidation results generally in increase of carbon dioxide, and decrease of oxalic acid, in the product. Results at 50° are identical for dextrose, lævulose, and *d*-mannose, and at 75° for dextrose and lævulose, which affords a verification of the results of de Bruyn with regard to the action of alkalis on these carbohydrates; it is concluded that these identities must be due to equilibria in aqueous solution leading, from either carbohydrate, to the same active component, in accordance with the views of Nef. At 50—100°, with increasing concentrations of alkali, the yield of oxalic acid from lævulose reaches a maximum, a minimum, and a second maximum, the yield of carbon dioxide varying conversely. It is concluded that this is due to the intermediate formation, in amount varying with the alkali concentration, of formaldehyde, glycollaldehyde, and glyceraldehyde, the first being oxidised to carbon dioxide, and the last two to oxalic acid and carbon dioxide. The second maximum of oxalic acid is ascribed to the intermediate formation of lactic acid.

F. G. WILLSON.

Mechanism of carbohydrate oxidation. II. Oxidation of *d*-galactose. W. L. EVANS and C. A. BUEHLER (J. Amer. Chem. Soc., 1925, **47**, 3098—3101; cf. preceding abstract).—The oxalic acid–carbon dioxide ratio in the product of oxidation of *d*-galactose varies with the alkalinity, owing to the shifting of the equilibria between the above carbohydrate and its isomerides with varying alkalinity. With increase in alkalinity, the above ratio tends to become identical for dextrose and *d*-galactose, a result ascribed to the increasing predominance of glyceraldehyde in the equilibria derived from both carbohydrates. As elevation of temperature shifts the equilibria also in the direction of glyceraldehyde, it also tends to identity in the oxalic acid–carbon dioxide ratio in the oxidation products from the two carbohydrates. F. G. WILLSON.

Mechanism of carbohydrate oxidation. III. Oxidation of the hexitols *d*-mannitol, *d*-sorbitol, and dulcitol. W. L. EVANS and C. W. HOLL (J. Amer. Chem. Soc., 1925, **47**, 3102—3105; cf. preceding abstracts).—The oxidation of the above hexitols by aqueous potassium permanganate yields results qualitatively similar to those reported for dextrose and galactose; it is concluded that the oxidation proceeds through the intermediate formation of aldohexoses. F. G. WILLSON.

Oxidation of dextrose by means of copper in sodium carbonate solution (Soldaïni's reagent). F. W. JENSEN and F. W. UPSON (J. Amer. Chem. Soc., 1925, **47**, 3019—3024).—Copper chloride (275 g.) was added, in aqueous solution, to an aqueous solution of sodium carbonate (275 g., anhydrous). Dextrose (25 g.) was then added, the mixture diluted to 2500 c.c., and vigorously agitated at 100° until precipitation of cuprous oxide was complete, the reaction requiring about 8 hrs. After removal of the cuprous oxide, the filtrate was acidified with hydrochloric acid and excess of copper removed as sulphide, the filtrate from this being then evaporated at 50—70°/20—30 mm., and the residue freed from volatile acids by several distillations to dryness with 100-c.c. portions of distilled water. The following products, in amounts quoted, were in this way obtained from 200 g. of dextrose. Formic acid, 30·86 g.; glycollic acid, 15·3 g.; gluconic acid, 1—2 g.; mannonic acid, small amount; arabonic acid, 6 g., isolated as the brucine salt; erythronic acid, 3·6 g., isolated as the brucine salt and identified as the lactone; *dl*-glyceric acid, 6·2 g., isolated as the brucine salt; and *d*-threonic acid, trace. These products differ from those obtained by oxidation with Fehling's solution only in the relatively smaller amount of hexonic acids present in the oxidation product. F. G. WILLSON.

Behaviour of dextrose and certain other carbohydrates towards dyes and towards potassium ferricyanide in an alkaline medium. E. KNECHT and E. HIBBERT (J.C.S., 1925, **127**, 2854—2860).—In the presence of potassium or sodium hydroxide, under specified conditions, certain carbohydrates are oxidised to a definite degree by methylene-blue or by potassium indigotintetrasulphonate, the excess of which is titrated with titanous chloride. The amount of indigotin reduced corresponds with 3 atoms of oxygen per mol. of dextrose, galactose, or glucosamine hydrochloride, 4 atoms per mol. of lævulose, 3½ per mol. of invert-sugar, and 6 per mol. of maltose, whence it appears that maltose has undergone hydrolysis. 2:2′-Bis-oxythionaphthendisulphonic acid behaves similarly with dextrose and lævulose, whilst with dextrose, lævulose, and glucosamine, potassium ferricyanide gives the same results as does indigotin. It is concluded that dextrose and galactose are converted into tetrahydroxyhexanedicarboxylic acids, and that lævulose gives equimolecular proportions of a mono- and a di-carboxylic acid. On using potassium ferricyanide to oxidise dextrose, titration with alkali yields results which confirm the hypothesis that a dicarboxylic acid is formed. Use of an alkali carbonate and hydrogen carbonate in the titration of dextrose with indigotin does not give rise to a higher degree of oxidation. If dextrose or lævulose is boiled for 2 min. with excess of sodium hydroxide, the amount of alkali neutralised corresponds with 2 mols. of lactic acid. Glycuronic acid can be determined volumetrically by means of potassium indigotintetrasulphonate, or by the osazone titration method. In presence of alkali hydroxide, kitone-blue A supplies two atomic proportions of oxygen to both dextrose and lævulose, corresponding with production of glycuronic acid and hydroxygluconic acid, respectively; by superimposing an indigotin titration on the kitone-blue titration, one more atom of oxygen is taken up in each case. Rosinduline 2B (or G) supplies one atomic proportion of oxygen to dextrose, and on superimposing a methylene-blue titration no further oxidation occurs; it is suggested that gluconic acid is the oxidation product. F. M. HAMER.

Reducing power of methylated sugars. G. ZEMPLÉN and G. BRAUN (Ber., 1925, **58**, [*B*], 2566—2570).—A method is described for the identification of partly methylated sugars if obtained in small amount by the hydrolysis of methylated disaccharides and thus not actually isolable in substance. The sugar is hydrolysed with boiling 2·5% hydrochloric acid for 3 hrs. and the reducing power determined by Bertrand's method. The following data are obtained on the basis that the reducing power of dextrose=100: βγε-trimethyl-lævoglucosan, after hydrolysis, 10·6; βγε-trimethylglucose, 9·8; βγε-trimethylmethylglucoside, after hydrolysis, 9·4; βγζ-trimethylglucose, 27·1; βγεζ-tetramethylglucose, 13·6; βγεζ-tetramethylmethylglucoside, after hydrolysis, 12·5; heptamethylmethylgentiobioside, after hydrolysis, 12·1; heptamethylmethylcellobioside, after hydrolysis, 20·2. H. WREN.

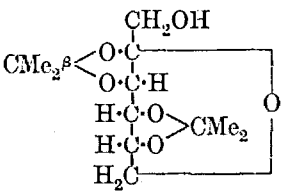
Synthesis of βγε(or βγδ)-trimethylglucose. J.C. IRVINE and J. W. H. OLDHAM (J.C.S., 1925, **127**, 2729—2735).—The constitution of βγε-trimethylglucose has been confirmed by the following synthesis: triacetylglucosan was converted into triacetyldibromoglucose; from this was formed triacetylmethylglucoside bromohydrin, which with alcoholic ammonia yielded methylglucoside bromohydrin. The bromo-

hydrin when methylated gave a mixture from which pure trimethylmethylglucoside bromohydrin was isolated. This, when heated at 150° with alcoholic potassium acetate, gave a 72% yield of a pure crystalline trimethyl-β-methylglucoside identical with that obtainable from the trimethylglucose under investigation. In the glucoside finally obtained, the hydroxy-group occupies the position of the bromine atom in triacetylmethylglucoside bromohydrin, and as Fischer reduced the latter to triacetylmethyl*iso*rhamnoside, the group must be in the ζ-position and the methyl groups in the corresponding sugar must be in the positions β, γ, and ε. Dibromotriacetyl-glucose, -maltose, and -glucosan are all convertible into the same form of trimethylglucose.

B. W. ANDERSON.

Acetone [*iso*propylidene] compounds of sugars and their derivatives. III. Constitution of β-di*iso*propylidenefructose. H. OHLE [with I. KOLLER and G. BEREND] (Ber., 1925, **58**, [*B*], 2577—2584; cf. A., 1924, i, 1168).—To elucidate the structure of β-di*iso*propylidenefructose (*loc. cit.*), the compound has been converted by the methods of Purdie, Freudenberg, and Hixon, and, most advantageously, by methyl sulphate and sodium hydroxide, into β-*diisopropylidenemethylfructose*, m. p. 48—49°, $[\alpha]_D^{20}$ −38·26° in alcohol, −29·53° in chloroform, and the latter substance has been hydrolysed with alcoholic sulphuric acid at 38—40°. The specific rotation of the solution during the hydrolysis varies in the manner characteristic of β-di*iso*propylidenefructose, thus showing that structural alteration has not occurred during methylation, and that during removal of the acetone residues the derivative of an unstable fructose passes into the derivative of a stable form. The failure of the resulting methylfructose to solidify in contact with γ-methylfructose (cf. Irvine and Hynd, J.C.S., 1909, **95**, 1220) and its inability to yield an osazone preclude the possibility of the presence of the methyl group in the γ- or ζ-position, and hence the annexed formula is the only possible expression of the constitution of β-di*iso*propylidenefructose. To obtain evidence of a positive nature, β-di*iso*propylidenefructose has been oxidised by potassium permanganate in aqueous alkaline solution, whereby an acid, $C_{12}H_{18}O_7$, is obtained which retains all the carbon atoms of the parent sugar. The acid has not been obtained crystalline, but is characterised as the *potassium* salt, $C_{12}H_{17}O_7K,H_2O$, $[\alpha]_D^{21}$ −31·75° in water, and the *aniline* salt, m. p. 120°, $[\alpha]_D^{20}$ −31·3° in chloroform. Removal of the acetone residues results in the production of a ketohexonic acid, of which the *potassium* salt, $C_6H_9O_7K,H_2O$, $[\alpha]_D^{22}$ −70° in water, *brucine* salt, $C_{29}H_{36}O_{11}N_2,3H_2O$, $[\alpha]_D^{20}$ −56·9° in water, and *phenylhydrazine* salt of the corresponding phenylosazone, $C_{24}H_{28}O_5N_4$, m. p. 102—103°, are described. The acid is not identical with the expected α-ketogluconic acid, but is possibly an isomeride thereof.

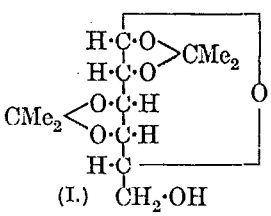
H. WREN.



Acetone [*iso*propylidene] compounds of sugars and their derivatives. IV. Constitution of diacetonegalactose [galactose di*iso*propylidene ether]. H. OHLE and G. BEREND (Ber., 1925, **58**, [*B*], 2585—2589).—Even under the mildest experimental conditions, the oxidation of galactose di*iso*propylidene ether by potassium permanganate proceeds less definitely than that of β-di*iso*propylidenefructose (preceding abstract), yielding oxalic acid in addition to *diisopropylidenegalacturonic acid*, m. p. 157° (*potassium* salt, $C_{12}H_{17}O_7K,0{\cdot}5H_2O$, $[\alpha]_D^{20}$ −61·09° in water). The acid is hydrolysed to *d*-galacturonic acid, which could not be caused to crystallise; the specific rotation, as judged from the behaviour of the barium salt dissolved in dilute hydrochloric acid, is $[\alpha]_D^{20}$ +46·7°, whereas Ehrlich gives +53·4° for the pure acid. The solution does not exhibit mutarotation. The acid gives a sparingly soluble basic lead salt and a characteristic *brucine* salt,

$C_{29}H_{36}O_{11}N_2,H_2O$,

m. p. 189° (decomp.), $[\alpha]_D^{20}$ −7·5° in water, but the characteristic cinchonine salt could not be obtained. With phenylhydrazine it gives the *phenylhydrazine* salt of the phenylosazone of *d*-galacturonic acid, $C_{24}H_{28}O_5N_6$, m. p. 140° (decomp.). The behaviour of the acid leaves no doubt as to its identity with *d*-galacturonic acid (cf. Svanberg and Bergman, A., 1924, i, 1285), and thereby establishes the presence of the terminal ·CH_2·OH group in galactose di*iso*propylidene ether. Contrary to Svanberg, however, the authors do not accept the presence of an αγ-bridge in the sugar, since galactose di*iso*propylidene ether is obtained by treatment of galactose with acetone in the presence of anhydrous copper sulphate (the *acetate* of galactose *di*isopropylidene ether has m. p. 108°, $[\alpha]_D^{20}$ −48·08° in chloroform), and in these conditions it is scarcely possible to assume a displacement of the oxygen bridge which Haworth, Ruell, and Westgarth (J.C.S., 1924, **125**, 2468) have shown to be in the αε-position. The constitution (I) is most probable for galactose di*iso*propylidene ether.

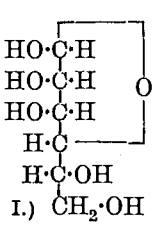


(I.)

H. WREN.

Acetone [di*iso*propylidene] compounds of sugars and their derivatives. V. Constitution of diacetonemannose [mannose di*iso*propylidene ether]. H. OHLE and G. BEREND (Ber., 1925, **58**, [*B*], 2590—2592).—Mannose di*iso*propylidene ether is very readily oxidised by potassium permanganate in dilute aqueous-alkaline solution, but the action practically ceases when one atomic proportion of oxygen has been utilised and *potassium* d-*diisopropylidenemannonate*, $C_{12}H_{18}O_7K,H_2O$, m. p. above 210° (decomp.), $[\alpha]_D^{20}$ −31·8° in water, is obtained in more than 80% yield. The corresponding free acid could not be isolated on account of the readiness with which it becomes converted into d-*diisopropylidenemannonolactone*, $C_{12}H_{18}O_8$, m. p. 126°, $[\alpha]_D^{20}$ +51° in chloroform, which is also obtained when the potassium salt is treated with benzoyl chloride in the presence of pyridine. The acetone residues are very easily

removed from the potassium salt by means of *N*-sulphuric acid, yielding *d*-mannonolactone, m. p. 149—151°, $[\alpha]_D^{20}$ +54° in water. The constitution of mannose di*iso*propylidene ether is thereby established, and, since it can be prepared from acetone and mannose in the presence of anhydrous copper sulphate, the similar structure (I) may be assigned to mannose; this is contrary to the conception of Haworth (A., 1925, i, 1133), who has assigned the amylene oxide structure to all aldoses.

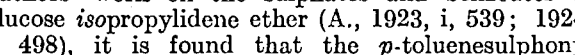


I.)

H. WREN.

Acetone (di*iso*propylidene) compounds of sugars and their derivatives. VI. Acyl derivatives of monoacetoneglucose [glucose *iso*propylidene ether]. H. OHLE and E. DICKHÄUSER (Ber., 1925, **58**, [*B*], 2593—2606).—In continuation of the authors' work on the sulphates and benzoates of glucose *iso*propylidene ether (A., 1923, i, 539; 1924, i, 498), it is found that the *p*-toluenesulphonyl derivatives resemble the sulphates and that the differences observed between the latter compounds and the benzoates are therefore to be ascribed to the presence of the sulphur atom.

γ-p-*Toluenesulphonylglucose* iso*propylidene ether* is prepared as an amorphous substance, $[\alpha]_D^{20}$ −11·65° in chloroform, by the partial hydrolysis of γ-*p*-toluenesulphonylglucose di*iso*propylidene ether (Freudenberg and Ivers, A., 1922, i, 523) with aqueous acetic acid; it is readily reconverted by acetone in the presence of anhydrous copper sulphate into 3-*p*-toluenesulphonylglucose di*iso*propylidene ether, and does not exhibit any tendency to pass into the ζ-isomeride in the presence of sodium hydroxide solution. It is transformed by benzoyl chloride in the presence of pyridine at 40° into the amorphous γ-p-*toluenesulphonyl-ζ-benzoylglucose di*iso*propylidene ether*, $[\alpha]_D^{21}$ −11·21° in chloroform, or by a larger proportion of the acid chloride into the crystalline γ-p-*toluenesulphonyl-εζ-dibenzoylglucose di*iso*propylidene ether*, m. p. 156°, $[\alpha]_D^{22}$ −68·38° in chloroform. With *p*-toluenesulphonyl chloride in the presence of chloroform at 40°, it affords *γζ-di*-p-*toluenesulphonylglucose* iso*propylidene ether*, an amorphous substance, $[\alpha]_D^{20}$ −4·92° in chloroform, which, with benzoyl chloride and pyridine, gives an amorphous compound not identical with γε-di-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether. ζ-p-*Toluenesulphonylglucose* iso*propylidene ether*, m. p. 108°, $[\alpha]_D^{20}$ −9·29° in chloroform, is prepared by the action of the acid chloride on glucose *iso*propylidene ether in the presence of pyridine and chloroform; with benzoyl chloride and pyridine, it affords amorphous ζ-p-*toluenesulphonyl-γε-dibenzoylglucose di*iso*propylidene ether*, $[\alpha]_D^{21}$ −51·38° in chloroform. The action of a considerable excess of *p*-toluenesulphonyl chloride on glucose *iso*propylidene ether or ζ-*p*-toluenesulphonylglucose *iso*propylidene ether in the presence of pyridine and chloroform leads to the production of *εζ-di*-p-*toluenesulphonylglucose* iso*propylidene ether*, m. p. 160°, $[\alpha]_D^{20}$ −6·37° in chloroform; the amorphous *εζ-di*-p-*toluenesulphonyl-γ-acetylglucose* iso*propylidene ether* has $[\alpha]_D^{22}$ −28·02° in chloroform. When εζ-di-*p*-toluenesulphonylglucose *iso*propylidene ether is treated with an excess of benzoyl chloride in the presence of pyridine, one of the *p*-toluenesulphonyl groups is replaced by benzoyl, and since the product is not identical with the crystalline ε-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether, it is regarded as ζ-p-*toluenesulphonyl-ε-benzoylglucose* iso*propylidene ether*, $[\alpha]_D^{20}$ −29·6° in chloroform. Confirmation of this view is found in the comparative difficulty in forming the di-*p*-toluenesulphonyl compound, for which a large excess of the reagent is necessary, and in the very ready loss of a *p*-toluenesulphonyl group by the hydrolysis of γ-di-*p*-toluenesulphonyl-ζ-benzoylglucose *iso*propylidene ether by alkali hydroxide. The same ease of replacement is observed in the hydrolysis by acid of εζ-di-*p*-toluenesulphonylglucose *iso*propylidene ether, which, somewhat unexpectedly, yields a compound, $[\alpha]_D$ about +38·6°, regarded as ζ-p-*toluenesulphonylglucose anhydride*,



A third p-*toluenesulphonylglucose* iso*propylidene ether*, m. p. 132°, $[\alpha]_D^{21}$ +34·3° in chloroform, is prepared by the action of a large excess of *p*-toluenesulphonyl chloride on glucose *iso*propylidene ether dissolved in a boiling mixture of pyridine and chloroform.

γ-Benzoylglucose *iso*propylidene ether is obtained from the corresponding di*iso*propylidene ether by a modification of the method of Fischer and Noth (A., 1918, i, 225). Attempts to transform glucose *iso*propylidene ether into a dibenzoyl derivative were only partly successful, and the product was not transformed by *p*-toluenesulphonyl chloride into the crystalline γ-*p*-toluenesulphonyl-εζ-dibenzoylglucose *iso*propylidene ether. ζ-Benzoylglucose *iso*propylidene ether is transformed by benzoyl chloride in the presence of pyridine and chloroform into ε-p-*toluenesulphonyl-ζ-benzoylglucose* iso*propylidene ether*, m. p. 142°, $[\alpha]_D^{22}$ +9·34° in chloroform, or γε-*di*-p-*toluenesulphonyl-ζ-benzoylglucose* iso*propylidene ether*, m. p. 113°, $[\alpha]_D^{22}$ +1·61° in chloroform, according to the relative proportion of the reactants. In general, it appears that the primary alcoholic group, if free, reacts most readily in the substitution of glucose *iso*propylidene ether. If the ζ-position is already substituted, the acyl group enters mainly in the ε-position. The preparation of γ-monosubstituted derivatives does not appear directly possible.

H. WREN.

Reaction of lævulose with alanine. C. NEUBERG and M. KOBEL (Biochem. Z., 1925, **162**, 496—501).—When a lævulose solution is mixed at the ordinary temperature with a solution of *dl*-alanine, a momentary increase in rotation occurs. Dextrose does not show this phenomenon.

P. W. CLUTTERBUCK.

Transformations of the sugar nitrates. J. W. H. OLDHAM (J.C.S., 1925, **127**, 2840—2845).—Although αζ-diacetyl-βγε-trimethylglucose yields a non-crystallising syrup when treated with fuming nitric acid, interaction of βγε-trimethylglucosan and

fuming nitric acid, in presence of chloroform and phosphorus pentoxide, yields *βγε-trimethylglucose αζ-dinitrate*, m. p. 86°, $[\alpha]_D$ +149·3° in chloroform; this dinitrate has no action on Fehling's solution. By boiling with methyl alcohol in presence of barium carbonate, it gives *trimethylmethylglucoside ζ-mononitrate*, m. p. 53—54°, n_D 1·4565, which is hydrolysed, by boiling with iron dust in acetic acid, to the same trimethylmethylglucoside as is obtained from trimethylglucosan; the mononitrate is unchanged by heating with alcoholic ammonia, but treatment with sodium iodide gives the same trimethylmethylglucoside iodohydrin as was obtained from Fischer's acetodibromoglucose (Irvine and Oldham, this vol., 149). Triacetylglucosan on treatment with fuming nitric acid in presence of chloroform, phosphoric oxide, and nitrogen pentoxide yields a syrup, together with *triacetylglucose αζ-dinitrate*, m. p. 132—133°, $[\alpha]_D$ +144·2° (in fuming nitric acid and chloroform); *tetra-acetylglucose ζ-mononitrate* has m. p. 142—143°, $[\alpha]_D$ +23·2° in acetic acid, and is hydrolysed to the corresponding *tetra-acetylglucose*, m. p. 126·5—127·5°, $[\alpha]_D$ +9·8° in chloroform. Reaction of triacetylglucose αζ-dinitrate with methyl alcohol yields *triacetylmethylglucoside ζ-mononitrate*, m. p. 133·5—134·5°, $[\alpha]_D$ −14·3° in chloroform, and this is hydrolysed to *triacetylmethylglucoside*, m. p. 134—134·5°, $[\alpha]_D$ −19·1° in chloroform, and converted by sodium iodide into *triacetylmethylglucoside ζ-iodohydrin*, m. p. 111—112·5°, $[\alpha]_D$ +0·9° in chloroform. Treatment of triacetylmethylglucoside ζ-mononitrate with methyl-alcoholic dimethylamine yields methylglucoside ζ-mononitrate in the form of a syrup, which on methylation by the silver oxide reaction gives trimethylmethylglucoside ζ-mononitrate, whilst triacetylmethylglucoside ζ-iodohydrin is converted by dimethylamine into *methylglucoside ζ-iodohydrin*, m. p. 157—158°, $[\alpha]_D$ −16·1° in chloroform. Mother-liquors from the recrystallisation of triacetylmethylglucoside ζ-mononitrate contain an *acetonitropentose*, m. p. 168—169°, $[\alpha]_D$ +92·0° in chloroform. The specific rotations of the compounds in various solvents are recorded. F. M. Hamer.

Soluble and insoluble salts of hexosediphosphoric acid. C. Neuberg and S. Sabetay (Biochem. Z., 1925, **161**, 240—243).—A pure calcium salt can be obtained from the commercial product "candiolin." It is sparingly soluble in cold or hot water, but a soluble form is obtained by adding ammonia to its solution in lactic acid and precipitating the filtered solution by alcohol. On heating a solution of this substance the less soluble modification is precipitated.

The barium salt has similarly been obtained in a soluble and an insoluble form. Magnesium yields a normal salt which is remarkably soluble in cold water, but separates on boiling. It is also more resistant to alkalis than hexosediphosphoric acid. The presence of ammonium chloride prevents the precipitation of the magnesium and also of the calcium salts by heat.

Hexosediphosphoric acid can be acetylated by the action of acetic anhydride on the calcium salt.

C. Rimington.

Glucosephosphoric acid. S. Sabetay and L. Rosenfeld (Biochem. Z., 1925, **162**, 469—478).—Sucrosephosphoric acid on hydrolysis with 1% oxalic acid solution gives a glucosephosphoric acid which is separated as the barium salt and purified by recrystallisation of the cinchonidine or brucine salts. The presence of dextrose is confirmed polarimetrically. Since treatment with phenylhydrazine gives glucosazone, phosphoric acid being eliminated, it seems probable that the substance is glucose-β-phosphoric acid. It is not identical with glucose-α-, -γ-, or -ζ-phosphoric acid, and from the structure of sucrose it appears unlikely that the phosphoric acid is attacked in the δ-position. The acid is not identical with Robison's glucosephosphoric acid.

P. W. Clutterbuck.

Nomenclature of polysaccharides. M. Bergmann (Ber., 1925, **58**, [*B*], 2647—2650).—The method of indicating the position of the oxygen bridge in saccharides by figures placed after the name of the compound, *e.g.*, methylglucoside (1 : 4), becomes involved when saccharide residues are linked through an oxygen atom and the points of union must also be indicated. It is proposed to indicate oxygen bridges which unite saccharide residues by a two-headed arrow placed over or, if necessary, under the name of the polysaccharide and extending at either end to the name of the component indicated; a figure at either end of the arrow shows the position of the bridge. Thus raffinose (cf. Haworth, Hirst, and Ruell, J.C.S., 1923, **123**, 3127) may be expressed,

$$\overset{1\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow 6}{\text{galactosido (1 : 5)-glucosido}}\ \overset{1\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow 2}{\text{(1 : 4)-fructoside (2 : 6)}}$$

and trihexosan may be written

$$\overset{1\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow 4}{\text{glucosido (1 : 6)-glucosido}}\ \overset{4\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow 1}{\text{(1 : 4)-glucosan}}\ \overset{6\leftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\rightarrow 1}{\text{(1 : 6).}}$$

It is proposed to use the suffix "osan" in naming the anhydride, $C_{12}H_{20}O_{10}$, of a disaccharide, $C_{12}H_{22}O_{11}$, only in those cases in which a carbonyl or lactol group is involved in the loss of water. The term anhydro-sugar, *e.g.*, anhydroglucose, is used for sugar derivatives which contain the intact lactol or carbonyl group.

H. Wren.

Syntheses of *iso*maltose and gentiobiose. A. Pictet and A. Georg (Compt. rend., 1925, **181**, 1035—1037).—That di-*l*-glucosan (A., 1921, i, 766) is the anhydride of *iso*maltose (Fischer, A., 1896, i, 119) is confirmed by the conversion of the former into the latter by two methods. Di-β-glucosan is allowed to remain in solution in concentrated hydrochloric acid, the acid is removed in a vacuum, and by means of silver carbonate, dextrose is removed by fermentation, and *iso*maltose is obtained. To obviate the possibility that the *iso*maltose is formed by hydrolysis of the di-β-glucosan to dextrose and conversion of the dextrose into *iso*maltose by the agency of the hydrochloric acid, a second synthesis has been effected. On treatment with acetyl bromide and pouring on ice, di-β-glucosan yields *octa-acetyliso-maltose bromohydrin*, which on treatment with barium hydroxide gives *iso*maltose. Acetylation of Fischer's *iso*maltose (*loc. cit.*) gives, in addition to an *iso-maltose*

acetate, 3% of gentiobiose octa-acetate (Zemplen, A., 1915, i, 119). L. F. HEWITT.

Digitoxin. A. WINDAUS and C. FREESE (Ber., 1925, **58**, [*B*], 2503—2510).—Pure digitoxin is prepared by extracting the crude glucoside with chloroform, whereby gitoxin remains undissolved. Ether is added to the chloroform extracts and the precipitated digitoxin is crystallised from ethyl acetate, dilute alcohol, or a mixture of chloroform and ether until the m. p. 255—257° is attained. Analyses of the air-dried substance agree with the formula $C_{42}H_{66}O_{13},H_2O$, whereas for the material dried in a vacuum they are in harmony with Cloetta's formula, $C_{44}H_{70}O_{14}$ (cf. A., 1921, i, 39). Determinations of *M* give low values for a compound $C_{44}H_{70}O_{14}$, and the composition $C_{42}H_{66}O_{13},0{\cdot}5H_2O$ is therefore suggested. Hydrolysis of digitoxin by acids leads, according to Cloetta (*loc. cit.*), to digitoxigenin (1 mol.), digitoxose (2 mols.), and an oily compound, $C_8H_{14}O_4$, obtained in the crystalline state by distillation of digitoxin in a high vacuum; analyses and determinations of mol. wt. agree with the formula $C_6H_{10}O_3$ better than with $C_8H_{14}O_4$ and it is therefore concluded that it is an anhydrodigitoxose analogous to β-glucosan. Hence, digitoxigenin and digitoxose may be regarded as the sole products of the hydrolysis of digitoxin, which probably proceeds thus: $C_{42}H_{66}O_{13}+3H_2O=C_{24}H_{36}O_4+3C_6H_{12}O_4$. The yield of digitoxigenin actually obtained is in good agreement with this conception. Digitoxin, $C_{42}H_{66}O_{13}$, and gitoxin, $C_{42}H_{66}O_{14}$, must therefore be closely related compounds. Both compounds yield digitoxose (3 mols.) when hydrolysed, together with digitoxigenin, $C_{24}H_{36}O_4$, and gitoxigenin, $C_{24}H_{36}O_5$, respectively, and the possibility therefore exists that the latter substance is oxydigitoxigenin. To test the presence of the same carbon skeleton in the compounds, digitoxigenin has been converted by the methods employed previously for gitoxigenin (cf. Windaus and Bandte, A., 1923, i, 1107; Windaus and Schwarte, A., 1925, i, 1295) into its anhydro-derivative, $C_{24}H_{34}O_3$, and subsequently hydrogenated in aqueous methyl alcohol in the presence of colloidal palladium to *tetrahydroanhydrodigitoxigenin*, $C_{24}H_{38}O_3$, m. p. 146—147°; in glacial acetic acid solution, hydrogenation proceeds less satisfactorily, the most sparingly soluble *product*, m. p. 163—164°, having also the composition $C_{24}H_{38}O_3$, so that probably a mixture of stereoisomerides is formed. Tetrahydroanhydrodigitoxigenin is isomeric with hexahydrodigitaligenin. *Tetrahydroanhydrodigitoxigenone*, m. p. 240—241° [*oxime*, m. p. 217° (decomp.)], prepared by oxidation of tetrahydroanhydrodigitoxigenin, is isomeric with the ketone, $C_{24}H_{36}O_3$, derived from gitoxigenin; this is also true of the *lactone*, $C_{24}H_{38}O_2$, m. p. 180—181°, obtained from it by reduction with zinc amalgam and concentrated hydrochloric acid.

In confirmation of Cloetta's observations (*loc. cit.*), it is found that digitoxigenin is converted by dehydrating agents into anhydrodigitoxigenin, $C_{24}H_{34}O_3$, m. p. 183—184°; the compound, m. p. 223°, described by Kiliani (A., 1899, i, 71) under this name appears to be a transformation product of the anhydro-compound which it is proposed to designate "β-anhydrodigitoxigenin." Toxigenone, obtained by oxidation of anhydrodigitoxigenin, for which Kiliani has proposed the formula $C_{19}H_{24}O_3$, certainly contains 24 carbon atoms in its molecule, since it can be converted into tetrahydroanhydrodigitoxigenin; the low analytical figures are probably due to obstinately retained solvent of crystallisation. Digitoxigenone, to which Kiliani has ascribed the formula $C_{19}H_{26}O_4$, is probably $C_{24}H_{34}O_4$. H. WREN.

Glycerol glucoside. H. S. GILCHRIST and C. B. PURVES (J.C.S., 1925, **127**, 2735—2745).—Glycerol glucoside is best obtained by heating a solution of dextrose in glycerol at 100° with 0·25% of dry hydrogen chloride. The product on methylation yields a *hexamethyl* derivative, b. p. 190—192°/12 mm., n_D 1·4497, and this on hydrolysis forms βγεζ-tetramethylglucose together with a dimethylglycerol. Thus the constitution of the parent glucoside is

$$CH_2(OH)\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH(OH)\cdot CH\cdot O\cdot CH_2$$
$$\qquad\qquad\qquad

dextrins with alcohol and hydrogen chloride, and subsequently hydrolysing, there is formed in each case a mixture of di-, tri-, and tetra-methylglucose; $\beta\gamma\varepsilon\zeta$-tetramethylglucose and $\beta\gamma\varepsilon$-trimethylglucose have been characterised. The tetramethylglucose is shown to be a genuine scission product of the methylated dextrins.

On a large scale, methylation of the total polymerised glucosan, followed by distillation, yields *trimethylglucosan*, b. p. 135°/0·2 mm., *di(trimethylglucosan)*, b. p. 205—210°/0·2 mm., n_D 1·4720, $[\alpha]_D^{20}$ +46·5° in chloroform, and *poly(trimethylglucosan)*. Treatment of di(trimethylglucosan) with methyl alcohol and hydrogen chloride yields approximately equimolecular proportions of dimethylmethylglucoside, $[\alpha]_D$ +108·4° in methyl alcohol, n_D 1·4743, and tetramethylmethylglucoside, together with a little trimethylmethylglucoside, and the proportions are confirmed by hydrolysis, which gives dimethylglucose and $\beta\gamma\varepsilon\zeta$-tetramethylglucose. Similarly, the poly(trimethylglucosan) is converted into approximately equimolecular proportions of $\beta\gamma\varepsilon\zeta$-tetramethylmethylglucoside, $\beta\gamma\varepsilon$-trimethylmethylglucoside, and dimethylmethylglucoside, together with a little monomethylmethylglucoside; hydrolysis yields equimolecular proportions of the tetra-, tri-, and di-methylglucoses. A series of polymerides from mono- to octa-glucosan is now complete with the exception of the penta-form; the specific rotations of the parent glucosides and their trimethyl derivatives are tabulated, as also are those of the methylated sugars to which the glucosans give rise.

From all the polyglucosans, invariable products are $\beta\gamma\varepsilon\zeta$-tetramethylglucose and dimethylglucose, which must be either the $\beta\gamma$- or, more probably, the $\beta\varepsilon$-derivative. As regards the mechanism of the polymerisation, it is supposed that glucosan is first converted into glucose, one molecule of which condenses with a second molecule of glucosan, and the process continues catalytically. Provisional formulæ are assigned to the di- and tri-glucosans; triglucosan may be regarded as glucosan maltoside. Besides the condensation type of reaction which occurs in polymerisation, a type involving association may take place. Evidence is adduced to show that the methylation process does not alter the configuration of a sugar, and does not disturb the positions in which sugar residues are attached, and that, during methylation and hydrolysis, non-glucosidic methoxy-groups do not migrate, whence it is concluded that the process is valid for determining the structure of carbohydrates. F. M. HAMER.

Distillation of cellulose etc. in presence of hydrogen under pressure and catalysts. H. E. FIERZ-DAVID and M. HANNIG.—See B., 1926, 35.

Action of diazomethane on cellulose. M. NIERENSTEIN (Ber., 1925, **58**, [*B*], 2625).—Contrary to the observations of Schmid (A., 1925, i, 1386), diazomethane causes slight methylation of cotton cellulose (cf. Geake and Nierenstein, A., 1914, i, 1146). H. WREN.

Stability of nitrocelluloses. J. DUCLAUX.—See B., 1926, 46.

Cellulose esters of higher fatty acids. G. KITA, T. MAZUME, I. SAKURADA, and S. NAKAJIMA.—See B., 1926, 45.

Solubility of lignins in phenols. A. HILLMER.—See B., 1926, 46.

Ionisation of ethoxytrimethylammonium hydroxide, trimethylamine oxide, and their derivatives. W. A. NOYES (J. Amer. Chem. Soc., 1925, **47**, 3025—3030; cf. A., 1923, i, 444).—The conductivities of phenyltrimethylammonium hydroxide, ethoxytrimethylammonium hydroxide, and trimethylamine oxide have been redetermined, in solutions of concentration 0·509, 0·159, and 0·5*M*, respectively. In the cases of the first two bases, addition of hydrobromic acid, in amount not quite sufficient for complete neutralisation, increased the resistance of the solutions, indicating that the association of the hydroxide is similar to that of the bromide. The conductance of the amine oxide solution was considerably increased by the addition of a similar proportion of hydrobromic acid. These results confirm the observation of Stewart and Maeser (A., 1925, i, 12) that ethoxytrimethylammonium hydroxide is completely ionised in dilute aqueous solution, the discordant results of previous experiments being probably due to the ease with which this compound decomposes into trimethylamine and acetaldehyde. The structure of trimethylamine oxide is discussed, and it is concluded that this base is correctly represented by the formula $[NMe_3{\cdot}OH]OH$. It is pointed out that the polar valency of nitrogen in ammonium salts is none the less a real valency because it is polar, and as this valency has been shown to be capable of holding a nitrogen atom in a stable ring formation in solution, it is to be regarded as attached to the nitrogen atom, and not belonging to the group as a whole (cf. Noyes and Potter, A., 1915, i, 79). The differences between "polar" and "non-polar" valencies are therefore of degree rather than of kind. F. G. WILLSON.

Action of Grignard reagent on amino-acids. VI. Decomposition of amino-alcohols by heat. F. BETTZIECHE and A. EHRLICH (Z. physiol. Chem., 1925, **150**, 191—196).—β-Amino-ααβ-triphenylethanol when heated in a sealed tube with 10% sodium hydroxide gives a good yield of a mixture of benzophenone and benzylamine, together with small amounts of benzoic acid. On heating this alcohol in a sealed tube with 5% ammonia or even with water to 130°, the same end-products are obtained. Heating alone in a sealed tube to 150° brings about the same decomposition. β-Amino-β-phenyl-αα-dibenzylethanol may be similarly decomposed by heating with water to 160°, yielding dibenzyl ketone and benzylamine. β-Amino-αα-diphenylethanol is decomposed by heating with water to 200° to give methylamine and benzophenone. β-Amino-αα-dibenzylethanol requires to be heated with water to 210° before decomposition ensues, when methylamine and dibenzyl ketone are produced. If this alcohol is heated alone in a sealed tube to 220°, the same decomposition takes place. The yields throughout are from 50 to 80% of the theoretical. H. D. KAY.

Action of Grignard reagent on amino-acids. VII. Deamination of β-amino-αα-dibenzylethanol. F. BETTZIECHE and A. EHRLICH (Z. physiol. Chem., 1925, **150**, 197—201).—By the action of nitrous acid on substituted β-amino-αα-diphenylethanols, a migration of a phenyl group between two neighbouring carbon atoms ensues, and a ketone is produced thus: $R{\cdot}CH(NH_2){\cdot}CPh_2{\cdot}OH \rightarrow R{\cdot}CHPh{\cdot}CO{\cdot}Ph$. The same type of reaction occurs with β-amino-αα-dibenzylethanol, with β-amino-αα-dibenzylpropanol, with β-amino-β-phenyl-αα-dibenzylethanol, and with β-amino-ααβ-tribenzylethanol, one of the benzyl groups migrating.

H. D. KAY.

Basis for the physiological activity of certain -onium compounds. III. Choline derivatives. R. R. RENSHAW and J. C. WARE (J. Amer. Chem. Soc., 1925, **47**, 2989—2995).—*Chloroacetylcholine chloroacetate*, m. p. 303° (indef.), obtained by heating choline chloride in a sealed tube with excess of chloroacetyl chloride at 100°, has about one-thousandth of the activity of acetylcholine (cf. Hunt and Renshaw, A., 1925, i, 861). *Iodomethyl acetate*, b. p. 65°/14 mm., α^{22} 1·902, obtained by the action of paraformaldehyde on acetyl iodide, condenses with trimethylamine in absolute alcohol with formation of *acetylformocholine iodide*, $NMe_3I{\cdot}CH_2{\cdot}OAc$, m. p. 152°, which is 12—24 times as active as formocholine (cf. Hunt and Renshaw, *loc. cit.*). *Acetylformocholine chloride* (*chloroplatinate*), obtained similarly, affords a 90% yield of formocholine chloride (cf. Hunt and Taveau, Hygienic Lab. Bull., 1911, **73**, 28; Dale, J. Pharmacol., 1914, **6**, 147) when warmed for 24 hrs. with 95% alcohol to which a few drops of concentrated hydrochloric acid have been added. Condensation of β-chloroethyldichloroarsine with trimethylamine in cold toluene yields *dichloroarsinylethyltrimethylammonium chloride*, $NMe_3Cl{\cdot}CH_2{\cdot}CH_2{\cdot}AsCl_2$, m. p. 181·1°, which, when treated with alcoholic sodium hydroxide, yields *arsinylethyltrimethylammonium chloride*, $NMe_3Cl{\cdot}CH_2{\cdot}CH_2{\cdot}AsO$, m. p. 194°, the toxicity of which is greater to animals infected with trypanosomes than to normal animals.

Neurine bromide is obtained in 90% yield by treating powdered bromocholine bromide, in suspension in an equal weight of absolute alcohol, with 1 mol. of potassium hydroxide in absolute alcoholic solution (0·094 g. per c.c.). When bromine is added to an alcoholic solution of neurine bromide, it is rapidly absorbed at first, but the reaction velocity diminishes considerably before 1 mol. of the halogen is absorbed, and considerable decomposition takes place when the solution is evaporated. An unstable *perbromide*, which decomposes in a few days when kept in a stoppered bottle, was isolated, and it is suggested that the retardation of the addition of bromine to neurine is due to the formation of this substance, the bromine in which is more active in substitution than in addition reactions. Bromoethenyltrimethylammonium bromide (cf. Bode, A., 1892, 806) melts sharply at 145° when heated 4° per min., and sharply at 155·5—156° when heated 7° per min.

When choline chloride is heated with phosphoryl chloride, the *compound* $NMe_3(O{\cdot}POCl_2){\cdot}CH_2{\cdot}CH_2Cl$ is obtained.

F. G. WILLSON.

Hydroxyamino-acids. I. F. BETTZIECHE (Z. physiol. Chem., 1925, **150**, 177—190).—Pyruvic acid is produced in small quantities when serine is boiled with 15% sulphuric acid. It is identified as the phenylhydrazone. From the same amino-acid, by warming with nitrous acid, a yield of 7·2% of the theoretical quantity of acetaldehyde is obtained. When phenylserine is boiled with 10% sulphuric acid, phenylacetaldehyde is produced in small yield, and also a very small quantity of β-phenylnaphthalene. Phenylpyruvic acid is present in the ethereal extract of the reaction mixture. The yield of β-phenylnaphthalene may be increased to 65% by conducting the reaction in a sealed tube at 160—170°. Concentrated sulphuric acid at the ordinary temperature produces traces of phenylpyruvic acid from phenylserine, and at a later stage phenylacetaldehyde, also in minute quantity. If the mixture is kept for 1—2 days, a poor yield of β-phenylnaphthalene is obtained. By boiling phenylserine with 10% sodium hydroxide, the benzylidene compound of β-amino-αα-diphenylethanol is obtained. The first action of the alkali is to decompose the phenylserine into benzaldehyde and glycine, which then react together to give the substituted ethanol.

H. D. KAY.

Trihydroxytriethylamine oxide and substituted hydroxylamines with hydroxyethyl radicals. L. W. JONES and G. R. BURNS (J. Amer. Chem. Soc., 1925, **47**, 2966—2973).—When treated with excess of ethylene oxide, first at 0° for 2 days, then at the ordinary temperature in a closed vessel for 2 weeks, hydroxylamine yields *trihydroxytriethylamine oxide*, $[CH_2(OH){\cdot}CH_2]_3N{\cdot}O$, m. p. 104—105·5° (*benzoyl* derivative and *hydrochloride*, oils; *picrate*, m. p. 73—74°; *chloroplatinate*, two forms, m. p. 99° and 158·0—158·5°). Reduction of trihydroxytriethylamine oxide with zinc dust and water affords trihydroxytriethylamine. When the latter is refluxed with acetyl chloride in excess, it yields the oily *hydrochloride* of *triacetoxytriethylamine*, b. p. 206—207°/27 mm. (*chloroplatinate*, m. p. 123·5°), which is oxidised to the above amine oxide when treated with ethereal benzoyl peroxide or aqueous hydrogen peroxide and the resulting ester hydrolysed with hydrochloric acid. When heated with aqueous sodium hydroxide, trihydroxytriethylamine oxide yields mainly dihydroxydiethylamine, whilst the action of concentrated hydrochloric acid at 100° affords trihydroxytriethylamine and probably an *oxidation product* of this base. The action of ethylene oxide on 1 mol. of hydroxylamine affords *dihydroxydiethylhydroxylamine* (*hydrochloride*; *picrate*, m. p. 104—106°; *chloroplatinate*, m. p. 117·5—118°; *tribenzoate*), which is converted into morpholine on reduction with zinc dust and hydrochloric acid, followed by treatment with 70% sulphuric acid, the primary reduction product being dihydroxydiethylamine. *O*-Ethylhydroxylamine reacts similarly with ethylene oxide, with formation of *O-ethyldihydroxydiethylhydroxylamine*, $[CH_2(OH){\cdot}CH_2]_2N{\cdot}OEt$ (*chloroplatinate*, m. p. 166—167°), together with the *ether*, $[CH_2(OH){\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2]_2N{\cdot}OEt$ (*chloroplatinate*,

mobile liquid), whilst *O* : *N*-diethylhydroxylamine yields analogously O-*ethyl*-N-*ethyl*-N-*hydroxyethyl-hydroxylamine*, b. p. 63°/10 mm., b. p. 170°/760 mm. (*hydrochloride*; *chloroplatinate*, m. p. 143—143·5°). When heated with ethylene oxide at 100° *O* : *N*-diethylhydroxylamine yields, in addition to the last-named base, a *base*, b. p. 150—165°/15 mm., probably $CH_2(OH)\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot NEt\cdot OEt$ (*chloroplatinate*, oily). Ethylene oxide has no action on hydroxyurethane at temperatures up to 100°. Addition of alcoholic potassium hydroxide to an alcoholic solution of hydroxyurethane causes precipitation of the *salt* $CO_2Et\cdot NH(OH)\cdot CO_2Et\cdot NH\cdot OK$, which puffs when heated. Ethylene oxide is without action on *m*-nitrobenzhydroxamic acid at the ordinary temperature. The sodium and potassium salts of hydroxyurethane are not alkylated by ethylene chloro- or iodo-hydrins. β-*Chloroethyl* 3 : 5-*dinitrobenzoate*, m. p. 92°, is described. When heated with ethylene glycol, naphthylcarbimide is converted into the *urethane*, $CH_2(OH)\cdot CH_2\cdot O\cdot CO\cdot NH\cdot C_{10}H_7$, m. p. 102—103°.

F. G. Willson.

Action of nitrous acid on amides and other "amino"-compounds. R. H. A. Plimmer (J.C.S., 1925, **127**, 2651—2659).—Amides and urethane do not react with nitrous acid in presence of acetic acid but react quantitatively in presence of 2*N*-hydrochloric acid. Similar results are given by guanine and creatine, but carbamide reacts quantitatively in presence of acetic acid. Biuret reacts with one nitrogen atom in presence of acetic acid, two nitrogen atoms in presence of small amounts of hydrochloric acid, and three nitrogen atoms in presence of 2*N*-hydrochloric acid (molecule disrupted). These results are best interpreted by giving to amides and similar compounds alternative formulæ, such as $R\cdot C(OH){:}NH$, which changes into the form $R\cdot CO\cdot NH_2$ in the presence of mineral acid. B. W. Anderson.

Behaviour of cyanamide in acid and alkaline solution. G. Grube and G. Motz.—See this vol., 131.

Preparation of *s*-trimethylguanidine. M. Schenck (Z. physiol. Chem., 1925, **150**, 121—132).—The hydriodide of *s*.-trimethylguanidine may be prepared as follows: (*a*) in 55% yield by heating cyanogen iodide with an alcoholic solution of methylamine in a sealed tube to 130°; (*b*) in 45% yield by similar treatment of symmetrical dimethylguanidine hydriodide; (*c*) in 27% yield by treating methylguanidine hydriodide in the same way; (*d*) in 23% yield from guanidine hydriodide in the same way. The same end-product is obtained if the hydrochloride of guanidine and methylamine are the reagents, and the reaction mixture after heating for 4 hrs. at 125—130° is treated with sodium iodide in absolute alcohol, giving a yield of 36%. *s*-Trimethylguanidine may be characterised by the insolubility of its hydriodide in absolute alcohol, and by the preparation and analysis of its chloroaurate and chloroplatinate.

H. D. Kay.

Acetyl derivatives of thiocarbamide and carbamide. Constitution of thiocarbamide. A. Hugershoff (Ber., 1925, **58**, [*B*], 2477—2487).—The action of acetic anhydride (1·5 mols.) on thiocarbamide at the lowest possible temperature gives a *triacetyl* derivative, $C_8H_{14}O_3N_4S_2$, m. p. 154°, which is also produced with 3 mols. of the anhydride or when mono- or di-acetylthiocarbamide is dissolved in hot alcohol and the solution is cooled. The compound dissolves unchanged in cold *N*-sodium hydroxide solution, but yields thiocarbamide and unchanged triacetyl compound when the solution is warmed. Warm 94% sulphuric acid hydrolyses it to monoacetylthiocarbamide, whereas an excess of hydrochloric acid (25%) converts it into thiocarbamide. It reacts with aromatic bases at 100°, giving monoacetylthiocarbamide and the corresponding acetylated amine. Its constitution is most readily explained by the hypothesis that it is a salt-like compound of the mono- and di-acetyl derivative in which the former functions as base and the latter as acid; attempts to prepare a similar substance from the more strongly basic thiocarbamide and diacetylthiocarbamide were, however, unsuccessful. The direct production of the triacetyl compound, non-formation of the mono- and di-acetylated product (cf. Kohmann, A., 1915, i, 944; Werner, J.C.S., 1916, **109**, 1120), and failure to obtain a compound from thiocarbamide and diacetylthiocarbamide are only explicable if the *M* usually assigned to thiocarbamide is doubled and the compound is regarded as a salt, $NH_2\cdot C(:NH)\cdot SH,H_2N\cdot C(:NH)\cdot SH$, in which only three hydrogen atoms can be acetylated. A diacetyl derivative can only be obtained from thiocarbamide when the salt-like union is dissolved by the addition of a stronger acid or a base (cf. Werner, *loc. cit.*). This conception of the constitution of thiocarbamide has not yet been confirmed by determinations of *M* in neutral solvents.

Thiocarbamide has m. p. 176° and, after resolidification, m. p. 147—148°. Acetylation of the resolidified product yields monoacetylthiocarbamide. It appears, therefore, that the basic half of the molecule undergoes transformation, but remains united to the acidic portion of the thiocarbamide molecule, thus preventing the salt-like union of the simple thiocarbamide molecules. It is probable that the thiocarbamide molecule suffers preliminary fission in all cases in which it appears to function in the unimolecular form.

Werner has assumed diacetylthiocarbamide to be a *NS*-derivative, thereby accounting for its formation from the potassium compound, $CH_3N_2\cdot SK$. Since, however, the author's work on the acetylation of arylated thiocarbamides (cf. Gibson, Diss., Göttingen, 1901) has led him to the conclusion that the first phase of the reaction consists in the addition of acetic anhydride to the thiocarbamide, this conception does not appear well founded and the behaviour of the diacetyl derivative toward sodium hydroxide is more readily harmonised with the structure

$$NAc{:}C(SH)\cdot NHAc.$$

The strongest argument in favour of the addition theory is found in the contrasted behaviour of *s*- and *as*-disubstituted thiocarbamides, the former of which alone yield acetyl derivatives, whereas according to the customary formulation the latter contain a free amino-group. If the *iso*-structure of the thiocarbamide derivatives be accepted, the constitutions

AcO·C(SH)(NHR)·NRAc and AcO·C(NR$_2$)(SH)·NHAc may be assigned to the additive compounds from which acetic acid can be eliminated only if a hydrogen atom is attached to the other nitrogen atom, as is the case with thiocarbamide, its monosubstituted and symmetrically disubstituted derivatives. The constitution NAc:C(SH)·NHAc,NH$_2$·C(SH):NAc, is therefore assigned to the triacetyl compound.

In contrast to thiocarbamide, carbamide yields directly a monoacetyl compound and cannot give a triacetyl derivative, since it does not form a salt with itself. Carbamide reacts vigorously with acetic anhydride at 120—130°, giving monoacetylcarbamide in about 32% yield. With the object of causing isomerisation of CO(NH$_2$)$_2$ to NH:C(OH)·NH$_2$, Werner has added sulphuric acid, thereby increasing the yield to 78%, but this yield is also attained in the absence of acid if the reactants are heated cautiously on the water-bath. The production of acetylcarbamide is attributed to the initial addition of the anhydride to the *iso*-form of carbamide, and the constitution NAc:C(OH)·NHAc is ascribed to the diacetyl derivative. In this case, also, the acetyl group attached to the amido-nitrogen is more readily removed than that present in the imido-group. Werner's conception that the readily removed acetyl group is attached to oxygen is regarded as improbable.

H. WREN.

Catalytic hydrogenation of azines. III. Hydrogenation of di*iso*butylideneazine. K. A. TAIPALE (J. Russ. Phys. Chem. Soc., 1925, **56**, 81—107).—Much of this paper has been already published (A., 1923, i, 547). The hydrogenation of *iso*butaldazine proceeds in two stages. One molecule of hydrogen first combines in the α : β (γ : δ)- and α : δ-positions, with formation of *iso*butyl*iso*butylidenehydrazine and azo*iso*butane. Union of a second hydrogen molecule with these compounds then yields *s*-di*iso*butylhydrazine, which on further hydrogenation gives *iso*butylamine and di*iso*butylamine. In certain of its properties, hydrazo*iso*butane resembles hydrazo-methane and -ethane, but in others it differs from these and from hydrazo*iso*propane.

Hydrazoisobutane (*diisobutylhydrazine*), CHMe$_2$·CH$_2$·NH·NH·CH$_2$·CHMe$_2$, b. p. 169·5—170°/735 mm., 63·5°/10 mm., d_0^0 0·8166, n_D^{20} 1·42757, oxidises readily in the air; it reduces ammoniacal silver solution and Fehling's solution, and gives unstable violet-blue colorations with nitrous acid and with ferric chloride. Its acid *oxalate*, C$_8$H$_{20}$N$_2$,H$_2$C$_2$O$_4$, has m. p. 170° (decomp.).

αβ-Diisobutyl-δ-phenylsemicarbazide, NHPh·CO·N(C$_4$H$_9$)·NH·C$_4$H$_9$, has m. p. 68·5—69°. *Dicarbanilyldiisobutylhydrazine*, NHPh·CO·N(C$_4$H$_9$)·N(C$_4$H$_9$)·CO·NHPh, prepared by the action of phenylcarbimide on di*iso*butylhydrazine, has m. p. 219·5°. *αβ-Diisobutyl-δ-phenylthiosemicarbazide*, NHPh·CS·N(C$_4$H$_9$)·NH·C$_4$H$_9$, m. p. 118·5—119°.

Azoisobutane, CHMe$_2$·CH$_2$·N:N·CH$_2$·CHMe$_2$, prepared by oxidation of hydrazo*iso*butane, by decomposition of the nitroso-compound of di*iso*butylhydrazine, or by partial reduction of the corresponding aldazine, has b. p. 145—145·5°/752 mm., d_0^0 0·7933—0·7947, n_D^{20} 1·41271—1·41291, remains unchanged at 150—160°, undergoes isomerisation into the hydrazone when heated with aqueous alkali hydroxide, and is readily reduced to hydrazo*iso*butane by hydrogen in presence of platinum-black. *isoButylhydrazine* forms a hygroscopic *dihydrochloride*, a *monohydrochloride*, m. p. 92—93°, a *hydrogen oxalate*, m. p. 168—169°, and a *dibenzoyl* derivative, m. p. 169·5—170°. *isoButylsemicarbazide*, NH$_2$·CO·N(NH$_2$)·C$_4$H$_9$, has m. p. 91·5—92°. *isoButylisobutylidenehydrazine*, CHMe$_2$·CH:N·NH·CH$_2$·CHMe$_2$, b. p. 175—176°/740 mm., 64·5°/12 mm., d_0^0 0·8389, n_D^{20} 1·44482—1·44502, reduces ammoniacal silver solution slowly and Fehling's solution when heated.

T. H. POPE.

Proposed international rules for numbering organic ring systems. A. M. PATTERSON (Rec. trav. chim., 1926, **55**, 1—18).—See A., 1925, i, 824.

Diphensuccindene series. XII. Colourless and coloured isomeric hydrocarbons of the diphensuccindene series. K. BRAND and T. SASAKI (Ber., 1925, **58**, [*B*], 2546—2550).—An extension of previous work (Brand and Schläger, A., 1924, i, 157) to compounds containing the propyl and *iso*propyl groups.

Diphensuccindane-9 : 12-dione is converted by magnesium propyl bromide in the presence of ether into 9 : 12-*di*-n-*propyldiphensuccindane*-9 : 12-*diol*, m. p. 121—122°, which is transformed by boiling formic acid or by boiling alcohol and hydrochloric acid into a mixture of colourless 9 : 12-*di*-n-*propylidenediphensuccindane*, m. p. 157—158°, and red 9 : 12-*di*-n-*propyl*-$\Delta^{9:11}$-*diphensuccindadiene*, $\begin{matrix} CPr^n:C\cdot C_6H_4 \\ C_6H_4\cdot C:CPr^n \end{matrix}$, m. p. 135—136°. The propylidene compound is oxidised by chromic acid in the presence of sulphuric acid to propaldehyde and diphensuccindanedione. Either hydrocarbon is hydrogenated in the presence of palladised charcoal and aqueous alcohol to 9 : 12-*di*-n-*propyldiphensuccindane*, m. p. 98—99°. Similarly, diphensuccindanedione and magnesium *iso*propyl bromide afford 9 : 12-*diiso*propyldiphensuccindane-9 : 12-*diol*, m. p. 132—133° (*compounds* +3MeOH and +3EtOH are also described), which, when boiled with a mixture of formic and glacial acetic acids, or with alcoholic hydrogen chloride, passes into red 9 : 12-*diiso*propyl-$\Delta^{9:11}$-*diphensuccindadiene*, m. p. 178—179°, and colourless 9 : 12-*diiso*propylidene-*diphensuccindane*, m. p. 189°. The latter hydrocarbon is oxidised by chromic acid to acetone and diphensuccindanedione. Either hydrocarbon is hydrogenated to 9 : 12-*diiso*propyldiphensuccindane, m. p. 80—81°.

H. WREN.

Parachor and chemical constitution. III. Orientation isomerism in aromatic compounds. S. SUGDEN and H. WILKINS (J.C.S., 1925, **127**, 2517—2522; cf. A., 1924, ii, 662; 1925, ii, 936, 937).—In order to show that the values of the parachor for benzene derivatives are not dependent on the orientation of the substituents and are in agreement with the values arrived at by summation of the atomic parachors, several *o*-, *m*-, and *p*-disubstituted benzenes have been investigated. The parachors,

together with the calculated values, are: xylenes, *o*-, 283·3, *m*-, 283·8, *p*-, 283·8, calc., 285·1; nitrotoluenes, *o*-, *301·1*, *m*-, *300·6*, *p*-, 302·8, calc., 303·1; chloronitrobenzenes, *o*-, *299·9*, *m*-, *298·9*, *p*-, 300·0, calc., 301·2; bromonitrobenzenes, *o*-, *312·9*, *m*-*313·5*, *p*-, *313·5*, calc., 315·0; toluonitriles, *o*-, *290·6*, *m*-, *295·6*, *p*-, *294·4*, calc., 292·9. Ten of these values (printed in italics) are based on new surface tension measurements carried out by the method of maximum bubble pressure (A., 1924, ii, 154). The values for *m*-toluonitrile given by Turner and Merry (J.C.S., 1910, **97**, 2075) are shown to be inaccurate.

E. E. WALKER.

Condensation of phenylacetylene under the influence of primary amines. K. KRASYSKI and A. KIPRIANOV (J. Russ. Phys. Chem. Soc., 1925, **56**, 1—10).—When heated in a sealed tube with an aqueous solution of methylamine or ethylamine, phenylacetylene is converted into *s*-triphenylbenzene, the yield with the former amine being quantitative. Under similar conditions, dimethylamine, diethylamine, trimethylamine, or piperidine converts phenylacetylene into an oily substance, whilst aqueous ammonia, potassium hydroxide solution, or water yields tarry products. *s*-Triphenylbenzene is formed by the condensation of phenylacetaldehyde with methylamine but not by that of acetophenone with methylamine. It seems probable that, when phenylacetylene and a primary amine are heated together, the former is converted by the action of the water into phenylacetaldehyde, which reacts with the amine to give either $CH_2Ph{\cdot}CH{:}NMe$ or $CHPh{:}CH{\cdot}NHMe$; polymerisation of the latter, with regeneration of the amine, would then yield triphenylbenzene.

T. H. POPE.

Derivatives of β-methylnaphthalene. K. DZIEWOŃSKI, (MLLE.) J. SCHOENÓWNA, and E. WALDMANN (Bull. Intern. Acad. Polonaise, 1925, **A**, 55—68).—See A., 1925, i, 1056.

Dissociation into free radicals of substituted dixanthyls. II. Dissociating influence of the *cyclo*hexyl group. J. B. CONANT and L. F. SMALL (J. Amer. Chem. Soc., 1925, **47**, 3068—3077; cf. A., 1925, i, 955).—Condensation of magnesium *p*-chlorobenzyl chloride and xanthone in ethereal suspension, followed by hydrolysis with ice and ammonium chloride, affords p-*chlorobenzylidenexanthen*, yellow, m. p. 131—131·5°, as a precipitate, whilst treatment of the dried ethereal layer with a cold acetic anhydride solution of perchloric acid yields p-*chlorobenzylxanthyl perchlorate*, m. p. 209° to a black liquid, after darkening at 200°. Reduction of the latter with vanadous sulphate affords *di*-p-*chlorobenzyldixanthylethane*, m. p. 147—149° in air, with brown coloration, 152° in carbon dioxide. In bromobenzene solution, this absorbs oxygen in amount corresponding with that required for complete formation of a *peroxide*. The power of absorbing oxygen is destroyed by heating the bromobenzene solution at 100° for 1 hr. Condensation of magnesium *iso*amyl bromide with xanthone affords similarly iso*amylxanthydrol*, m. p. 95—97°, decomposing into xanthone and *iso*amyl alcohol when kept. iso*Amylxanthyl perchlorate*, yellow, m. p. 165°, yields, when reduced with vanadous sulphate, *di*iso*amyldixanthylethane*, m. p. 137—145° in air, 158—160° in carbon dioxide. This absorbs oxygen in bromobenzene solution, the end-product of the oxidation being xanthone. It gives a colourless solution in naphthalene at 80° under carbon dioxide, which deepens to red at the b. p. of the solvent, and then rapidly fades if boiling is continued. n-*Hexylxanthyl perchlorate*, yellow, m. p. 126—127°, obtained similarly, is reduced by vanadous sulphate to *di*-n-*hexyldixanthylethane*, m. p. 119—133° in air, 138° in carbon dioxide. This absorbs oxygen in solution, and shows colour changes, in solution, typical of dissociable ethanes. cyclo*Hexylxanthydrol*, m. p. 152°, and cyclo*hexylxanthyl perchlorate*, m. p. 163° with blackening, after darkening at 160°, are obtained analogously. Reduction of the latter with vanadous sulphate affords *di*cyclo*hexyldixanthyl*, light yellow, which absorbs oxygen instantaneously and exhibits the usual colour changes in solution, increased dissociation on dilution being indicated by deviation from Beer's law. cyclo*Hexylxanthyl peroxide*, m. p. 147—148° (decomp.), decomposes violently when heated in hydrogen at 145—150°, with formation of xanthone and a yellow *liquid*.

F. G. WILLSON.

Replacement of halogens from aromatic compounds. R. H. CLARK and R. N. CROZIER (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 153—156).—Various aromatic halogen compounds were heated with an alcoholic solution of potassium hydroxide, sodium methoxide, or sodium ethoxide in sealed tubes. The following numbers represent the percentage replacement of halogen after 42 hrs. at 151°, the numbers in parentheses representing the replacement calculated from a consideration of the electronic theory as elaborated by Fry ("Electronic Conception of Valency and the Constitution of Benzene"): *o*-dichlorobenzene 6·8 (50); *m*-dichlorobenzene 9·3 (100); 1 : 2 : 4-trichlorobenzene 29·4 (33·3); 1 : 2 : 4 : 5-tetrachlorobenzene 35 (50); hexachlorobenzene 38·7 (50); pentabromophenol 39·1 (40); 2 : 4-dichloroaniline 0 (0); 2 : 4 : 6-trichlorophenol 0 (0); 2 : 6 : 4-dichloronitroaniline 0 (0); *p*-chloroaniline 0 (0); *m*-chloroaniline 1·5 (100); *o*-bromotoluene 2·4 (100); *m*-bromotoluene 2·1 (100).

J. S. CARTER.

Sulphuryl chloride. IV. New chlorinating agent. Preparation of polychloro-derivatives of toluene. O. SILBERRAD (J.C.S., 1925, **127**, 2677—2684).—When sulphuryl chloride containing about 1% of sulphur chloride is run into a mixture of toluene and anhydrous aluminium chloride at 70°, aluminium sulphur chloride is instantaneously formed, and by adjusting the relative proportions of hydrocarbon and reagent an almost theoretical yield of mono- (1 : 2 and 1 : 4), di- (1 : 2 : 4), tri- (1 : 2 : 3 : 4 and 1 : 2 : 4 : 5), and penta-chlorotoluene may be obtained. The new reagent does not attack the side chain.

B. W. ANDERSON.

Reactions of aromatic compounds containing multivalent iodine. C. WILLGERODT (J. pr. Chem., 1925, [ii], **111**, 353—367).—A systematic review

of the known facts regarding the formation and reactions of this type of compound.

R. W. WEST.

Halogen derivatives of diphenylmethane. A. E. TSCHITSCHIBABIN and A. A. SCHESLER (J. Russ. Phys. Chem. Soc., 1925, **56**, 149—152).—The method previously used for the reduction of alcohols of the diphenyl- and triphenyl-methane series (A., 1911, i, 277) serves for the preparation of various halogenated diphenylmethane derivatives (cf. also A., 1911, i, 278).

Phenyl-p-chlorophenylcarbinol, $C_6H_4Cl{\cdot}CHPh{\cdot}OH$, m. p. 61°, prepared from *p*-chlorobenzaldehyde and magnesium phenyl bromide, is reduced by means of hydriodic acid in glacial acetic acid to phenyl-*p*-chlorophenylmethane. *Phenyl-o-chlorophenylcarbinol*, m. p. 65—65·5°, similarly obtained, yields *phenyl-o-chlorophenylmethane*, m. p. 13·2°, b. p. 164·5°/19 mm., d_0^0 1·1530. *Phenyl-m-chlorophenylcarbinol*, similarly obtained, has m. p. 38°. T. H. POPE.

Derivatives of toluene. R. POGGI (Atti R. Accad. Lincei, 1925, [vi], 2, 423—427).—m-*Nitrobenzyl iodide*, m. p. 84·5—86°, and 2 : 4-*dinitrobenzyl iodide*, m. p. 75·5—76°, are obtained by boiling the alcoholic solutions of the corresponding chlorides with a slight excess of potassium iodide. By boiling *p*-nitrobenzyl thiocyanate with concentrated sulphuric acid, p-*nitrobenzyl thiocarbamate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}CO{\cdot}NH_2,$$

m. p. 140—141°, is obtained. By prolonged boiling of this compound with 20% hydrochloric acid, hydrogen sulphide, carbon dioxide, and ammonia are eliminated, giving p-*nitrobenzyl mercaptan*. m-*Cyanobenzyl bromide*, m. p. 94—95·5°, is prepared by the Sandmeyer reaction from *m*-toluonitrile. m-*Cyanobenzyl iodide*, m. p. 113—114°, and o-*cyanobenzyl iodide*, m. p. 77—78°, were prepared by boiling the corresponding chloro-derivatives in alcoholic solution with potassium iodide. By boiling an alcoholic solution of *p*-cyanobenzyl chloride with sodium thiosulphate for an hour, *sodium* p-*cyanobenzyl thiosulphate*, $CN{\cdot}C_6H_4{\cdot}CH_2{\cdot}S_2O_3Na$, was obtained, which on prolonged heating at 70° with concentrated sulphuric acid gave p-*cyanobenzyl mercaptan*, m. p. 43°. Oxidation of this compound in the cold by alcoholic iodine solution gave pp'-*dicyanobenzyl disulphide*, m. p. 147·5°. F. G. TRYHORN.

Two forms of *o*-nitrotoluene. R. H. CLARK and R. N. CROZIER (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 157—158).—The α- and β-forms of *o*-nitrotoluene (Knoevenagel, A., 1907, i, 202) have practically the same refractive index and density and the same *M* as determined by the f. p. method. It is, however, claimed that the assumption of the existence of two electronic forms, $C_6H_4\overset{-}{M}e{\cdot}\overset{+}{N}O_2$ and $C_6H_4\overset{+}{M}e{\cdot}\overset{-}{N}O_2$, as an explanation for the existence of the two modifications is supported by the results of chemical tests.

J. S. CARTER.

2-Nitro-3 : 4-dimethoxy-1-methylbenzene (2-nitrohomoveratrole). E. MERCK CHEM. FABR.—See B., 1926, 30.

Reactions of organic thiosulphates. H. B. FOOTNER and S. SMILES (J.C.S., 1925, **127**, 2887—2891).—The organic sodium thiosulphates,

$$RS{\cdot}SO_2{\cdot}ONa$$

(cf. Price and Twiss, *ibid.*, 1907, **91**, 2021) share with the disulphoxides (A., 1925, i, 391) certain characteristic reactions of the thiol-sulphone group, due to instability of the dithio-system in substances of the type $RS{\cdot}SO_2X$; this group is readily split by alkali mercaptides and with varying ease by other reagents, the activity depending on the character of the group X. The organic thiosulphates are readily decomposed in aqueous solution by sodium mercaptides: $R{\cdot}S{\cdot}SO_3Na+NaSR' \longrightarrow RS{\cdot}SR'+Na_2SO_3$. When R and R' are the same, a single symmetrical disulphide is produced; when they are dissimilar, a mixture of the two possible symmetrical disulphides is usually obtained, probably because of secondary reaction of the mercaptide with the disulphide (Lecher, A., 1920, i, 433), $RS{\cdot}SR'+NaSR \rightleftharpoons RS{\cdot}SR+R'SNa$. The organic thiosulphates are quickly and almost quantitatively decomposed by aqueous alkali cyanide, giving the corresponding thiocyanates in excellent yield, $RS{\cdot}SO_3Na+NaCN \longrightarrow R{\cdot}SCN+Na_2SO_3$. The disulphoxides behave similarly but are much less reactive, $RS{\cdot}SO_2R+NaCN \longrightarrow R{\cdot}SO_2Na+R{\cdot}SCN$.

Di-*p*-toluenesulphonyl sulphide (Tröger, A., 1899, i, 905) behaves similarly towards the mercaptans, the sulphur chain being ruptured with formation of sulphinate and thiosulphonate together with the disulphide corresponding with the mercaptan used, $(C_7H_7{\cdot}SO_2)_2S+2RSNa \rightarrow C_7H_7{\cdot}SO_2{\cdot}SNa+C_7H_7{\cdot}SO_2Na+(RS)_2$. Whilst sodium dithionate is not attacked by alkali mercaptides, the tri- and tetra-thionates are rapidly decomposed, giving the disulphide $Na_2S_3O_6+2R{\cdot}SNa \longrightarrow (RS)_2+Na_2SO_3+Na_2S_2O_3$; $Na_2S_4O_6+2R{\cdot}SNa \longrightarrow (RS)_2+2Na_2S_2O_3$. This result is, in the authors' opinion, adequately explained by the structures proposed by Mendeléev for the polythionates. o-*Nitrophenyl benzyl disulphide* has m. p. 54°; *benzyl* 9-*anthryl disulphide*, m. p. 128°; p-*nitrobenzyl thiocyanate*, m. p. 79°, and 9-*anthryl thiocyanate*, m. p. 181°. M. JOHNSON.

Dependence of rotatory power on chemical constitution. XXVII. Optical properties of *n*-alkyl *p*-toluenesulphinates. H. PHILLIPS (J.C.S., 1925, **127**, 2552—2587).—When an optically inactive *n*-alkyl ester of *p*-toluenesulphinic acid is heated gently with *l*-β-octanol a mixture of a lævorotatory *n*-alkyl *p*-toluenesulphinate and a lævorotatory β-octyl *p*-toluenesulphinate is produced which can be separated by fractional distillation under very low pressures. Alcoholysis of the *l*-β-octyl *p*-toluenesulphinate thus produced yields an optically active *n*-alkyl ester of opposite sign. By these methods, using *l*-β-octanol, *n*-alkyl *p*-toluenesulphinates have been prepared with α^{25}_{5461} −6·72° and +0·92° and *n*-butyl esters with α^{25}_{5461} −3·46° and +16·52° (*l*=1 dm. in each case). The asymmetry must be attributed to the sulphur, and since only three groups are attached to this atom, the reason for this asymmetry is sought in the electronic structure. According to Lowry's theory, the oxygen should be

attached to the sulphur atom through a semipolar linking, the oxygen atom being negatively and the sulphur atom positively charged. The parachor (A., 1924, ii, 662) of ethyl *p*-toluenesulphinate has been determined by S. Sugden, and this confirms the presence of a semipolar linking (A., 1925, ii, 936). The observed asymmetry might have been attributed to the tetrahedral arrangement of three different groups and one lone pair of electrons, but the view that the asymmetry is due to the three groups not being coplanar with the positively charged sulphur atom is shown to be more in accordance with cognate facts. The existence of a positive charge is regarded as the essential factor making optical activity possible for a ter-covalent atom containing three different groups. The corresponding sulphonic acid and its *n*-alkyl esters do not give any indication that they can exist in optically active forms.

It is suggested that carboxylic esters contain a small proportion of an isodynamic form possessing a semipolar linking, the constitution of which is analogous to that of the sulphinic esters. The additional centre of asymmetry thus introduced would explain the complex dispersion of these esters.

Optically active *p*-toluenesulphinic esters undergo changes analogous to the Walden inversion. Thus if *l*-β-octanol is heated with ethyl *p*-toluenesulphinate, a lævorotatory ethyl ester remains. If this in turn is heated with *n*-butyl alcohol, a dextrorotatory *n*-butyl *p*-toluenesulphinate is obtained. On the other hand, if the inactive butyl ester is heated with *l*-β-octanol, a lævorotatory *n*-butyl *p*-toluenesulphinate is produced.

By means of a cycle of changes involving the oxidation of *p*-toluenesulphinic esters to the corresponding sulphonic esters, *l*-β-octanol has been converted into *d*-β-octanol and *l*-menthol into *d*-*neo*-menthol. It is shown that when the *p*-toluenesulphinate of an optically active carbinol (such as *l*-β-octanol) is treated with potassium acetate and ethyl alcohol the optically active alcohol is regenerated without inversion, but when the sulphinate is oxidised to the sulphonate and this then treated with potassium acetate and ethyl alcohol the acetate of *d*-β-octanol is produced, showing that inversion has taken place. The slow mutarotation of *p*-toluenesulphinic esters of *l*-β-octanol and of *l*-menthol caused by the labile nature of the rotation due to the sulphinic acid group has been studied. An equilibrium value of a^{25}_{5893} −35·1° is obtained after about 1000 hrs.

Ethyl dl-p-*toluenesulphinate* has b. p. 99—104°/0·1 mm., n^{25}_D 1·5309, d^{25}_4 1·114; *butyl* dl-p-*toluenesulphinate*, b. p. 90—95°/0·1 mm., n^{25}_D 1·5195, d^{25}_4 1·066; l-*menthyl* dl-p-*toluenesulphinate*, m. p. 108—109°, in acetone solution (*c*=2·609) gave $[\alpha]^{17}_{5461}$ −239·9° and $[\alpha]^{17}_{4359}$ −433·8°. E. E. Walker.

Constitution of the so-called diphenyl*cyclo*butane. R. Stoermer and C. Thier [and, in part, E. Laage] (Ber., 1925, **58**, [*B*], 2607—2615).—The "diphenyl*cyclo*butane" obtained by Stoermer and Biesenbach (A., 1905, i, 524) by the action of alcoholic potassium hydroxide on phenylacetaldehyde at high temperature and pressure is identified as αγ-diphenylpropene. The reaction appears to consist in the primary formation of the aldol,

$$CH_2Ph{\cdot}CH(OH){\cdot}CHPh{\cdot}CHO,$$

which passes into the corresponding, unsaturated aldehyde by loss of water and subsequently loses the aldehydic group as formic acid, thus giving αγ-diphenylpropene. The hydrocarbon, b. p. 178—179° (corr.)/14 mm., m. p. 15—16°, may be conveniently prepared in 67% yield by heating phenylacetaldehyde with alcoholic potassium hydroxide under reflux. It is identical with the compound obtained from α-benzylcinnamic acid by Dieckmann and Kämmerer (A., 1906, i, 820) and yields the same dibromide, m. p. 109°, and *pseudo*nitrosite, m. p. between 142° and 150°, according to the manner of heating; the latter compound is converted by diethylamine in boiling alcoholic solution into the *substance*, $C_{19}H_{24}O_2N_2$, m. p. 93°. The *nitrosochloride* has m. p. 166° (decomp.). αγ-Diphenylpropene is readily converted into αγ-diphenylpropane, b. p. 301—303° (corr.), 166—168°/16 mm., by sodium and boiling alcohol or hydrogen in the presence of palladised calcium carbonate. Oxidation of αγ-diphenylpropene by permanganate in alkaline solution yields only benzaldehyde, benzoic and phenylacetic acids; in acetone solution, particularly in the presence of sulphuric acid, benzaldehyde and *βγ-diphenylpropaldehyde hydrate*, $CH_2Ph{\cdot}CHPh{\cdot}CHO,H_2O$, m. p. 116—117° (*semicarbazone*, m. p. 189°), are produced. Ozonisation of αγ-diphenylpropene and subsequent decomposition of the ozonide yields only benzaldehyde, and benzoic and phenylacetic acids.

Under the modified conditions of preparation of αγ-diphenylpropene, three isomeric *β-benzyl-αγ-diphenyl-δ-valerolactones*, m. p. 109°, 133°, and 165°, respectively, are obtained as by-products. A fourth *isomeride*, m. p. 135°, was prepared during attempts to obtain the methyl ester from the dry sodium salt from the lactone, m. p. 109°, and methyl sulphate. Further, the lactone, m. p. 109°, exists in a dimorphous *form*, m. p. 122°. Apparently, the primary aldol passes into the corresponding unsaturated aldehyde which unites with a further molecule of phenylacetaldehyde, yielding the dialdehyde,

$$CH_2Ph{\cdot}CH(CHPh{\cdot}CHO)_2,$$

this is transformed by Cannizzaro's reaction into the compound,

$$CH_2Ph{\cdot}CH(CHPh{\cdot}CH_2{\cdot}OH){\cdot}CHPh{\cdot}CO_2H,$$

from which four isomeric β-benzyl-αγ-diphenyl-δ-valerolactones are derived by loss of water.

H. Wren.

Diacene [diacenaphthylidene] and its ketonic derivatives. K. Dziewoński and T. Lityński (Ber., 1925, **58**, [*B*], 2539—2544).—Diacenaphthylidenedione, $\begin{matrix}C_{10}H_6\\CO\end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix}C_{10}H_6\\CO\end{matrix}$, m. p. 287—288°, is conveniently prepared by the oxidation of acenaphthene in glacial acetic acid with potassium dichromate at 40—50°. The most advantageous method for the preparation of diacenaphthylidenone,

$$\begin{matrix}C_{10}H_6\\CO\end{matrix}\!\!>\!C{:}C\!<\!\!\begin{matrix}C_{10}H_6\\CH_2\end{matrix},$$

m. p. 258°, consists in boiling acenaphthylene dibromide in concentrated alcoholic solution with concentrated hydrochloric acid, whereby acenaphthen-

one is formed as by-product. Diacenaphthylidene, $C_{10}H_6>C:C<C_{10}H_6$ (CH_2 bridges), m. p. 271—273° [*picrate*, m. p. 214° (decomp.)] (cf. Doliński and Dzievoński, A., 1916, i, 138), is prepared by the reduction of diacenaphthylidenedione or diacenaphthylidenone by zinc dust in the presence of acetic anhydride and anhydrous sodium acetate. H. WREN.

Composition of rubicene. K. DZIEVOŃSKI and J. SUSZKO (Ber., 1925, **58**, [*B*], 2544—2546).—New analyses of rubicene confirm the composition, $C_{26}H_{12}$, assigned to it by Dzievoński and Suszko (A., 1922, i, 730) in place of the formula, $C_{26}H_{14}$, suggested by Pummerer and Ulrich (A., 1925, i, 1259; cf. also Pummerer, A., 1912, i, 182). H. WREN.

Action of amines on di- and tri-chloroacetic acids. A. S. WHEELER and E. DE W. JENNINGS (J. Elisha Mitchell Sci. Soc., 1924, **40**, 112).—When substituted amines are used, the di- and tri-chloroacetates are formed, respectively. However, with such amines as aniline and *o*-toluidine the dichloro-acid produces trichloroacetates.

CHEMICAL ABSTRACTS.

Action of aromatic amines on semicarbazide hydrochloride. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **56**, 55—60).—When semicarbazide hydrochloride is boiled with a primary aromatic amine, such as aniline, *o*- or *p*-toluidine, 2 : 3-xylidine, or benzylamine, the corresponding substituted carbamides are obtained: $NH_2R+NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2=NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_3$ and $NH_2{\cdot}NH{\cdot}CO{\cdot}NHR+NH_2R=NHR{\cdot}CO{\cdot}NHR+N_2H_4$ (cf. A., 1925, i, 984). T. H. POPE.

Action of magnesium butyl bromide on aromatic thiocarbimides. D. E. WORRALL (J. Amer. Chem. Soc., 1925, **47**, 2974—2976).—The following substituted amides of thiovaleric acid were obtained by the action of magnesium butyl bromide on the appropriate thiocarbimides (cf. Sachs and Loevy, A., 1903, i, 334; 1904, i, 307; Gilman, A., 1924, i, 382); *thiovaleryl-anilide*, m. p. 38—39°; -p-*toluidide*, m. p. 69—70°; -p-*anisidide*, m. p. 62—63°; -p-*chloroanilide*, m. p. 101·5—102°; -p-*bromoanilide*, m. p. 112°; -*diphenylamide*, m. p. 147—148°; -β-*naphthylamide*, m. p. 79—80°; and *bisthiovaleryl-p-phenylenediamide*, m. p. 198—199°. The action of hydroxylamine on these derivatives affords *oximes*, hydrogen sulphide and some ammonia being liberated. F. G. WILLSON.

Isomeric change in aromatic compounds. I. Conversion of diacylanilides into acylamino-ketones. A. W. CHAPMAN (J.C.S., 1925, **127**, 2818—2820).—When a current of dry hydrogen chloride is passed through fused diacetanilide or dibenzanilide, the acyl chloride and monoacylanilide result. Diacylanilides, when heated in presence of either hydrogen chloride or zinc chloride, are converted into the corresponding acylamino-ketones. The catalytic activity of the zinc chloride, which is ineffective when absolutely dry, is ascribed to the presence of a little free hydrogen chloride, without which rearrangement does not occur. Since the necessary conditions are exactly those under which hydrogen chloride decomposes the diacylanilides, it is suggested that this change, previously regarded as intramolecular (Chattaway, J.C.S., 1904, **85**, 386), is, in reality, a decomposition followed by recondensation, thus: $NPhAc_2+HCl \rightarrow NHPhAc+AcCl \rightarrow Ac{\cdot}C_6H_4{\cdot}NHAc+HCl$. M. JOHNSON.

Preparation of *p*-bromophenylhydroxylamine by the emulsification process. R. D. HAWORTH and A. LAPWORTH (J.C.S., 1925, **127**, 2970).—Reduction of *p*-bromonitrobenzene by the method previously described (*ibid.*, 1921, **119**, 770) is frequently unsuccessful. Good results are obtained by the use of more solvent benzene and more reducing solution. *p*-Bromonitrobenzene (5 g.), benzene (40 c.c.), hydrosulphide solution (120 g., *loc. cit.*, p. 769), and calcium chloride (5 g., in a little water) are emulsified. After 1½ hrs., solid ammonium chloride (5 g.) is added. After shaking, the precipitated *p*-bromophenylhydroxylamine (about 2·9 g.) is collected. A further yield (0·5 g.) can be obtained from the benzene layer by precipitation with petroleum (b. p. 40—60°). The sodium sulphide crystals used in making the reducing solution must be of good quality.

M. JOHNSON.

Dibromination of aceto-*m*-toluidide. S. C. J. OLIVIER (Rec. trav. chim., 1925, **44**, 1109—1112).—By the action of 2 mols. of bromine on an acetic acid solution of aceto-*m*-toluidide, a mixture is obtained which after hydrolysis consists of 73% of 4 : 6-dibromo-*m*-toluidine and 27% of 2 : 6-*dibromo*-m-*toluidine*, m. p. 66·5—67°. It is shown that the 2 : 6-dibromo-compound, m. p. 33—35°, previously described (Neville and Winther, J.C.S., 1880, **37**, 440) is a eutectic mixture of the two isomerides.

R. W. WEST.

Trinitrophenylnitroaminoethyl nitrate. R. C. MORAN.—See B., 1926, 78.

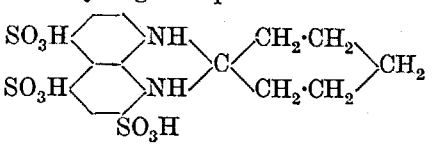
Preparation of some primary amines by the catalytic reduction of nitriles. W. H. CAROTHERS and G. A. JONES (J. Amer. Chem. Soc., 1925, **47**, 3051—3057).—*p*-Toluonitrile is reduced smoothly in acetic anhydride solution by hydrogen in presence of platinum oxide, with formation of *p*-methylbenzylacetamide, m. p. 110—111° (cf. Lustig, A., 1895, i, 162), in 88% yield. The reduction requires over 5 hrs. with hydrogen under 3 atm. pressure. In glacial acetic acid, a 71% yield of *pp'*-dimethyldibenzylamine, together with small proportions of the corresponding primary and tertiary amines, was obtained similarly in 6½ hrs. In absolute alcohol, reduction proceeds more slowly, and both primary and secondary amines are produced. In *n*-butyric anhydride, a 74% yield of p-*methylbenzyl*-n-*butyramide*, m. p. 71—72°, was obtained. Benzonitrile affords similarly, in acetic anhydride solution, benzylacetamide; in glacial acetic acid, benzylamine and dibenzylamine, the former predominating; and in absolute alcohol, ammonia and the primary and secondary amines. *o*-Toluonitrile is reduced similarly in acetic anhydride solution to *o*-methylbenzylacetamide, m. p. 76—76·5° (cf. Strassmann, A., 1888, 474), whilst phenylacetonitrile affords β-phenylethyl-

acetamide, in 63% yield. The above acetyl derivatives of primary amines are soluble in cold dilute hydrochloric acid, from which they are precipitated unchanged on addition of alkali; the corresponding aromatic sulphonyl derivatives are only slightly soluble in dilute alkali. The following acyl-derivatives of the above amines are described: p-*methylbenzyl-phenylcarbamide*, m. p. 188—188·2°, -p-*toluenesulphonamide*, m. p. 94·7—95·5°, and p-*bromobenzenesulphonamide*, m. p. 126·5—127·5°; o-*methylbenzylphenylcarbamide*, m. p. 167·5—168°, -*benzenesulphonamide*, m. p. 128·3—129·1°, -p-*toluenesulphonamide*, m. p. 118·7—119·2°, and -p-*bromobenzenesulphonamide*, m. p. 106·5—107°; β-*phenylethyl*-p-*bromobenzenesulphonamide*, m. p. 88·5—89·5°, and -phenylcarbamide, m. p. 153·5—154·5° (cf. Forster and Stötter, J.C.S., 1911, **99**, 1338). The success of the preparation of primary amines by reduction of nitriles in acid anhydride solution is ascribed to prevention of hydrolysis of the imine usually assumed to be formed intermediately, and to prevention of its condensation with the primary amine by the prior acylation of the latter. F. G. WILLSON.

Benzidine derivatives of thiocarbamide and azo dyes therefrom. L. PINTO.—See B., 1926, 43.

Action of sulphites on aromatic amino- and hydroxy-compounds. XII. Products of the action of sulphites on 1 : 8-dinitronaphthalene. H. T. BUCHERER and H. BARSCH (J. pr. Chem., 1925, [ii], **111**, 313—339; cf. A., 1925, i, 1338).—When 1 : 8-dinitronaphthalene is boiled with aqueous sodium hydrogen sulphite solution (8·3 mols. per mol. of dinitro-compound), and the cooled, filtered solution acidified, a naphthylenediaminetrisulphonic acid separates (cf. Fischesser, D.R.-P. 79577) in a yield of 8·8% of the theoretical, calculated on the dinitronaphthalene used, whilst the mother-liquor contains a further 15·4% yield of the acid, together with the sulphurous ester of an aminonaphtholtrisulphonic acid. The latter is hydrolysed by boiling with alkali, after which the above mother-liquor contains active material (evaluated by titration with diazo-solution) corresponding with 31·9% of the applied dinitronaphthalene. When the naphthylenediaminetrisulphonic acid is boiled with aqueous sodium hydrogen sulphite, it is converted into the sulphurous ester of an aminonaphtholtrisulphonic acid. As this reaction is hindered by a sulphonic group *ortho* or *meta* to the amino-group, it is concluded that the trisulphonic acid is actually 1 : 8-*naphthylenediamine*-2 : 4 : 5-*trisulphonic acid*, both of the alternative constitutions suggested by Fischesser (*loc. cit.*) being untenable. When the trisulphonic acid is boiled with *cyclo*hexanone in presence of concentrated hydrochloric acid, a condensation *product*, probably (I), is formed, which is not attacked by boiling sodium hydrogen sulphite solution.

(I.)



When 1 : 8-dinitronaphthalene is treated at 90° with sodium hydrogen sulphite solution in presence of ammonia (cf. D.R.-P. 215338), the cooled, filtered solution deposits, on acidification, a small proportion of α-naphthylamine-4 : 7-disulphonic acid, containing traces of the corresponding aminonaphtholdisulphonic acid and naphthylenediaminedisulphonic acid. The total yield of disulphonic acids corresponds with 6·9% of the dinitronaphthalene used, whilst the mother-liquor contains further an approximately equal proportion of the sulphurous ester of the aminonaphtholdisulphonic acid. When boiled with aqueous sodium hydrogen sulphite, α-naphthylamine-4 : 7-disulphonic acid is converted into the sulphurous ester of the corresponding naphtholdisulphonic acid.

Treatment of 1 : 8-naphthylenediamine with 11 pts. of 2% fuming sulphuric acid at 95—100° for several hrs. affords 1 : 8-naphthylenediamine-4-sulphonic acid, which, when warmed with 5 pts. of 20% fuming sulphuric acid, yields a disulphonic acid, probably 1 : 8-naphthylenediamine-4 : 5-disulphonic acid (cf. D.R.-P. 72584). F. G. WILLSON.

Reactions of azoxy-compounds. I. Action of light. W. M. CUMMING and G. S. FERRIER (J.C.S., 1925, **127**, 2374—2379).—*o*-Hydroxyazo-compounds result when solutions of certain azoxy-compounds are exposed to the light of a mercury-vapour lamp. The yields are highest in alcohol and lowest in benzene. Azobenzene in 85% alcohol gives a 63·3% yield of *o*-hydroxyazobenzene, m. p. 82—83°, in 200 hrs. (44% in 100 hrs.). The same transformation occurs under the influence of sunlight or electric light (filament lamp). 2 : 2′-, 3 : 3′-, and 4 : 4′-Azoxytoluene, 4 : 4′-dichloroazoxybenzene, 2 : 2′-diamino-4 : 4′-azoxytoluene, and 4 : 4′-azoxyanisole react similarly. 2-*Hydroxy*-3 : 3′-*azotoluene* has m. p. 61·5—62·5°. 4 : 4′-Azoxyphenetole and 4 : 4′-dinitroazoxybenzene are unchanged.

The existence of an isomeric 4 : 4′-azoxytoluene, m. p. 75° (Janovsky and Reimann, A., 1889, 392), is unconfirmed, and a setting-point curve shows that it cannot be a solid solution of *p*-azo- in *p*-azoxytoluene. C. HOLLINS.

Azo dyes. BRITISH DYESTUFFS CORP., LTD., K. H. SAUNDERS, and H. GOODWIN.—See B., 1926, 7.

***o*-Hydroxyazo dyes.** A.-G. F. ANILIN-FABR.—See B., 1926, 7.

Azo dyes. SOC. OF CHEM. IND. IN BASLE.—See B., 1926, 43.

Azo dyes. G. KALISCHER, K. KELLER, and L. CASSELLA U. CO.—See B., 1926, 44.

Phenylhydrazine and factors affecting hydrazone formation. E. G. R. ARDAGH and J. G. WILLIAMS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 75, and J. Amer. Chem. Soc., 1925, **47**, 2976—2983).—The iodometric method (Ardagh and Williams, this vol., 189) for the determination of phenylhydrazine gives low results when a buffer solution is present. Correct results are obtained when the solution is just acid to methyl-orange. Aqueous solutions of phenylhydrazine and its salts oxidise fairly rapidly on exposure to air, the solutions being stable when prepared with water free from oxygen and preserved in an atmosphere of nitrogen.

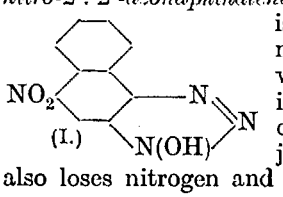
Hydrazone formation is a reversible process, the equilibrium being greatly influenced by the acidity of the medium. Acetonephenylhydrazone formation is almost complete over the p_H range 5—7, provided the hydrazone is at the same time salted out. If the hydrazone be extracted with some suitable solvent, immiscible with water, the reaction is quantitative. The rôle of sodium acetate in hydrazone formation is solely that of a buffer. J. S. CARTER.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. I. E. MÜLLER (J. pr. Chem., 1925, [ii], **111**, 273—276).—A summary of previous researches in this field, introductory to the following three papers. F. G. WILLSON.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. II. Action of hydrazine hydrate on some nitro- and chloronitro-compounds. E. MÜLLER and G. ZIMMERMANN (J. pr. Chem., 1925, [ii], **111**, 277—292).—Whilst the action of hydrazine hydrate on *m*-nitrobenzoic acid in alcoholic solution affords only the corresponding *hydrazine* m-*nitrobenzoate*, m. p. 182°, in absence of solvent the nitrobenzoic acid is reduced at water-bath temperature in 30 min. with formation of *m*-aminobenzoic acid. *p*-Nitrobenzoic acid behaves similarly (cf. Curtius and Bollenbach, A., 1907, i, 1078). *p*-Nitrotoluene is reduced to *p*-toluidine when heated with hydrazine hydrate for 4 hrs. at 130° in a sealed tube, *o*- and *m*-toluidines being also analogously produced. At 150°, hydrazine hydrate reduces *o*-, *m*-, and *p*-nitroanilines to the corresponding phenylenediamines. 2 : 4-Dinitrotoluene is reduced by alcoholic hydrazine hydrate at water-bath temperature to *o*-nitro-*p*-toluidine, and this is further reduced to 2 : 4-tolylenediamine when heated with hydrazine hydrate at 140°. Reduction of *m*-chloronitrobenzene to *m*-chloroaniline by the action of hydrazine hydrate proceeds at water-bath temperature, but *o*-chloronitrobenzene, when boiled with hydrazine hydrate, yields hydroxybenzotriazole as the *hydrazine* salt, m. p. 110—120° with loss of hydrazine; *o*-nitrophenylhydrazine is probably the primary product. 2 : 4-Dichloronitrobenzene reacts with hydrazine hydrate in hot alcoholic solution with formation of the *hydrazine* salt, m. p. 182—183° (decomp.), of the corresponding 4-*chloro-hydroxybenzotriazole*, exploding at 204—205° (*potassium* salt, explodes above 300°; *ethyl ether*, m. p. 59—60°; *benzoyl* derivative, m. p. 126°). The 5-*chloro*-2 : 4-*dinitrophenylhydrazones* of *benzaldehyde*, orange, m. p. 242°, *acetone*, yellow, m. p. 123°, *ethyl acetoacetate*, m. p. 115°, and *formaldehyde*, yellow, m. p. 124°, are described. *Benzoyl*-5-*chloro*-2 : 4-*dinitrophenylhydrazine*, reddish-yellow, has m. p. 219°. When treated with sodium nitrite in suspension in cold aqueous-alcoholic hydrochloric acid, 5-chloro-2 : 4-dinitrophenylhydrazine affords an unstable *nitrosoamine*, yellow, decomp. at 85°, which, when heated, loses water and nitrogen with formation of 5 : 5′-*dichloro*-2 : 4 : 2′ : 4′-*tetranitroazobenzene*, yellow, m. p. 93°, exploding at higher temperatures with evolution of a yellow, irritant vapour. 5-Chloro-2 : 4-dinitrophenylhydrazine dissolves in alkali with darkening and evolution of gas. Acidification of the solution affords brown flocks which could not be purified, but which did not appear to represent a hydroxytriazole derivative. The *dihydrochloride*, pale yellow, readily hydrolysed, the *sulphate*, pale yellow, decomp. at 213°, and the *dibenzoyl* derivative, pale orange-yellow, m. p. above 300°, of 2 : 4-*dinitro*-1 : 5 *dihydrazinobenzene*, are described. F. G. WILLSON.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. III. Action of hydrazine hydrate on 2 : 4 : 5-trichloronitrobenzene. E. MÜLLER and W. HOFFMANN (J. pr. Chem., 1925, [ii], **111**, 293—306).—Hydrazine hydrate reacts with 2 : 4 : 5-trichloronitrobenzene in boiling alcoholic solution with formation of 3 : 4-*dichloro*-6-*nitrophenylhydrazine*, orange-yellow, m. p. 194·5°, and 4 : 5-*dichlorohydroxybenzotriazole*, $C_6H_2Cl_2\langle\overset{\qquad N}{N(OH)}\rangle N$, exploding at 194—196° after becoming brown at 190° [*hydrazine* salt, m. p. 205° (decomp.); *potassium* salt, explodes at 230—250°; *barium*, *magnesium*, *copper*, and *silver* salts; *aniline* salt, m. p. 168° (decomp.); *methyl ether*, m. p. 129°; *ethyl ether*, m. p. 90°; *benzoyl* derivative, m. p. 152°; *acetyl* derivative, m. p. 150°; *carbethoxymethyl* derivative, m. p. 109°; *carbethoxy*-derivative, m. p. 123°]. Formation of the triazole is favoured by the application of excess of hydrazine hydrate, and by the action of hydrazine or of alkalis on the dichloronitrophenylhydrazine. The following 3 : 5-*dichloro*-6-*nitrophenylhydrazones* are described: *benzaldehyde*-, yellowish-red, m. p. 184°; *salicylaldehyde*-, yellowish-green, m. p. 207°; *resorcylaldehyde*-, orange-red, m. p. 251°; *acetone*-, lemon-yellow, m. p. 157°; and *benzophenone*-3 : 5-*dichloro*-6-*nitrophenylhydrazone*, pale yellow, m. p. 162°. Treatment with nitrous acid converts the dichloronitrophenylhydrazine into 3 : 4-*dichloro*-6-*nitrophenylazoimide*, yellowish-brown, m. p. 56°, which is decomposed by alkalis into azoimide and a *compound*, m. p. 34°, possessing phenolic properties. The action of anhydrous hydrazine on 2 : 4 : 5-trichloronitrobenzene affords, together with the above triazole, 2 : 3-*dichloro*-6-*nitrophenylhydrazine*, red, m. p. 172° [*hydrochloride*, m. p. 195° (decomp.); *benzylidene* derivative, red, m. p. 225°]. F. G. WILLSON.

Action of hydrazine on nitro- and chloronitro-derivatives of benzene and naphthalene. IV. Action of hydrazine on 1-chloro-2 : 4-dinitronaphthalene. E. MÜLLER and K. WEISBROD (J. pr. Chem., 1925, [ii], **111**, 307—312).—When treated with hydrazine hydrate in hot alcoholic solution, 1-chloro-2 : 4-dinitronaphthalene affords 2 : 4-dinitronaphthalene, the *hydrazine* salt of 2 : 4-*dinitro*-α-*naphthol*, m. p. 203—205°, 5-*nitro*-3-*hydroxynaphthotriazole*, (I), yellow, m. p. 215° (decomp.), and 4 : 4′-*dinitro*-2 : 2′-*azonaphthalene*. The primary product is probably 2 : 4-dinitronaphthylhydrazine, from which the triazole derivative is derived by reduction and condensation with the adjacent nitro-group, but which also loses nitrogen and hydrogen with formation of



(I.)

dinitronaphthalene, the latter being then further reduced to the azo-derivative, whilst the naphthol is formed by hydrolysis of the chlorodinitronaphthalene. The same products are obtained when the reaction is carried out at the ordinary temperature, but when anhydrous hydrazine is used, neither the dinitronaphthol nor the triazole derivative is formed.

F. G. WILLSON.

Nitrogen tetroxide as a reagent for diazotisation. B. HOUSTON and T. B. JOHNSON (J. Amer. Chem. Soc., 1925, **47**, 3011—3018).—Nitrogen tetroxide forms a convenient reagent for diazotising primary aromatic amines in anhydrous solvents. The reaction proceeds according to the equation $R{\cdot}NH_2+N_2O_4=R{\cdot}N{:}N{\cdot}O{\cdot}NO_2$, and is in accordance with the structure $ON{\cdot}O{\cdot}NO_2$ for nitrogen tetroxide. When *m*-nitroaniline, dissolved in dry benzene, is treated with pure nitrogen tetroxide in the cold until the reddish colour of the solution indicates an excess of the gas, 3 : 3′-*dinitrodiazoaminobenzene*, yellow, m. p. 195—196° (violent decomp.), is precipitated in practically quantitative yield. By using 3 mols. of nitrogen tetroxide to 1 mol. of *m*-nitroaniline, a yield of 69% of *m*-nitrobenzenediazonium nitrate can be obtained, together with 24% of the diazoamino-compound. In the case of *p*-nitroaniline, a molar ratio of nitrogen tetroxide to base of 1 : 2 affords 84% of diazoamino-derivative with 12% of diazonium nitrate, whilst a corresponding ratio of 2·25 : 1 yields 91% of diazonium nitrate, the diazoamino-compound not being formed under these conditions. *o*-Nitroaniline yields, with corresponding ratios of nitrogen tetroxide, 12% of diazoamino-compound and 8% of diazonium nitrate, and 64% of diazonium nitrate free from diazoamino-compound, respectively.

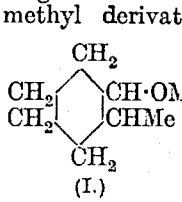
F. G. WILLSON.

Decomposition of diazo-compounds under the influence of copper. J. S. P. BLUMBERGER (Chem. Weekblad, 1925, **22**, 599—604).—A consideration of the various methods of reaction of diazo- and diazonium-compounds in presence of copper and copper compounds in relation to the theory of induced alternate polarity. Many of the configurations assumed are found to be contradictory.

S. I. LEVY.

Stereoisomerism in the *cyclo*hexane series. I. 2-Methyl*cyclo*hexanols. M. GODCHOT and P. BEDOS (Bull. Soc. chim., 1925, [iv], **37**, 1451—1466).—*cyclo*Hexene oxide, obtained in 55% of the theoretical yield by the action of potassium hydroxide on 2-chloro*cyclo*hexanol, reacts readily with magnesium methyl iodide, yielding first a magnesium methyl derivative which gives 2-iodo*cyclo*hexanol with water. Further reaction on distilling off the ether in place of decomposing with water yields a product (I), which when finally treated with water gives 2-methyl*cyclo*hexanol, b. p. 163—164°/763 mm., in 63% yield. The *phenylurethane* has m. p. 71° and the *acid phthalate*, m. p. 128°. Since *cyclo*hexene oxide should itself from spatial considerations be a *cis*-compound, it is concluded that the 2-methyl*cyclo*hexanol is itself the *cis*-isomeride, the alternative possibility of its being 1-methyl*cyclo*hexan-1-ol being excluded by the fact that on oxidation with chromic and acetic acids it yields 2-methyl*cyclo*hexanone. The 2-chloro*cyclo*hexanol, m. p. 29°, previously described (A., 1923, i, 327; cf. Detœuf, A., 1922, i, 327) similarly reacts with magnesium methyl iodide in two stages (cf. Grignard, A., 1905, i, 593), giving finally 50% of the theoretical yield of a mixture of two stereoisomeric 2-methyl*cyclo*hexanols, b. p. 163—164°/763 mm. Since the phenylurethane of the *cis*-isomeride has m. p. 71°, the isomeride yielding a phenylurethane, m. p. 105° (cf. Sabatier and Mailhe, A., 1905, i, 275), and an *acid phthalate*, m. p. 122°, is regarded as the *trans*-compound. Accordingly the original chloro*cyclo*hexanol is either a mixture of *cis*- and *trans*-forms or some interconversion has taken place in the reaction. It is possible that the product obtained by Detœuf (b. p. 84—85°/16 mm., m. p. 8°) is the other isomeride. *cis*-2-Methyl*cyclo*hexanol obtained by hydrolysis of the acid phthalate, m. p. 128°, has b. p. 166·5°/760 mm., d_{26}^{26} 0·9187, n_D^{26} 1·45437; the *trans*-isomeride, similarly obtained from the phthalate m. p. 122°, has b. p. 167—167·5°/760 mm., d_{26}^{26} 0·9236, n_D^{26} 1·4581. Commercial 2-methyl*cyclo*hexanol, obtained by catalytic reduction of *o*-cresol in the presence of nickel, consists of a mixture of about 80% of the *trans*- with 20% of the *cis*-form. Hydrogenation of the 2-methyl*cyclo*hexanone in acetic acid in the presence of platinum-black similarly yields a mixture of the *cis*- and *trans*-isomerides, but reduction with sodium and alcohol yields almost entirely the *trans*-form of 2-methyl*cyclo*hexanol (cf. Skita, A., 1922, i, 534; 1923, i, 460).

R. BRIGHTMAN.


(I.)

Sulphonation of *p*-chlorophenol. J. M. GAUNTLETT and S. SMILES (J.C.S., 1925, **127**, 2745—2746).—Sulphonation of *p*-chlorophenol yields an acid which on methylation forms 4-chloroanisole-2-sulphonic acid (*sodium* salt, loses $2H_2O$ at 120°; *chloride*, m. p. 104°). Reduction of the acid chloride yields 4-*chloroanisole*-2-*sulphinic acid*, m. p. 116°, and from this 4-*chloroanisole*-2-*methylsulphone*, m. p. 94°, and 4-*chloroanisole*-2-*disulphoxide*, m. p. 125°, are obtained. 4-*Chloroanisole*-2-*mercaptan*, m. p. 42°, and 4-*chloroanisole*-2-*disulphide*, m. p. 105°, were also prepared.

B. W. ANDERSON.

Complete synthesis of thymol from *iso*propyl alcohol. L. BERT and P. C. DORIER (Compt. rend., 1926, **182**, 63—65).—*p*-Chloromethyl*iso*propylbenzene is obtained from *iso*propyl alcohol (Blanc, A., 1923, i, 549) and yields a magnesium derivative which when treated with water gives *p*-cymene; this may be transformed into 5-bromo-2-amino-*p*-cymene (Wheeler and Smithey, A., 1922, i, 332; Wheeler and Taylor, J. Amer. Chem. Soc., 1925, **47**, 178), which when diazotised and heated with ethyl alcohol gives 5-bromo-*p*-cymene. The last-named yields a magnesium derivative which when treated with oxygen and water gives thymol.

L. F. HEWITT.

Derivatives of azoimide—a correction. A. KORCZYNSKI and ST. NAMYSLOVSKI (Bull. Soc. chim., 1925, [iv], **37**, 1397).—Picryl azide (2 : 4 : 6-trinitro-1-azidobenzene) described by the authors

(A., 1924, i, 1354) had previously been described by Schrader (A., 1917, i, 595). W. HUME-ROTHERY.

Pyrocatechol compounds of bi-, ter-, and quadri-valent metals. R. WEINLAND and H. SPERL (Z. anorg. Chem., 1925, **150**, 69—83).—When a solution of manganous acetate is treated with pyrocatechol and an alkaline hydroxide, the manganese is rapidly oxidised by the air, and complex *salts* of tervalent manganese are obtained of the formulæ: $[Mn(C_6H_4O_2)_3]Na_3,0{\cdot}5NaOH,6H_2O$; $[Mn(C_6H_4O_2)_3]K_3,3H_2O$;

$$[Mn(C_6H_4O_2)_3]H(NH_4)_2,5H_2O;$$

these are decomposed by acids. If dilute ammonia is used, an unstable *base*, $Mn_6(C_6H_4O_2)_5(OH)_2,10H_2O$, is precipitated. Pyridine yields a crystalline *compound*, $4[Mn(C_6H_4O_2)_2]H_2,2C_5H_5N,C_6H_4(OH)_2$; nickel forms a similar *compound*, but the zinc *compound* has the normal formula $[Zn(C_6H_4O_2)_2]H_2,2C_5H_5N$. Unlike most complex pyrocatechol compounds, these pyridine salts are stable in air. From stannous chloride a *compound*, $[ClSnC_6H_4O_2]H,C_5H_5N$, is obtained, and thorium nitrate yields a *substance*, $Th(O{\cdot}C_6H_4{\cdot}OH)_4,2C_5H_5N$. The yellow colour of this latter compound is surprising because an ammonium salt, containing 3 mols. of pyrocatechol, is colourless; it may be a pseudo-ammonium salt. The *zirconium* compound,

$$[Zr(C_6H_4O_2)_3]H_2,C_5H_5N,0{\cdot}5[C_6H_4(OH)_2,C_5H_5N],$$

is also yellow, whilst aluminium forms a yellow, tarry compound which rapidly changes to a colourless, powdery *substance*, $[Al(C_6H_4O_2)_2]H,C_5H_5N,H_2O$. From bismuth nitrate a *compound*, $Bi(C_6H_4O_2)(O{\cdot}C_6H_4{\cdot}OH)$, is obtained, the constitution of which is uncertain, and also an *acid*, $Bi(NO_3)(O{\cdot}C_6H_4{\cdot}OH)_2$.

A. GEAKE.

2-Nitro-3 : 4-dimethoxytoluene [2-nitro-homoveratrole]. E. MERCK.—See B., 1926, 28.

Reduction of cinnamaldehyde to cinnamyl alcohol in presence of platinum oxide–platinum-black and promoters. XI. W. F. TULEY with R. ADAMS (J. Amer. Chem. Soc., 1925, **47**, 3061—3068).—Reduction of cinnamaldehyde with hydrogen in presence of platinum oxide–platinum-black ceases when 0·15 mol. of hydrogen has been absorbed per mol. of aldehyde. The catalyst can be reactivated by shaking with air, but many reactivations are necessary before reduction is complete, and the product, when 1 mol. of hydrogen has been absorbed, contains unchanged aldehyde, phenylpropaldehyde, cinnamyl alcohol, and phenylpropyl alcohol. A quantitative yield of cinnamyl alcohol is obtained when the aldehyde (0·2 mol. in 100 c.c. of 95% alcohol) is treated with an equivalent of hydrogen in presence of 0·2 g. of catalyst and 0·00002 mol. of ferrous chloride. Increase in the proportion of ferrous chloride to 0·0005 mol. results in a less pure product. Phenylpropyl alcohol is obtained by allowing a second mol. of hydrogen to be absorbed, but this takes place much more slowly. If 0·00002 mol. of zinc acetate is substituted for the ferrous chloride, reduction proceeds similarly, but much more slowly, to phenylpropyl alcohol, whilst 0·0006 mol. of zinc acetate completely inhibits the reduction. In presence of 0·0002 mol. of ferrous chloride and 0·00003 mol. of zinc acetate, reduction proceeds rapidly until 1 mol. of hydrogen is absorbed, when it ceases abruptly, and the product is very pure cinnamyl alcohol. The optimum proportions of the two salts are specific for each set of reaction quantities. Best results are obtained when the platinum oxide is reduced before the aldehyde is added to the solvent, and by keeping the temperature of reaction below 40°.

F. G. WILLSON.

***cyclo*Hexylglycerol.** R. DELABY and M. M. JANOT (Compt. rend., 1925, **181**, 1146—1147; cf. Klages and Klenk, A., 1906, i, 638; Moureu and Gallagher, A., 1922, i, 34; Delaby, A., 1923, i, 85).—cyclo*Hexylvinylcarbinol*, b. p. 93—94°, d_0^0 0·9352, $n_D^{17\cdot5}$ 1·4811, *allophanate*, m. p. 169—170°, when treated with bromine in acetic acid yields the *dibromide*, m. p. 73·5° (cf. Valeur and Luce, Bull. Soc. chim., 1920, [iv], **27**, 611). The dibromide when treated with potassium acetate gives cyclo*hexylglyceryl triacetate*, which is hydrolysed by hydrochloric acid and methyl alcohol, yielding cyclo*hexylglycerol*, b. p. 188—190°/20 mm., m. p. 73·5°. L. F. HEWITT.

[Syntheses by means of organic peroxides.] E. O. VON LIPPMANN (Ber., 1925, **58**, [*B*], 2706).—The observations attributed to the author by Gelissen and Hermans (this vol., 63) were made by E. Lippmann. H. WREN.

Chlorination of *o*- and *p*-aminobenzoic acids. L. ELION (Rec. trav. chim., 1925, **44**, 1106—1108).—By passing the calculated amount of chlorine into an acetic acid solution of anthranilic acid, a 75% yield of 3 : 5-dichloroanthranilic acid, m. p. 231°, is conveniently obtained. On boiling with acetic anhydride, this acid yields 3 : 5-*dichloroacetylanthranil*, m. p. 151°, which is converted by alkali hydroxides into 3 : 5-*dichloro-2-acetamidobenzoic acid*, m. p. 203°. By this method, *p*-aminobenzoic acid yields trichloroaniline and 35% of 3 : 5-dichloro-4-aminobenzoic acid. R. W. WEST.

Action of formaldehyde and secondary amines on acids with mobile hydrogen atoms. C. MANNICH and L. STEIN (Ber., 1925, **58**, [*B*], 2659—2662).—The synthesis of β-amino-acids from malonic and acetoacetic esters by means of formaldehyde and secondary amines has already been reported (A., 1922, i, 351; 1924, i, 946, 947). Attempts to extend the synthesis to other similar acids are irregularly successful. Phenylacetic acid does not condense, but its hydrogen atoms become sufficiently mobile if the negative character of the phenyl group is strengthened by the introduction of one or more nitro-groups. *o*-Nitromandelic acid may also be used, but *o*-nitrophenylacetic, *m*- and *p*-nitromandelic, *o*-nitrophenylpyruvic, sulphoacetic, ββ3-trichloro-α-hydroxypropionic, and *o*- and *p*-hydroxydiphenylacetic acids are unsuitable. *p*-Nitrophenylacetic acid, piperidine, and formaldehyde afford β-*piperidino*-α-p-*nitrophenylpropionic acid*,

$$C_5H_{10}N{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NO_2){\cdot}CO_2H,$$

m. p. 138—139° (decomp.), which is readily converted by boiling water into piperidine and α-p-*nitrophenylacrylic acid*, m. p. 176—177°. Reduction of the

nitro-acid by tin and hydrochloric acid yields β-piperidino-α-*p*-aminophenylpropionic acid, isolated as the *dihydrochloride*, m. p. 213° (decomp.). *β-Dimethylamino-α-p-nitrophenylpropionic acid* has m. p. 167—168°. *β-Methylamino-α-p-nitrophenylpropionic acid*, decomp. about 177°, its *hydrochloride*, decomp. 170°, and *phenylacetyl* derivative, m. p. 175°, are described. The action of formaldehyde and secondary amines on 2 : 4-dinitrophenylacetic acid leads to diamines in place of amino-acids, since carbon dioxide is lost during the reaction. Thus with piperidine, *αγ-dipiperidino-β-2 : 4-dinitrophenylpropane*, m. p. 133—134° [dihydrochloride, m. p. about 144° (decomp.)], is obtained. *αγ-Bisdimethylamino-β-2 : 4-dinitrophenylpropane*, m. p. 85—86°, and *αγ-bisdiethylamino-β-2 : 4-dinitrophenylpropane* (*picrate*, decomp. 165—166°) are described. *o*-Nitromandelic acid, formaldehyde, and piperidine afford *β-piperidino-α-hydroxy-α-o-nitrophenylpropionic acid*, $C_{14}H_{18}O_5N_2,H_2O$, decomp. 109°. H. WREN.

Chemical isomerism of the three *cis*-cinnamic acids. H. STOBBE (Ber., 1925, **58**, [*B*], 2620—2626).—A reply to De Jong (A., 1920, i, 162), a critical review of whose experiments shows that the *cis*-cinnamic acids, m. p. 68° and 58°, respectively, can be recrystallised unchanged from concentrated solutions if the operation is effected rapidly so that there is little chance of infection. If these conditions are not fulfilled and the solutions are dilute, are preserved for 8—14 days or longer, and are decanted from one vessel to another in the laboratory so that the risk of infection is increased, the acid of m. p. 42° separates from solutions of the other two acids. The acid of m. p. 68° is never obtained from solutions of that of m. p. 58°, and the reverse transformation is never observed; it follows, therefore, that the solutions of the two acids are not identical. De Jong's arguments against the chemical isomerism of the three *cis*-cinnamic acids are regarded as refuted from his own observations. The supposed identity of the three double acids obtained from *trans*-cinnamic acid and the three *cis*-acids rests on the identity of the very indefinite m. p. of the compound, and cannot be regarded as established until the crystals have been measured and further constants established. H. WREN.

Qualitative resemblance between the velocity of hydration of acid anhydrides and the velocity of hydrolysis of diacyl peroxides. J. BÖESEKEN and H. GELISSEN (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 624—629).—By an examination of the existing data on the hydrolysis of diacyl peroxides and acid anhydrides, the authors show that in both cases (1) it is the C·O linking that is ruptured by the water; (2) the reaction products are two acids; (3) the velocity is accelerated by alkali hydroxides, carbonates, and hydrogen carbonates (cf. Orton and Jones, J.C.S., 1912, **101**, 1708; Baeyer and Villiger, A., 1900, i, 437); and (4) the reaction is catalytically affected by acids (cf. Clover and Richmond, A., 1903, i, 396; Orton and Jones, *loc. cit.*). They conclude, therefore, that the diacyl peroxides are anhydrides of peracids and acids, and that those derived from acid anhydrides which have a small hydration constant do not hydrolyse, or do so exceedingly slowly, the velocity of hydrolysis of the peroxide being always smaller than that of the corresponding anhydride. This conclusion is supported by existing data and by the preparation of the following new peroxides, derived from acids the anhydrides of which are not attacked by water, and which are themselves stable towards that reagent: *cinnamoyl peroxide*, m. p. 144°; *phenylpropionyl peroxide*, m. p. 38·5°; *trichloroacrylyl peroxide*, m. p. 49°. The agreement also holds for the corresponding derivatives of benzenesulphonic acid. J. W. BAKER.

Derivatives of *p*-hydroxymethylbenzoic acid. II. Ether esters. F. H. CASE (J. Amer. Chem. Soc., 1925, **47**, 3003—3005; cf. A., 1925, i, 815).—*p*-Chloromethylbenzoic acid is obtained in 78% yield by hydrolysis of *p*-chloromethylbenzonitrile with concentrated hydrochloric acid. When boiled with water until solution is complete, this is converted into *p*-hydroxymethylbenzoic acid. Hydrolysis of *p*-bromomethylbenzonitrile with hydrobromic acid yields similarly *p*-bromomethylbenzoic acid (cf. Swiss Pat. 93500). p-*Ethoxymethylbenzoyl chloride*, b. p. 136—138°/8 mm., obtained by the action of thionyl chloride on the corresponding acid, was used for preparing the following esters: *benzyl*, b. p. 198—201°/5 mm.; p-*carbethoxybenzyl*, m. p. 36—37°, b. p. 243—244°/3 mm.; and *β-diethylaminoethyl* p-*ethoxymethylbenzoate*, b. p. 183—185°/5 mm. (*hydrochloride*, m. p. 122—123°). The last-named salt appears to possess local anæsthetic properties. F. G. WILLSON.

Derivatives of *p*-hydroxymethylbenzoic acid. III. Amino-esters. F. H. CASE (J. Amer. Chem. Soc., 1925, **47**, 3005—3008; cf. preceding abstract).—*Ethyl* m-*nitro*-p-*chloromethylbenzoate*, yellow, b. p. 170—174°/4 mm., is obtained by heating *m*-nitro-*p*-chloromethylbenzonitrile (cf. Banse, A., 1894, i, 574) with absolute alcohol and sulphuric acid. When boiled with 1 mol. of anhydrous sodium acetate in alcohol, it affords *ethyl* m-*nitro*-p-*acetoxymethylbenzoate*, yellow, m. p. 57—58°, which, on hydrolysis with alcoholic hydrogen chloride, yields *ethyl* m-*nitro*-p-*hydroxymethylbenzoate*, yellow, m. p. 115—116° (*benzoate*, pale yellow, m. p. 129—130°; *phenylurethane*, m. p. 125—126°). Reduction of ethyl *m*-nitro-*p*-hydroxymethylbenzoate with tin and hydrochloric acid, or with hydrogen in presence of colloidal palladium or platinum oxide, affords *ethyl* m-*amino*-p-*hydroxymethylbenzoate*, m. p. 85—86° [*hydrochloride*, m. p. 129—130° (decomp.)]. n-*Butyl* m-*nitro*-p-*hydroxymethylbenzoate*, yellow, b. p. 198—203°/3 mm., and n-*butyl* m-*amino*-p-*hydroxymethylbenzoate*, m. p. 76—77°, obtained analogously, are described. F. G. WILLSON.

6-Thiol-*m*-toluic acid. F. KROLLPFEIFFER [with H. SCHULTZE and E. SOMMERMEYER] (Ber., 1925, **58**, [*B*], 2698—2701).—6-Thiol-*m*-toluic acid has been obtained by Krollpfeiffer (A., 1925, i, 1306) by the action of alkali on 3-bromo-2 : 6-dimethylthiochromanone and also by Arndt (*ibid.*, 1309) from 2 : 2-dichloro-6-methylthiochromonol, but the properties of the compounds are not in agreement.

Re-examination of Arndt's product shows that it cannot possibly be a homologue of *o*-thiolbenzoic acid, since it evolves carbon dioxide and does not yield a disulphide when oxidised by potassium ferricyanide. Further, when treated with molten potassium hydroxide it affords 4-methylthionaphthenquinone. Analysis of Arndt's compound suggests that it is 2 : 3 : 4-triketothiochroman.

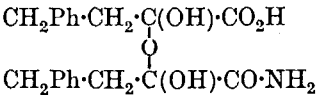
6-Thiol-*m*-toluic acid is prepared synthetically as follows: 6-amino-*m*-toluic acid is diazotised and the solution is treated successively with sulphur dioxide and copper powder; the sulphinic acid thus produced is reduced by zinc dust in the presence of alcohol to 6-thiol-*m*-toluic acid, m. p. 155°, identical with the product derived from 3-bromo-2 : 6-dimethylthiochromanone. Either acid reacts with chloroacetic acid to form *o-carboxy-p-tolylthiolacetic acid*, decomp. 220°, which is transformed by fusion with sodium hydroxide into 3-hydroxy-5-methylthionaphthen.

The conversion of 3-bromochromanone into chromone by boiling pyridine or dimethylaniline is incidentally recorded. H. WREN.

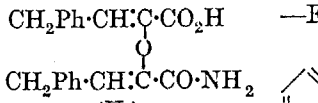
Some peculiarities of inactive mandelic acid. N. KISHNER (J. Russ. Phys. Chem. Soc., 1925, **56**, 15—17).—When inactive mandelic acid is heated to 130° either in the anhydrous state or in a sealed tube with water, its m. p. at first has the normal value, 118°, but if the resulting acid is allowed to solidify and is then re-melted in the same capillary tube, it melts at 105—106°; if this acid is then recrystallised from benzene, its m. p. is 118° at the first, and 103° at the second, fusion. Further, if the molten acid with the abnormal m. p. is seeded with a crystal of the ordinary acid, the crystals separating melt at 118° at the first time and at 101—103° at the second time.

Crystallisation of the abnormal acid from hot benzene solution gives long, hexagonal plates which, in the mother-liquor, gradually change into rhombohedral crystals, $C_8H_8O_3,C_6H_6$, which lose their benzene and their form when kept. T. H. POPE.

α-Hydroxy-γ-phenylcrotonamide. An example of an ether of a ketone hydrate. J. BOUGAULT (Bull. Soc. chim., 1925, [iv], **37**, 1420—1436).—A general account of work which has in part been published previously (A., 1912, i, 770; 1913, i, 269, 366; 1925, i, 921). The structure (I), representing the ether of a ketone hydrate assigned to the acid amide obtained by the action of dilute sodium hydroxide on an alcoholic solution of α-hydroxy-γ-phenylcrotonamide, has now been confirmed. The sodium salt of the amide is first precipitated and converted into the acid amide by

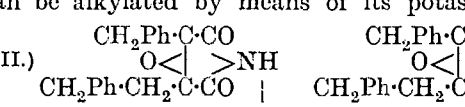


(I.)



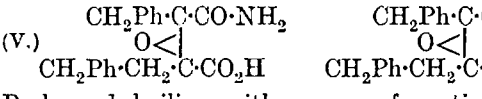
(II.)

treatment with hydrochloric acid. On account of the ease with which the amide undergoes dehydration, its m. p. could not be determined. Alkalis, even sodium carbonate, produce hydrolysis to benzylpyruvic acid, but with ammonia phenylpropionylbenzylalanineamide is produced, as a result of secondary reaction with the benzylpyruvic acid (cf. A., 1921, i, 177). Dehydration at 100° yields the acid amide (II), which is only slightly soluble in acetone and is precipitated from its solutions in alkali by acetic acid. Boiling alkalis hydrolyse it to benzylpyruvic acid. Besides the acid amide (I), a small amount of the corresponding *diamide*, m. p. 198°, is formed in the action of sodium hydroxide on α-hydroxy-γ-phenylcrotonamide, and this similarly yields benzylpyruvic acid on hydrolysis. Potassium permanganate in acetic acid oxidises (I) to an imide, m. p. 120°, which is now regarded as possessing the structure (III) for the following reasons: (1) it is only feebly acid and can be alkylated by means of its potassium salt;



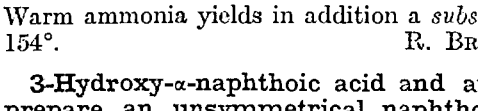
(III.) (IV.)

(2) the *methylimide*, m. p. 86°, on treatment with sodium carbonate, yields a mixture of two acids, m. p. 175° and 150°, which probably possess the structures (V) and (VI), and are decomposed by boiling potassium or sodium hydroxide into methylamine and a dibasic acid, m. p. 204°, regarded as *benzyl-β-phenylethyloxidomaleic acid* (IV) (*dimethyl* ester, m. p. 74°); (3) hydrolysis with dilute sodium hydroxide yields ammonia and a mixture of benzylpyruvic and phenylpropionic acids. Partial hydrolysis of the imide (III) yields a new *acid amide*, m. p. 170° (decomp.), possessing the structure (V) or (VI) (*methyl* derivative, m. p. 154°); boiling dilute sodium hydroxide or a mixture of acetic and hydrochloric acids converts it into (IV) and the *anhydride*, m. p. 104°.



(V.) (VI.)

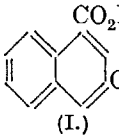
Prolonged boiling with excess of acetic anhydride yields a second *anhydride*, m. p. 75°, which is considered to have formula (VII) or (VIII). It forms a *methyl ether*, m. p. 53°, and an *imide* with ammonia, m. p. 122°, whilst sodium amalgam converts it into α-benzyl-α′β-phenylethylsuccinic acid, m. p. 170°.



(VII.) (VIII.)

Warm ammonia yields in addition a *substance*, m. p. 154°. R. BRIGHTMAN.

3-Hydroxy-α-naphthoic acid and attempts to prepare an unsymmetrical naphthoxthin. R. LESSER and S. SAD (Ber., 1925, **58**, [*B*], 2551—2559).—Examination of a series of derivatives of 3-hydroxy-α-naphthoic acid leads the authors to assign to the acid the normal constitution (I) (cf. Lesser, Kranlpuhl, and Sad, A., 1925, i, 1424). This conception depends largely on the difference of the behaviour of the anilide and 2-hydroxy-3-naphthanilide towards vegetable fibres and of 4-amino-3-hydroxynaphthoic acid and 1-amino-2-hydroxy-3-

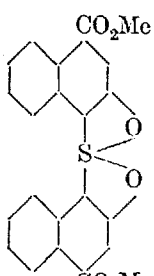


(I.)

naphthoic acid towards sodium nitrite. Since the presence of the double linking between the carbon atoms 2 and 3 in 2-hydroxy-3-naphthoic acid is regarded as established (*loc. cit.*), the alternative position of the double linking must be assumed in the acid under consideration.

The following compounds are described: 3-hydroxy-α-naphthoic acid, m. p. 248—249° (corr.); 3-acetoxy-α-naphthoic acid, m. p. 173—174° [Royle and Schedler (J.C.S., 1923, **123**, 1641) record m. p. 169—170°]; 3-*benzoyloxy-α-naphthoic acid*, m. p. 222—223°; 3-*methoxy-α-naphthoic acid*, m. p. 159°; 3-*acetoxy-α-naphthoyl chloride*, m. p. 96—97°; 3-*acetoxy-α-naphthamide*, m. p. 180—181°, from which 3-*hydroxy-α-naphthamide*, m. p. 209—211°, is obtained by cautious hydrolysis; 3-*acetoxy-α-naphthanilide*, m. p. 178—179°, and thence 3-*hydroxy-α-naphthanilide*, m. p. 112—113°; 4-p-*nitrobenzeneazo*-3-*hydroxy-α-naphthanilide*, m. p. 295—296°; *methyl* 3-*hydroxy-α-naphthoate*, m. p. 91—92°; 4-*bromo*-3-*hydroxy-α-naphthoic acid*, m. p. 231—232°; 4-*benzeneazo*-3-*hydroxy-α-naphthoic acid*, m. p. 273° (decomp.). 3-Hydroxy-α-naphthoic acid couples with *p*-diazobenzenesulphonic acid, and the product (*disodium* salt) is reduced by sodium hyposulphite in faintly alkaline solution to 4-*amino*-3-*hydroxy-α-naphthoic acid*, m. p. 204° (decomp.), of which the *sodium* salt and *hydrochloride* are described. The acid readily loses carbon dioxide in boiling dilute hydrochloric acid solution, forming 1-amino-β-naphthol. 4-*Acetamido*-3-*acetoxy-α-naphthoic acid* has m. p. 225° (decomp.). 4-Amino-3-hydroxy-α-naphthoic acid is readily oxidised by nitric acid to 3 : 4-naphthaquinonecarboxylic acid, m. p. 173° (decomp.); the corresponding *oxime* has m. p. 181—182° (decomp.). 4-*Nitroso*-3-*hydroxy-α-naphthoic acid*, m. p. above 300°, is prepared with difficulty by the action of a large excess of sodium nitrite on a solution of the hydroxynaphthoic acid in dilute hydrochloric acid. 4-Amino-3-hydroxy-α-naphthoic acid is converted by sodium nitrite in the presence of copper sulphate into β-*naphthoxadiazole*-4-*carboxylic acid*, decomp. 151°. 1-Amino-2-hydroxy-3-naphthoic acid, m. p. 241° (decomp.), can be similarly converted into the corresponding *oxadiazole* (*diazo-oxide*), m. p. 182—183° (decomp.), but the compound can be obtained with equal readiness by the usual method.

Methyl 3-hydroxy-α-naphthoate is converted by sulphur chloride in the presence of carbon tetrachloride into *di*-4-*carbomethoxy*-2-*hydroxynaphthyl sulphide*, m. p. 210—211° (*dibenzoate*, m. p. 225°), which is transformed by bromine and alkali, but not by potassium ferricyanide, into the corresponding *dehydrosulphide* (II), m. p. 188—189°; this substance does not react with phenylhydrazine, *p*-nitrophenylhydrazine, phenylcarbamhydrazide, or hippurylhydrazine, thus strongly indicating the spiran structure, since there can be no question of steric hindrance with a compound which does not contain a substituent in the *ortho*-position (cf. von Auwers and Kehrmann, Ber., 1923, **56**, 1802). The dehydrosulphide is reduced by excess of zinc dust and fuming hydrochloric acid in boiling benzene to the corresponding iso*sulphide*, $C_{24}H_{18}O_6S$, m. p. 146° (*dibenzoate*, m. p. 147—148°). Di-4-carbomethoxy-2-hydroxynaphthyl sulphide gives a *dipotassium* salt, whereas β-naphthol sulphide, di-6-bromo-β-naphthol 1-sulphide, di-3-carbomethyl-2-hydroxynaphthyl sulphide, and di-5-chloro-2-hydroxy-4 : 6-dimethylphenyl sulphide yield only *monopotassium* salts.



(II.)

Unsuccessful attempts to prepare unsymmetrical naphthoxthins are described. Thus α-naphthol-2-sulphonic acid is converted by ethyl chloroformate into 1-ethylcarbonatonaphthalene-2-sulphonic acid, which is transformed into the corresponding *sulphonyl chloride*, m. p. 127—128°, and subsequently reduced to 2-thiol-α-naphthol, which could not be obtained in the pure condition; the compound could not be condensed with 1-iodo-β-naphthol. 4-*Chloro*-1-*hydroxynaphthyl* 2′-*hydroxynaphthyl* 2 : 1′-*sulphide*, m. p. 167—168° (decomp.), is obtained by the action of sulphur chloride on 4-chloro-α-naphthol and β-naphthol dissolved in chloroform. H. Wren.

Lactonic esters derived from phenacyl bromide by condensation with ethyl sodiomalonate and analogous substances. R. M. Rây and J. N. Rây (J.C.S., 1925, **127**, 2721—2723).—Phenacyl bromide condenses with ethyl sodiomalonate in presence of alkali to form the *lactone* of α-carbethoxy-γ-hydroxy-γ-phenyl-Δ$^{\beta}$-propenecarboxylic acid, m. p. 105°; similarly, with ethyl acetylsodiomalonate, the *lactone* of α-acetyl-α-carbethoxy-γ-hydroxy-γ-phenyl-Δ$^{\beta}$-propenecarboxylic acid, m. p. 136°, is formed. Another *lactone*, m. p. 135°, is formed with ethyl sodioethylmalonate, and the condensation with ethyl sodiobenzylmalonate and with ethyl sodio*iso*propylmalonate yields *lactones*, m. p. 125° and 151°, respectively. On oxidation, the lactones yield benzoic acid. Phenacyl bromide and ethyl sodiocyanoacetate heated in alcoholic solution yield *ethyl diphenacylcyanoacetate*, m. p. 141°, together with a *substance*, m. p. 125—127°. B. W. Anderson.

Constitution of chlorine derivatives of the phthalonic acid series. A. Cornillot (Compt. rend., 1925, **181**, 1071—1073).—Ethyl α-chlorophthalide-α-carboxylate (cf. A., 1924, i, 515, 1071) in benzene solution on treatment with aluminium chloride yields *ethyl α-phenylphthalide-α-carboxylate*, $CO<\overset{C_6H_4}{\underset{O}{}}>CPh\cdot CO_2Et$, m. p. 70°, and a small amount of benzhydrol-*o*-carboxylic acid. Ethyl α-phenylphthalide-α-carboxylate does not react with semicarbazide, but reacts readily with alkalis and rather less so with acids, giving α-phenylphthalide, ethyl alcohol, and carbon dioxide. The mobility of the terminal carboxyl group is thus increased by the introduction of the phenyl group into ethyl α-chlorophthalide-α-carboxylate, of which the suggested structure (*loc. cit.*) is hereby confirmed.

L. F. Hewitt.

Radical dissociation of arylated succinic acid derivatives. II. Radical dissociation of tetraarylsuccinodinitriles. A. Löwenbein and R. F. Gagarin (Ber., 1925, **58**, [*B*], 2643—2644; cf. Löwenbein, A., 1925, i, 552; Blicke, *ibid.*, 811).—Since tetraphenylsuccinodinitrile undergoes radical

dissociation at a somewhat inconveniently high temperature, *tetra*-p-*anisylsuccinodinitrile*, m. p. (indef.) 220—240°, has been prepared by the action of potassium ferricyanide on di-*p*-anisylacetonitrile in boiling sodium hydroxide solution. The colourless solutions of the compound in cold chloroform, alcohol, benzene, or glacial acetic acid become vivid pink when warmed, and exhibit an intense yellow fluorescence which slowly disappears when they are cooled. The presence of free di-*p*-anisylcyanomethyl radicals is established by the conversion of the product with phenylhydrazine in boiling solution into di-*p*-anisylacetonitrile. H. WREN.

Dichlorodiphenylmethanedicarboxylic acids. H. WEIL.—See B., 1926, 8.

Chenodeoxycholic acid. II. A. WINDAUS and A. VAN SCHOOR (Z. physiol. Chem., 1925, **148**, 225—231).—Oxidation of sodium chenodeoxycholate with sodium hypobromite solution gives deoxybiliobanic acid, m. p. 253°, yield 20% of the pure acid (from ethyl acetate), together with 10% of the crude acid; the dimethyl ester has m. p. 107°. Chenodehydrodeoxycholic acid on oxidation with nitric acid gives a *dinitroketotricarboxylic acid*, m. p. 222° (decomp.), yield 10%; *trimethyl* ester, m. p. 156° (cf. A., 1925, i, 405). P. W. CLUTTERBUCK.

Naphthalene-1 : 4 : 5 : 8-tetracarboxylic acid and its derivatives. FARBW. VORM. MEISTER, LUCIUS, U. BRÜNING.—See B., 1926, 7.

Vat dyes [from perylenetetracarboxymonoimide]. KALLE U. CO. A.-G.—See B., 1926, 7.

Substituted *iso*diazomethanes. F. D. CHATTAWAY and A. J. WALKER (J.C.S., 1925, **127**, 2407—2414; cf. A., 1925, i, 1193).—The chlorination and bromination of *o*-nitrobenzaldehydephenylhydrazone proceeds exactly as for the *m*- and *p*-nitro-compounds (*loc. cit.*). The ω-halogen derivatives (I), however, when treated with sodium acetate and acetic acid, or with pyridine or ammonia, or even by recrystallisation from alcohol, readily lose a molecule of hydrogen halide and form 1-aryl-3-*o*-nitrophenyl*iso*diazomethanes (II). These compounds explode when

(I.) $Ar{\cdot}NH{\cdot}N{:}CX{\cdot}C_6H_4{\cdot}NO_2$ $Ar{\cdot}N\overset{\diagup N\diagdown}{=\!=}C{\cdot}C_6H_4{\cdot}NO_2$ (II.)

heated to a definite temperature in each case, which is lower for mixtures than for pure substances and may be used as a means of identification, in the same way as the mixed m. p.

Addition of bromine to a suspension of *o*-nitrobenzaldehydephenylhydrazone in acetic acid gives, with 1 mol. of halogen, *o*-nitrobenzaldehyde-*p*-bromophenylhydrazone, m. p. 183°, and with 2 mols. of halogen, the 2 : 4-dibromophenylhydrazone, m. p. 204°, and *ω-bromo-o-nitrobenzaldehyde-p-bromophenylhydrazone*. This, shaken in benzene solution with a little aqueous ammonia, is converted readily into 1-p-*bromophenyl*-3-*o*-*nitrophenyl*iso*diazomethane*, which explodes at 144°, and is conveniently prepared by adding bromine (2 mols.) in acetic acid to *o*-nitrobenzaldehydephenylhydrazone or -*p*-bromophenylhydrazone and sodium acetate suspended in acetic acid. With 3 mols. of bromine, the product is *ω-bromo-o-nitrobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 110°, from which 1-(2′ : 4′-*dibromophenyl*)-3-*o*-*nitrophenyl*-iso*diazomethane*, exploding at 145—146°, is prepared (cf. Ciusa and Vecchiotti, A., 1916, i, 437, who give an erroneous constitution).

The following ω-bromo-*o*-nitrobenzaldehydearylhydrazones are also described, together with the related *iso*diazomethanes: 2 : 4-*dichlorophenyl*-, m. p. 122° (iso*diazomethane* explodes at 140°); 2 : 4 : 6-*trichlorophenyl*-, m. p. 115—116° (iso*diazomethane* explodes at 163°); 3 : 4 : 5-*trichlorophenyl*-, m. p. 170° (decomp.; iso*diazomethane* explodes at 151°). 1-p-*Chlorophenyl*-3-*o*-*nitrophenyl*iso*diazomethane* (explodes at 147°) is prepared directly.

Chlorination is more vigorous than bromination and proceeds best in chloroform. The first isolable product is *o*-nitrobenzaldehyde-2 : 4-dichlorophenylhydrazone, m. p. 192°. *ω-Chloro-o-nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone*, m. p. 132°, and the 2 : 4 : 6-*trichloro*-compound, m. p. 107°, yield the same *iso*diazomethanes as the corresponding ω-bromo-derivatives. C. HOLLINS.

Chloro-1-methyl*cyclo*hexan-2-one. M. GODCHOT and P. BEDOS (Compt. rend., 1925, **181**, 919—921).—On direct chlorination in presence of chalk, or on treatment with chlorocarbamide, 1-methyl*cyclo*hexan-2-one yields 1-*chloro*-1-*methyl*cyclo*hexan*-2-*one*, b. p. 78—79°/14 mm., d^{14} 1·099, n_D^{15} 1·4696; these physical constants and the constitution assigned to the reaction product differ from those given by Kötz and Steinhorst (A., 1911, i, 210). This chlorinated ketone gives a red coloration with ferric chloride, but no tautomeride has been obtained. On distillation with pyridine, it yields 1-methyl-Δ^6-*cyclo*hexen-2-one, which on treatment with magnesium methyl iodide gives cantharenol (Haworth, J.C.S., 1913, **103**, 1246), phenylurethane, m. p. 105°. 1-Chloro-1-methyl-*cyclo*hexan-2-one when treated with magnesium methyl iodide gives 1 : 1 : 2-*trimethyl*-Δ^2-cyclo*hexene*, b. p. 144—146°, d^{14} 0·862, n_D^{15} 1·459, together with a small amount of a *dimethyl*cyclo*hexadiene*.
L. F. HEWITT.

Preparation of thiosemicarbazones and semicarbazidesemicarbazones of *cyclo*hexenones and investigation of the properties of the latter compounds. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **56**, 19—44; cf. A., 1914, i, 292; 1924, i, 969).—The introduction of aromatic or heterocyclic radicals into the nuclei of *cyclo*hexenones does not influence the union of semicarbazide with the double linking, the reaction proceeding normally. If the hydroaromatic ketone contains conjugated linkings, that is, if a double linking occurs outside the nucleus, as with pulegone, or if, as in carvone, there is a second double linking within the nucleus, the double linking becomes inactive towards semicarbazide. The inactivity of the double linking of aliphatic–aromatic ketones towards semicarbazide is confirmed. Replacement of the oxygen atom of semicarbazide by a sulphur atom prevents the formation of compounds

analogous to semicarbazidesemicarbazones; unsaturated αβ-hydroaromatic ketones give only thiosemicarbazones, which crystallise well and may be used for characterising *cyclo*hexenones.

The action of cold, dilute mineral or organic acid solution on semicarbazidesemicarbazones results in the detachment of the semicarbazide molecule united with the αβ-double linking of the nucleus, with formation of the semicarbazones of the *cyclo*hexenones. Semicarbazidesemicarbazones of *cyclo*hexenones are decomposed by nitrous acid, with formation of the original ketones; with those of the aliphatic series, this decomposition to ketone may be effected by change in the conditions of the reaction. Attempts to prepare nitroso-compounds of semicarbazidesemicarbazones of *cyclo*hexenones proved unsuccessful. When boiled with water, semicarbazidesemicarbazones of *cyclo*hexenones first yield semicarbazide and the corresponding semicarbazones, which then decompose into semicarbazide and the ketones and, in some cases, partly into azine and hydrazine. Boiling alkali hydroxide solutions rapidly decompose semicarbazidesemicarbazones into the ketones and tarry products. Cold hydrocyanic acid combines with neither the semicarbazones nor the semicarbazidesemicarbazones of *cyclo*hexenones. The latter are decomposed at a high temperature into ammonia, tarry matters, and probably hydrazodicarbonamide. Di- and in some instances tri-hydrochlorides of semicarbazidesemicarbazones are obtainable; the third hydrogen chloride molecule probably combines at the double linking, with the carbonyl oxygen atom united with the semicarbazide residue.

3-*Methyl*-5-*furyl*-Δ^2-cyclo*hexenonesemicarbazone*, $C_{12}H_{15}O_2N_3$, decomp. 177—178·5°, is accompanied by another *compound*, $C_{13}H_{20}O_3N_6$, when 2 mols. of the semicarbazide act on 1 mol. of the ketone. The *semicarbazidesemicarbazone*, $C_{15}H_{22}O_2N_6$, decomposes at about 201—202°.

Thiosemicarbazones of the following are described: 3-*methyl*-Δ^2-cyclo*hexenone*, $C_8H_{13}N_3S$, m. p. 136—138°; 3:5-*dimethyl*-Δ^2-cyclo*hexenone*, m. p. about 187°, decomp. at 194·5—195·5°; 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone*, m. p. 150—151°; 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone*, m. p. 160—161°; 3-*methyl*-5-iso*butyl*-Δ^2-cyclo*hexenone*, m. p. 128—129° (decomp.); 5-*furyl*-3-*methyl*-Δ^2-cyclo*hexenone*, decomp. at 186—187·5°; 5-*phenyl*-3-*methyl*-Δ^2-cyclo*hexenone*, m. p. 201—203° (decomp.). T. H. POPE.

Preparation of phenylcarbamic acid hydrazones of *cyclo*hexenones. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **56**, 45—53; cf. preceding abstract).—Borsche and Merkwitz (A., 1902, i, 186; 1904, i, 945; 1905, i, 305) have shown that the action of the semicarbazones of aliphatic, aromatic, and hydroaromatic aldehydes and ketones on primary aromatic amines results in liberation of ammonia and formation of phenylcarbamic acid hydrazones of the aldehydes or ketones, these ultimately undergoing transformation into azines. The author has investigated the reactions taking place when aniline is boiled with the semicarbazones and semicarbazidesemicarbazones of 3-methyl-, 3:5-dimethyl-, 3-methyl-5-ethyl-, and 3-methyl-5-*iso*propyl-Δ^2-*cyclo*hexenones, and with mesityl oxide semicarbazidesemicarbazone.

The last of these compounds, when boiled with aniline, yields hydrazocarbonamide and a *compound* containing 13·6—13·8% of nitrogen and decomposing at 234—236°. The latter is also formed, under similar conditions, from 3-methyl-5-ethyl-Δ^2-*cyclo*hexenone-semicarbazone and -semicarbazidesemicarbazone. In every case, the reaction with aniline gives as final product the *cyclo*hexenonephenylsemicarbazone (phenylcarbamic acid hydrazone), which does not react further with aniline to form an azine (see above). These results are in agreement with Borsche's statement (A., 1902, i, 186) that, with the semicarbazones of ketones, the reaction usually stops at the first phase.

The phenylsemicarbazones obtained, which may be used for characterising the *cyclo*hexenones, are as follows: 3-*methyl*-Δ^2-cyclo*hexenone*, m. p. 173—174°; 3:5-*dimethyl*-Δ^2-cyclo*hexenone*, decomp. at 191—192°; 3-*methyl*-5-*ethyl*-Δ^2-cyclo*hexenone*, m. p. (decomp.) about 210—211°; 3-*methyl*-5-iso*propyl*-Δ^2-cyclo*hexenone*, m. p. (decomp.) 152—153°.

T. H. POPE.

Superheating of uniform organic compounds. II. Mono- and di-ketones. S. SKRAUP and S. GUGGENHEIMER (Ber., 1925, **58**, [*B*], 2488—2500).—*p*-Anisyl methyl, ethyl, propyl, and *iso*propyl ketones are considerably more stable to heat than the corresponding hydrocarbons (cf. Skraup and Nieten, A., 1924, i, 1185), but at a relatively high temperature they lose water and undergo autocondensations which rapidly lead to resinification and carbonisation without apparently yielding simple organic fission products. In this respect they differ strikingly from acetophenone, which at 330° gives dypnone, diphenylfuran, and triphenylbenzene in 70% yield.

Well-defined products are obtained by superheating diketones of the type $Ar{\cdot}CO{\cdot}[CH_2]_n{\cdot}CO{\cdot}Ar$ (n=2—5), the compounds with an even number of carbon atoms being more reactive than those with an odd number. Loss of water from αδ-, αζ-, and αη-diketones occurs in much the same manner as under the influence of condensing agents, and the abnormal behaviour of αε-diketones which results in scission of the carbon chain is also observed under the influence of chemical agents. αδ-Diketo-αδ-diphenylbutane at 300—310° yield 2:5-diphenylfuran in 80% yield. αε-Diketo-αε-diphenylpentane at 330° affords acetophenone and, presumably, phenyl vinyl ketone, which undergoes further condensation; αε-*diketo*-αε-*di*-p-*chlorophenylpentane*, m. p. 117°, prepared in unsatisfactory yield from glutaryl chloride and chlorobenzene, appears to yield *p*-chloroacetophenone. αζ-Diketo-αζ-diphenylhexane appears to be converted at 300—310° into a mixture of 2-benzoyl-1-phenyl-Δ^5-*cyclo*pentene and 2-benzoyl-1-phenyl-Δ^1-*cyclo*pentene. Adipyl chloride and chlorobenzene in the presence of aluminium chloride yield αζ-*diketo*-αζ-*di*-p-*chlorophenylhexane*, m. p. 166—167°, and δ-p-*chlorobenzoylvaleric acid*, m. p. 130°; if excess of aluminium chloride is employed and the temperature is allowed to rise during the reaction, a partial condensation of the diketone to 2-p-*chloro*-

benzoyl-1-p-*chlorophenyl*-Δ^5-cyclo*pentene*, m. p. 130°, occurs, although this substance could not be obtained by the action of aluminium chloride on pre-formed diketone. When concentrated sulphuric acid is used as condensing agent the diketone affords 2-p-*chlorobenzoyl*-1-p-*chlorophenyl*-Δ^1-cyclo*pentene*, m. p. 108°. A mixture of the *cyclo*pentene derivatives is obtained from the diketone at 255—265°, whereas at a higher temperature secondary changes occur, causing polymerisation and carbonisation with production of *p*-chlorobenzoic acid. $\alpha\eta$-Diketo-$\alpha\eta$-diphenyl-*n*-heptane at 325—330° affords a mixture of 2-benzoyl-1-phenyl-Δ^6-*cyclo*hexene and 2-benzoyl-1-phenyl-Δ^1-*cyclo*hexene. Pimelyl chloride and chlorobenzene in the presence of aluminium chloride yield $\alpha\eta$-*diketo*-$\alpha\eta$-*di*-p-*chlorophenylheptane*, m. p. 112°, and ε-p-*chlorobenzoylhexoic acid*, m. p. 139—140°. The diketone is not affected by concentrated sulphuric acid at 100°, but when heated at 285—295°, gives *p*-chlorobenzoic acid and a *substance*, $C_{19}H_{15}OCl_2$, m. p. 156°, thus indicating the probable production of a mixture of 2-*p*-chlorobenzoyl-1-*p*-chlorophenyl-Δ^6- and -Δ^1-*cyclo*hexenes. H. WREN.

Mechanism of reduction. VI. H. J. PRINS (Rec. trav. chim., 1925, **44**, 1093—1100; cf. A., 1925, ii, 1169).—The difference between reducing agents is discussed in terms of the degree of activation of the hydrogen atom. Experiments on the reduction in acid media of benzophenone with formation of benzopinacone and benzhydrol show that the theory of alkalinity of the metallic surface (Böeseken and Cohen, A., 1913, i, 1062) is incorrect. The formation of hydrol depends on the ratio between the velocity of condensation and of reduction of the half-pinacone, $CPh_3{\cdot}OH$, both of these reactions taking place on the metallic surface. Increase in the active surface and decrease in the reduction velocity both tend towards pinacone formation, so that with aluminium amalgam in alcoholic hydrochloric acid solution only pinacone is obtained. R. W. WEST.

Transformation of trisubstituted aldehydes into disubstituted ketones. A. ORÉKHOV and M. TIFFENEAU (Compt. rend., 1926, **182**, 67—69).—The transformation of aldehydes of the type $CR'_2R''{\cdot}CHO$ into the ketones $CHR'R''{\cdot}CO{\cdot}R'$ and $CHR'_2{\cdot}CO{\cdot}R''$ by the agency of cold sulphuric acid has been studied (cf. Danilov, A., 1923, i, 680, 787, 788). $\alpha\alpha$-Diphenylpropaldehyde yields exclusively phenyl α-phenylethyl ketone; $\alpha\alpha$-diphenylbutaldehyde gives a mixture of about 66% of phenyl α-phenylpropyl ketone and about 33% of diphenylmethyl ethyl ketone; α-phenyl-α-methylpropaldehyde gives solely α-phenylethyl methyl ketone and α-phenyl-α-ethylbutaldehyde yields exclusively α-phenylpropyl ethyl ketone. These products are the same as those obtained by the action of sulphuric acid on the corresponding glycols from which the aldehydes are obtained (cf. A., 1921, i, 565, 788; 1922, i, 458; 1923, i, 333, 788, 789; 1924, i, 729). It would thus seem that the transformation of the glycols and hydrobenzoins into ketones is not a semipinacolinic transformation, but takes place *via* the trisubstituted aldehyde. L. F. HEWITT.

Phenyl α-acenaphthyl ketone and phenyl-α-acenaphthylmethane. K. DZIEWOŃSKI and M. RYCHLIK (Bull. Intern. Acad. Polonaise, 1925, A., 179—195).—See this vol., 70.

Synthesis of substituted indones and *cyclo*pentadienones. A. LÖWENBEIN and G. ULICH (Ber., 1925, **58**, [*B*], 2662—2667).—Benzylidenediphenylmaleide, dissolved in benzene, is converted by an ethereal solution of magnesium phenyl bromide into the *compound*, $\begin{matrix}CPh{\cdot}C(:CHPh)\\CPh{\cdot}CPh(OH)\end{matrix}\!>\!O$, m. p. 210° (decomp.), the constitution of which rests on analyses, indifference towards ketonic reagents, insolubility in aqueous sodium hydroxide, and indifference towards Grignard's reagents. It is converted by treatment with alcoholic sodium hydroxide, or, preferably, with sulphuric acid or hydrogen chloride in glacial acetic acid, into 2 : 3 : 4 : 5-*tetraphenyl*-$\Delta^{2:4}$-cyclo*pentadien*-1-*one*, having an intense violet-black colour, m. p. 218°. The ketone is transformed by magnesium benzyl chloride into 1-*benzyl*-2 : 3 : 4 : 5-*tetraphenyl*-$\Delta^{2:4}$-cyclo*pentadien*-1-*ol*, m. p. 155—156° after softening, which, with glacial acetic acid and hydrogen chloride, yields 2 : 3 : 4 : 5 : 6-*pentaphenylfulvene*, $\begin{matrix}CPh{:}CPh\\CPh{:}CPh\end{matrix}\!>\!C{:}CHPh$, m. p. 204°; the latter compound is also obtained by condensing 2 : 3 : 4 : 5-tetraphenyl-$\Delta^{2:4}$-*cyclo*pentadiene with benzaldehyde.

Benzylidenephthalide is converted by magnesium phenyl bromide into 2 : 3-diphenylindone, m. p. 150—151°; the compound does not appear to be the primary product of the change, since the yield is increased by increasing the relative proportion of the Grignard reagent and the solution is only pale yellow in colour, passing into the intensely red colour of the indone after hydrolytic decomposition of the solution. H. WREN.

Methylation of the oximes of benzil. O. L. BRADY and H. M. PERRY (J.C.S., 1925, **127**, 2874—2882).—A reinvestigation of the methyl ethers of the oximes of benzil, using methyl sulphate as the methylating agent, abolishes confusion in the literature of these compounds (cf. Auwers and Meyer, A., 1889, 403; Dittrich, A., 1891, 317). The constitutions of the ethers are established by heating with hydriodic acid and determining the methyl iodide obtained from the *O*-ethers and by detecting the methylamine from the *N*-ethers by Valton's method (A., 1925, ii, 446). The usual configurations are adopted for the oximes, and not those suggested by Meisenheimer. α-Benzildioxime yields α-*benzildioxime* NN-*dimethyl ether*, $C_{16}H_{16}O_2N_2,\frac{1}{2}C_6H_6$, m. p. 185° [anhyd., m. p. 192° (decomp.)], and α-benzildioxime *NO*-dimethyl ether, m. p. 109° (Auwers and Meyer, m. p. 109—110°). Methylation with methyl iodide yields the latter compound together with α-benzildioxime *OO*-dimethyl ether, m. p. 163—164° (Auwers, m. p. 165°), which could not be obtained by use of methyl sulphate. β-Benzildioxime, obtained by an improved method by solution of α-benzildioxime in boiling aniline and removal of aniline of crystallisation from the crystalline deposit, gives β-benzildioxime *NO*-dimethyl ether, m. p. 102—103°

(identical with Auwers' compound, m. p. 88—89°), and β-benzildioxime *OO*-dimethyl ether, m. p. 72—73° (Auwers, m. p. 72°). Attempts to prepare the *NN*-dimethyl ether were unsuccessful. γ-Benzildioxime gives γ-benzilmonoxime *O*-methyl ether and benzil, probably formed respectively by hydrolysis of an *ON*-dimethyl ether and of an *NN*-dimethyl ether, since the *N*-methyl compounds are unusually easily hydrolysed. Methylation with methyl iodide gave crystals of a *compound*, m. p. 145—157°, insufficient for further purification. α-Benzilmonoxime gives α-benzilmonoxime *O*-methyl ether, m. p. 58—59° (Dittrich, m. p. 62—63°). The *N*-methyl ether could not be obtained. γ-Benzilmonoxime gives *γ-benzilmonoxime N-methyl ether*, m. p. 109—110°, and γ-benzilmonoxime *O*-methyl ether, m. p. 63° (Dittrich, m. p. 64—65°). The latter gives curiously low analytical results for methoxyl. A possible explanation, based on Meisenheimer's configuration, and involving reduction of the carbonyl group and ring formation by elimination of water, is being investigated :

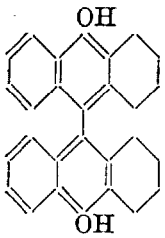
$$\mathrm{Ph{\cdot}\overset{\overset{\mathrm{N{\cdot}OMe}}{\|}}{C}{\cdot}COPh} \longrightarrow \mathrm{Ph{\cdot}\overset{\overset{\mathrm{N{\cdot}OMe}}{\|}}{C}{\cdot}CHPh{\cdot}OH} \longrightarrow \mathrm{Ph{\cdot}\overset{\overset{\mathrm{N{\cdot}O{\cdot}CH_2}}{|}}{C}{-}CHPh}$$

On boiling with hydrochloric acid, α-benzildioxime *NN*-dimethyl ether gives benzil, whilst the *ON*-dimethyl ether gives γ-benzilmonoxime *O*-methyl ether, probably through α-benzilmonoxime *O*-methyl ether, which is converted into the γ-compound under these conditions. β-Benzildioxime *ON*-dimethyl ether also gives γ-benzilmonoxime *O*-methyl ether. α-Benzildioxime *OO*-dimethyl ether, when heated with concentrated hydrochloric acid in a sealed tube at 110°, gives β-benzildioxime *OO*-dimethyl ether. The *O*-ethers are exceptionally stable to hydrolysing agents, whereas the *N*-ethers are readily hydrolysed; the latter form hydrochlorides, the former do not; and the β-forms of the dioximes and the γ-forms of the monoximes are the most stable at high temperatures. M. JOHNSON.

Hydrobenzoin transformation. II. *s*-Phenylanisyl glycol (*p*-methoxyhydrobenzoin). A. OREKHOV and M. TIFFENEAU (Bull. Soc. chim., 1925, [iv], **37**, 1410—1420; cf. A., 1923, i, 333).—*s*-Phenylanisyl glycol, $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHPh{\cdot}OH$, on dehydration with 20% sulphuric acid, partly undergoes the usual "pinacoline dehydration," yielding phenyl-*p*-anisylacetaldehyde, $OMe{\cdot}C_6H_4{\cdot}CHPh{\cdot}CHO$, but is also partly converted into *p*-methoxydeoxybenzoin, $OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}COPh$, by "vinyl dehydration," thus $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CHPh{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH{:}CPh{\cdot}OH \longrightarrow OMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}COPh$. Since the alternative "vinyl dehydration" $\longrightarrow OMe{\cdot}C_6H_4{\cdot}C(OH){:}CHPh \longrightarrow OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$, does not take place, it is concluded that the hydroxyl group in the neighbourhood of the anisyl group is less stable than that attached to the carbon atom carrying the phenyl group, a result which indicates that the affinity of the anisyl group is greater than that of the phenyl group. Since hydrobenzoin under similar conditions gives exclusively diphenylacetaldehyde, it is evident that the introduction of a *p*-methoxy-group diminishes the tendency of the eliminated hydroxyl group to take with it hydrogen from the adjacent hydroxyl group rather than from the carbon in the dehydration process. p-*Anisylbenzyl carbinol*, $OMe{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CH_2Ph$, m. p. 57—58°, obtained in 88% yield from magnesium benzyl chloride and anisaldehyde (cf. C. Hell, A., 1904, i, 242), is readily converted (yield 84%) by 50% sulphuric acid into s-*phenyl*-p-*anisylethylene* (p-*methoxystilbene*), m. p. 135—136°. This gives a *dibromide*, m. p. 175—176° (decomp.), reconverted by aqueous acetone into *p*-methoxystilbene; potassium carbonate converts it into p-*methoxytolane*, m. p. 89—90° [*dibromide*, m. p. 166—167° (decomp.)], whilst sodium acetate and acetic acid yield a mixture of a crystalline, m. p. 65—75°, and an oily *diacetate*, probably stereoisomerides. On hydrolysis with alcoholic potassium hydroxide the former yields *phenyl*-p-*anisyl glycol*, m. p. 111—112°, whilst from the oily diacetate the stereoisomeric glycol, m. p. 134—135°, is obtained similarly. Both isomerides on dehydration yield a mixture of *p*-methoxydeoxybenzoin and *phenyl*-p-*anisylacetaldehyde*, a viscous oil (*semicarbazone*, m. p. 127—128°), oxidised to phenyl-*p*-anisyl ketone by chromic and acetic acids. Phenyl-*p*-anisylacetaldehyde is obtained more readily by the action of dry potassium hydroxide on the iodohydrin of *as*-phenyl-*p*-anisylethylene in ethereal solution. The oily product, probably the ethylene oxide, on treatment with sodium hydrogen sulphite yields the hydrogen sulphite compound of phenyl-*p*-anisylacetaldehyde, from which the aldehyde is obtained on hydrolysis with 10% sodium carbonate. R. BRIGHTMAN.

Catalytic hydrogenations under pressure in the presence of nickel salts. IX. Anthraquinone, phenanthraquinone, and benzanthrone. J. VON BRAUN and O. BAYER (Ber., 1925, **58**, [*B*], 2667—2685).—Confirmation of the view of von Braun (A., 1924, i, 545) and Schroeter (A., 1925, i, 127) that 9 : 10-dihydroanthracene is the primary product of the catalytic hydrogenation of anthracene and that this compound passes subsequently into 1 : 2 : 3 : 4-tetrahydroanthracene is found in the behaviour of dihydroanthranol, which is reduced in decahydronaphthalene solution to 1 : 2 : 3 : 4-tetrahydroanthranol (yield 15%), 9 : 10-dihydroanthracene, and 1 : 2 : 3 : 4-tetrahydroanthracene. Whether catalytic hydrogenation of anthracene occurs exclusively through the 9 : 10-dihydro-compound or whether the primary attack takes place also at the side nucleus cannot be decided for the hydrocarbon, but a decision can be reached for its oxygenated derivatives using anthranol as starting point; if hydrogenation occurs initially in the 9 : 10-position, the yield of tetrahydroanthranol from this substance cannot, under identical conditions, exceed that from dihydroanthranol. Actually the yield is far greater, so that for anthranol the primary attack occurs mainly or possibly exclusively at the side nucleus. The possibility that tetrahydroanthranol is readily attacked by hydrogen with elimination of the hydroxy-group and formation of tetrahydroanthracene is invalidated by the observation that it absorbs hydrogen less readily than

anthranol or dihydroanthranol and yields successively 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthranol and 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroanthracene, m. p. 39° (Schroeter, *loc. cit.*, records m. p. 35°). Anthraquinone is hydrogenated with great ease under pressure, the first isolable product being anthranol, which, if the supply of hydrogen is suitably controlled, is obtained in quantitative yield; further addition of hydrogen leads to the production of tetra- and octa-hydroanthranols. 1 : 2 : 3 : 4-*Tetrahydroanthranol*, m. p. 108°, its *acetate*, m. p. 109°, *benzoate*, m. p. 142°, and *methyl ether*, b. p. 197° /14 mm. (slight decomp.), are described. It does not give a coloration with ferric chloride. With bromine in glacial acetic acid, it affords a *monobromo*-derivative, m. p. 123°. Chromic acid in glacial acetic acid oxidises it to a mixture of little anthraquinone and much 1 : 2 : 3 : 4-tetrahydroanthraquinone, m. p. 154° (cf. Schroeter, *loc. cit.*).

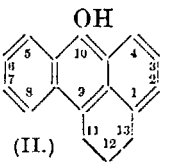


(I.)

It is converted by nitric acid into black, smeary products. Nitrous acid acts on a 10% solution of it in alcohol, precipitating *di-tetrahydrodianthranol*, (I), m. p. 167°, and giving also tetrahydroanthraquinone and the *nitroso*-derivative, $C_{14}H_{13}O_2N$, m. p. 210°; in more concentrated solution, the nitroso-compound is obtained in better yield, accompanied by tetrahydroanthraquinone substances, difficult to characterise, but ditetrahydrodianthranol is not formed. It couples very readily with diazonium salts, but the products crystallise with difficulty; reduction of the benzeneazo-derivative by sodium hyposulphite gives *aminotetrahydroanthranol*, which could not be caused to crystallise; the *hydrochloride* is described. 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*Octahydroanthranol*, m. p. 125°, is very sparingly soluble in alkali hydroxide solutions; the *acetyl* derivative, m. p. 52°, *benzoyl* compound, m. p. 128°, and p-*bromo*-derivative, m. p. 123°, are described. It is oxidised by chromic acid in acetic acid solution to *octahydroanthraquinone*, m. p. 182°, which is quantitatively reduced by sodium hyposulphite to *octahydroanthraquinol*, m. p. 234—236°. Nitric acid transforms it into an amorphous compound, m. p. above 300°. Nitrous acid yields the corresponding *nitroso*-derivative, m. p. 190°, together with octahydroanthraquinone and *dioctahydrodianthranol*, which could not be obtained in the homogeneous state. *Benzeneazo-octahydroanthranol*, m. p. 163°, is smoothly reduced by sodium hyposulphite in alcoholic solution to 9-*amino-octahydroanthranol*, which is insoluble in alkali hydroxide solutions and very sparingly soluble in acids; its constitution is, however, established by its oxidation to octahydroanthraquinone.

Hydrogenation of phenanthraquinone proceeds similarly to that of anthraquinone, affecting first the quinone complex and subsequently one side nucleus after the other. Differences are found in the possibility of so moderating the reduction of phenanthraquinone that phenanthraquinol in addition to 9-phenanthrol can be isolated, thus clearly establishing the first step in the action. Also, owing to the lower stability of the hydrogenated derivatives of phenanthrene in comparison with those of anthracene, the individual products are obtained in lower yield, and it is not possible to trace the several phases of the change in so quantitative a manner. Phenanthraquinone dissolved in decahydronaphthalene readily absorbs two atomic proportions of hydrogen at 160°, yielding 9-phenanthrol, m. p. 149—150° (acetate, m. p. 76°), and phenanthraquinol, m. p. 148°. Further hydrogenation occurs only at a much higher temperature and, after eight atomic proportions of hydrogen have been absorbed, gives a mixture of di- and *tetra-hydrophenanthrol*, m. p. 114—115°; the acetyl, benzoyl, *p*-nitrobenzoyl, bromo-, and benzeneazo-derivatives are oily or badly crystallised, pointing to the possibility that the tetrahydro-compound is a mixture of two isomeric forms, although this view is not supported by its definite m. p. and non-separability by solvents. It is oxidised by chromic acid in glacial acetic acid solution to *tetrahydrophenanthraquinone*, decomp. 90—100°, according to the rate of heating. More complete hydrogenation of phenanthraquinone or 9-phenanthrol affords a mixture of octahydrophenanthrene (cf. Schroeter, *loc. cit.*) and *octahydrophenanthrol*, m. p. 133° (*acetyl* derivative, m. p. 133°; *monobromo*-derivative, m. p. 110°). The phenol is oxidised by chromic acid to *octahydrophenanthraquinone*, decomp. 150°. It couples with diazobenzene, yielding *benzeneazo-octahydrophenanthrol*, m. p. 140°, which is reduced by sodium hyposulphite to *aminohydroxyoctahydrophenanthrene*, m. p. 184°.

Technical benzanthrone is readily purified by recrystallisation from decahydronaphthalene and in this solvent absorbs four atomic proportions of hydrogen at 160°, a further four somewhat more slowly at 200°, and the final two at 250°. 1 : 9-*Trimethyleneanthranol*, (II), m. p. 148°, readily yields a *benzoyl* derivative, m. p. 135°. [In naming these derivatives, it does not appear possible to express the genetic relationship to benzanthrone in any simple manner, and the authors propose to regard them as substituted anthracene derivatives in which the fourth ring is 1 : 9-trimethylene.] 1 : 9-*Trimethylene*-5 : 6 : 7 : 8-*tetrahydroanthranol*, m. p. 137° (*acetate*, m. p. 123°), is obtained together with 1 : 9-*trimethylene*-5 : 6 : 7 : 8-*tetrahydroanthracene*, b. p. 228—230°/16 mm. (*picrate*, m. p. 125°), at 180—200°; at 250°, the hydrocarbon is practically the sole product of the change, even when the reaction is very prolonged. It is not smoothly dehydrogenated by sulphur or oxidised by nitric acid. Treatment of 1 : 9-trimethylene-5 : 6 : 7 : 8-tetrahydroanthracene with sodium and alcohol yields a hydrocarbon, b. p. 212—214°/13 mm., which by analogy with the mode of reduction of naphthalene, is regarded as 1 : 9-*trimethylene*-1 : 4 : 5 : 6 : 7 : 8-*hexahydroanthracene*; it immediately decolorises permanganate and gives an oily dibromide. H. WREN.



(II.)

Preparation of hydrogenated, polynuclear quinones. A. SKITA [with K. WARNAT, C. WULFF, H. SIEGEL, and B. SCHREYER] (Ber., 1925, **58**, [*B*], 2685—2697).—The methods adopted previously for

the reduction of anthraquinone and similar substances lead to products poorer in oxygen. It is therefore remarkable that catalytic hydrogenation of *para*- and *ortho*-quinones in the presence of platinum affords nuclear-hydrogenated quinols or glycols which are readily oxidised to hydrogenated quinones.

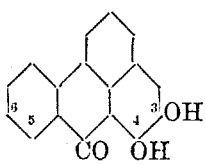
Phenanthraquinone in the presence of glacial acetic acid, concentrated hydrochloric acid, chloroplatinic acid, colloidal platinum, and water readily absorbs twelve atomic proportions of hydrogen at 50—60°, yielding 9 : 10-*dihydroxydecahydrophenanthrene*, b. p. 352—355°, m. p. 136° (*diacetate*, m. p. 160°), which is oxidised by boiling, dilute mercuric acetate solution to *octahydrophenanthraquinone*, m. p. 142° (cf. p. 173). If the mineral acid is omitted, the reaction terminates with the production of 9 : 10-*dihydroxy*-9 : 10-*dihydrophenanthrene* (*diacetate*, m. p. 183°).

Anthraquinone in acid solution in the presence of colloidal platinum affords octahydroanthraquinol, m.p. 242° (*acetate*, m. p. 224°), which is converted by the action of air on its solution in benzene or acetone into octahydroanthraquinone, m. p. 183°. The quinol or quinone is transformed by bromine into *octahydroanthraquinone dibromide*, m. p. 128°. The mother-liquors from the preparation of octahydroanthraquinol contain octahydroanthranol, m. p. 125° (benzoate, m.p. 129°); bromo-octahydroanthranol, m.p. 123°, and the *acetate*, m. p. 143°, are described (see p. 173). It is remarkable that the hydrogenation of anthraquinone under these conditions does not invariably proceed to the production of the octahydroanthraquinol, but sometimes ceases when tetra- or hexahydroanthraquinol has been produced; the phenomenon appears to depend on the size of the colloidal platinum particles. The isolation of *tetrahydroanthraquinol*, decomp. (indef.) 206—216° (*acetate*, m. p. 204—206°), is effected with certainty if mineral acid is omitted from the mixture; the quinol is readily oxidised by air to 1 : 2 : 3 : 4-tetrahydroanthraquinone. Certain reduction to the hexahydroanthraquinol stage is effected by careful regulation of the quantities of hydrochloric acid and platinum. 1 : 2 : 3 : 4 : 5 : 8-*Hexahydroanthraquinone*, m. p. 170°, and its *dibromide*, m. p. 118°, are described; the position of the hydrogen atoms is deduced from the conversion of the quinone by sodium acetate and acetic anhydride into 1 : 2 : 3 : 4-tetrahydroanthraquinol diacetate, m. p. 204—206° (see above). 1 : 2 : 3 : 4 : 5 : 8-*Hexahydroanthraquinol* has m. p. 229—230° (*diacetate*, m. p. 209°); an isomeric *diacetate* of hexahydroanthraquinol, m. p. 212°, is obtained by the reduction of tetrahydroanthraquinone with acetic acid and excess of zinc dust.

Reduction of 2-methylanthraquinone in the presence of mineral acid affords 2-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthraquinol*, m. p. 193° (*diacetate*, m. p. 143°), which is very readily oxidised to 2-*methyloctahydroanthraquinone*, m. p. 158—159°. Similarly, 2-aminoanthraquinone yields 2-amino-octahydroanthraquinol (*hydrochloride*, m. p. above 300°), which is converted by air into 2-*amino-octahydroanthraquinone*, m. p. 140—145°.

Hydrogenation of acenaphthenequinone under the conditions described for anthraquinone proceeds with unusual ease, and if reaction is stopped after the absorption of ten atomic proportions of hydrogen, gives a mixture of products from which the following compounds are isolated: a *dihydroxytetrahydroacenaphthene*, b. p. 185°/9 mm., which gives a *diacetate*, m. p. 115—116°; *hexahydroacenaphthene*, $C_{12}H_{16}$, b. p. 114—115°/10 mm.; more highly hydrogenated acenaphthenequinones from which individual substances could not be isolated; and a *substance*, $C_{24}H_{30}O_4$, m. p. 206°. H. WREN.

Reduction products of the hydroxyanthraquinones. VII. W. B. MILLER and A. G. PERKIN (J.C.S., 1925, **127**, 2684—2685).—Alizarin 2-methyl ether yields on reduction chiefly 1-*hydroxy*-2-*methoxyanthrone*, m. p. 135—137° (*diacetyl* derivative, m. p. 202°), with 4-*hydroxy*-3-*methoxyanthrone*, m. p. 202° (*acetyl* derivative, m. p. 186°), in smaller amounts. By the benzanthrone reaction *benzalizarin monomethyl ether*, m. p. 247—249° (*acetyl* derivative, m. p. 205—207°), is obtained from 4-hydroxy-3-methoxyanthrone, whilst 1-hydroxy-2-methoxyanthrone yields *iso-benzalizarin*, m. p. 260—262° (*acetyl* derivative, m. p. 243—245°; *diacetyl* derivative, m. p. 214°), in which the hydroxyl groups are in the 3 : 4- or 5 : 6-positions (annexed formula). Benzalizarin is akin to alizarin in its powerful dyeing properties with mordants; *iso*benzalizarin is much less powerful. This suggests that the dyeing properties of alizarin are due to the presence of a *para*-quinonoid rather than an *ortho*-quinonoid grouping. *Anthrapurpurin dimethyl ether*, m. p. 235° (*acetyl* derivative, m. p. 205°), has been prepared, and from it *diacetylanthrapurpurinanthranol dimethyl ether*, m. p. 178°, was obtained by reduction followed by acetylation.



B. W. ANDERSON.

Action of hydrazine hydrate on phenanthraquinone. Correction. S. DUTT (J.C.S., 1925, **127**, 2971; cf. *ibid.*, 1923, **123**, 3420).—Anhydrous hydrazine reacts with phenanthraquinone in absolute alcohol, giving a good yield of phenanthrone. In presence of small quantities of moisture or with ordinary commercial hydrazine hydrate, 9 : 10-dihydroxyphenanthrene is obtained almost exclusively. M. JOHNSON.

1-Benzoylbenzanthrone. FARBW. VORM. MEISTER, LUCIUS, U. BRÜNING.—See B., 1926, 44.

Menthone series. I. J. READ and A. M. R. COOK (J.C.S., 1925, **127**, 2782—2788).—The alkaline reduction of *dl*-piperitone yields some *dl*-α-phellandrene and a mixture of *dl-iso*menthols, from which *dl-iso*menthone is obtained by oxidation with chromic acid, and this on reduction yields crystalline *dl*-menthol with some *dl-iso*menthols. Reduction of *dl*-piperitone with hydrogen in presence of colloidal palladium yields *dl-iso*menthone direct. There exists a definite dynamic equilibrium between *iso*menthone and menthone in the presence of alkali. From pure *dl-iso*menthone have been obtained the *oxime*, m. p. 99—100°, *benzoyloxime*, m. p. 55·5°, and *iso*oxime, m. p. 94—95°. *dl*-Menthone yields an oxime, m. p. 81—82°, *benzoyloxime*, m. p. 72—73°, *iso*oxime, m. p.

114—115°, *α-semicarbazone*, m. p. 185—186°, and *β-semicarbazone*, m. p. 161—162°. B. W. ANDERSON.

Determination of menthol in alcoholic solution. DONATH and SEBOR.—See B., 1926, 75.

Carbylamines. XIII. Reaction of phenylcarbylamine with pernitrosomenthone. M. PASSERINI (Gazzetta, 1925, **55**, 721—726).—Pernitrosomenthone dissolved in the smallest possible quantity of ether is treated with phenylcarbylamine. The crystals collected after 8 to 10 days consist of *α-mentholcarboxy-δ-anilide* (I), m. p. 166—168°, $[\alpha]_D^{10}+62{\cdot}62°$; a small yield of an *isomeride*, m. p. 134—136°, is also obtained. When compound (I) is heated for 80 hrs. with alcoholic potassium hydroxide in a closed tube at 120—130°, *α-mentholcarboxylic acid*, m. p. 112—113°, is formed. Compound (I) is oxidised by potassium dichromate and sulphuric acid to *l*-menthone, which is characterised by its oxime and its semicarbazide. W. E. ELLIS.

Action of phosphoric acid on terpenes etc. P. G. CARTER, H. G. SMITH, and J. READ.—See B., 1926, 75.

Rhodesian eucalyptus oils. P. G. CARTER and J. READ.—See B., 1926, 76.

Chemico-physical investigations on certain acid phthalates of terpenic alcohols. V. PAOLINI (Annali Chim. Appl., 1925, **15**, 411—413).—The solution of a weak acid containing the salt of a strong base with the same acid obeys approximately the relationship: $\log(1/[H^+]) = \log(1/K_a) + \log([S]/[A])$, where $[H^+]$ is the hydrogen-ion concentration of the solution, K_a the dissociation constant of the weak acid, [S] the concentration of the salt, and [A] the concentration of the free acid in the same solution. Measurements made with acid phthalates at 25° in accordance with this equation give the following mean values for the dissociation constants: β-thujyl hydrogen phthalate, $7{\cdot}5\,.\,10^{-6}$; *l*-β-carvomenthyl hydrogen phthalate, $3{\cdot}02\,.\,10^{-6}$; *l*-α-terpinyl phthalate, $1{\cdot}42\,.\,10^{-5}$. T. H. POPE.

Isomeric thujones (tanacetones). *d*-α-Thujones. V. PAOLINI (Annali Chim. Appl., 1925, **15**, 414—416).—If α-thujonesemicarbazone is hydrolysed by phthalic anhydride (cf. A., 1912, i, 635), the resulting α-thujone has $[\alpha]_D+10{\cdot}23°$, whereas that obtained by Wallach by mineral acid hydrolysis has $[\alpha]_D-10{\cdot}23°$ (A., 1905, i, 147). When, however, the thujone given by the semicarbazone and phthalic anhydride is displaced, as it is formed, by a current of steam, the lævorotatory modification is obtained. Conversion into the dextrorotatory isomeride is evidently due to prolonged action of the hydrogen ions. T. H. POPE.

Camphor series. X. Synthesis of camphor. I. Catalytic action of reduced copper on borneols. B. MASUMOTO (Mem. Coll. Sci. Kyōtō, 1925, **9**, 219—224).—The oxidation of *d*- and *l*-borneols to camphor takes place without any side reactions when reduced copper at 200—220° is employed as a catalyst. Copper oxide, prepared from copper nitrate and sodium hydroxide and reduced with hydrogen at 200°, furnishes the best copper catalyst. No borneol is formed when camphor vapour and hydrogen are together passed over reduced copper. B. W. ANDERSON.

Camphor from turpentine oil. Y. MURAYAMA.—See B., 1926, 75.

Making *iso*bornyl esters. J. EBERT.—See B., 1926, 28.

Constituents of rosins and rosin oil, and polymerisation of turpentine oil. E. KNECHT and N. B. MAURICE.—See B., 1926, 21.

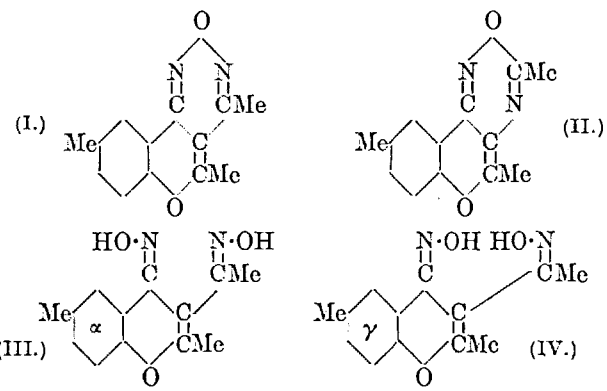
Nepetella, pennyroyal, and origanum oils. G. ROMEO and U. GIUFFRÈ.—See B., 1926, 107.

Vinylene-homologous furfuraldehydes. W. KÖNIG [with K. HEY] (Ber., 1925, **58**, [*B*], 2559—2566].—Aldehydes of the type, $C_4H_3O{\cdot}[CH{:}CH]_n{\cdot}CHO$, are obtained by the condensation of furfuraldehyde with acetaldehyde in cold, aqueous alkaline solution. The depth of colour of the compounds increases with increasing number of vinylene groups, but the increment per group, as measured by the displacement of the maximum of absorption, diminishes somewhat as the series is ascended. The depth of colour of the adducts of the aldehydes and stannic chloride or hydrogen chloride increases with increasing number of vinylene groups. 2-Furylacraldehyde (*strepto*-monovinylenefurfuraldehyde; for nomenclature see A., 1924, i, 669), m. p. 54° (*oxime*, m. p. 123°), is prepared in 60% yield by the interaction of furfuraldehyde and acetaldehyde at 0° in the presence of dilute aqueous sodium hydroxide. With more concentrated alkali hydroxide at 20° and with an increased proportion of acetaldehyde, a mixture of vinylene-homologous aldehydes is obtained, from which, by fractional distillation under reduced pressure followed by crystallisation of the solid fractions, the following individuals are isolated: ε-2-*furylpentadienal* (2-strepto*divinylenefurfuraldehyde*), m. p. 66° (*oxime*, m. p. 127°; *phenylhydrazone*, m. p. 153°); η-2-*furylheptatrienal* [2-strepto*trivinylenefurfuraldehyde*), m. p. 111° (*phenylhydrazone*, m. p. 183°). H. WREN.

Stereochemistry of the oximes of 1 : 3-diketones. I. Action of hydroxylamine on 3-acetyl-2 : 6-dimethylchromone. G. WITTIG and F. BAUGERT (Ber., 1925, **58**, [*B*], 2627—2636).—The possibilities of ring opening to compounds of the *cis*- or *trans*-configuration are critically discussed from a theoretical point of view (cf. Meisenheimer, A., 1922, i, 152; Kuhn and Ebel, A., 1925, i, 780, 1237; Böeseken, *ibid.*, 1237) and, for present purposes, the views of Meisenheimer are adopted.

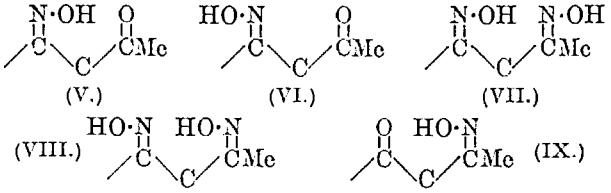
3-Acetyl-2 : 6-dimethylchromone is converted by hydroxylamine in acetic acid solution into a mixture of 3-*acetyl*-2 : 6-*dimethylchromone-γ-monoxime*, m. p. 100—100·5°, which is very stable towards hydrochloric acid and does not undergo the Beckmann change when treated with concentrated sulphuric and glacial acetic acids or with acetyl chloride, and 3-*acetyl*-2 : 6-*dimethylchromone-α-dioxime*, m. p. 222—224° (decomp.). Oximation of the yellow monoxime, m. p. 100—100·5°, in the presence of cold sodium hydroxide solution, affords 3-*acetyl*-2 : 6-*dimethyl-*

chromone-γ-dioxime, m. p. 159—159·5°, or, if slowly heated, m. p. 165—167° after softening at 159—159·5°, which is unaffected by sodium alkoxide solution, boiling water, or sodium carbonate solution, or by cold sulphuric acid; it is hydrolysed to the γ-monoxime by boiling hydrochloric acid. With acetyl chloride it yields the corresponding *diacetate*, m. p. 131—132°. When the γ-dioxime is boiled with 2*N*-sodium hydroxide solution or distilled under diminished pressure it is converted into 3 : 4-2′ : 6′-*dimethylchromo-5-methyl*-2 : 6-*oxdiazine* (I), m. p. 88—88·5°, whereas, when treated with concentrated sulphuric acid, phosphorus pentachloride, or acetyl chloride, it yields the isomeric 3 : 4-2′ : 6′-*dimethylchromo-6-methyl*-2 : 5-*oxdiazine*, (II), m. p. 144—144·5°. During the second change, the Beckmann isomerisation occurs in the oximated side-chain, leading to the production of a pyrazolone or oxdiazine ring; since the product is not basic and does not react with hydroxylamine, the former possibility is excluded. If Meisenheimer's views are adopted, the configuration (III) or (IV) follows for the dioxime, and its ability to lose water and form compound (I) decides in favour of (IV). Since the γ-monoxime is formed from the dioxime by concentrated hydrochloric acid and itself does not undergo the Beckmann change, and therefore has the oximino-group attached to the nucleus (which is also shown by the stability of the pyrone ring towards alkalis), it must have the configuration (V). Protracted treatment of the γ-monoxime with boiling 2*N*-sodium carbonate solution leads to the production of 3-*acetyl*-2 : 6-*dimethylchromone-α-monoxime*, m. p. 157°, which is not reconverted into the γ-oxime by hot, concentrated acids. Since further oximation transforms it into 3-acetyl-2 : 6-dimethylchromone-α-dioxime, it follows that the pyrone ring does not suffer fusion followed by re-closure to a structurally isomeric oxime during the action of the alkali. The monoxime must therefore have the constitution (VI). During the oximation of 3-acetyl-2 : 6-dimethylchromone in acetic acid solution, therefore, the γ- and α-monoximes are simultaneously produced and the latter is further converted into the α-dioxime. Since the α-dioxime is hydrolysed by acids to the α-monoxime and does not form the compound (I) (see above) by loss of water, it cannot be the δ-compound, and the α-configuration [formula (III) above] is regarded as established, which is in harmony with its stability towards alkali. With concentrated sulphuric acid, transformation does not occur in the side-chain, but the oximino-group is removed with production of the α-monoxime and, under definite conditions, of an intermediate *compound*, $C_{26}H_{24}O_5N_2$, m. p. 184—184·5°, the constitution of which has not been elucidated.



If the γ-monoxime reacts with hydroxylamine in boiling sodium carbonate solution, a mixture of the γ-dioxime and of a new *dioxime*, m. p. 156°, is formed, which, since it is hydrolysed by acids to the γ-monoxime, must have the β-configuration (VII), since the γ-form is already assigned. When distilled in a vacuum it yields the anhydride (I), together with the γ-dioxime, thus proving that the β- is first transformed into the γ-variety, which subsequently loses water. A similar transformation is observed when the β-form is digested with concentrated sulphuric acid. A fourth stereoisomeric *dioxime*, m. p. 195°, is obtained together with the anhydride (I) by prolonged treatment of the γ-form with boiling sodium hydroxide solution; for this only the δ-configuration (VIII) is available. Hydrolysis of the δ-dioxime leads to the formation of a new *monoxime*, m. p. 126°, in place of the expected α-oxime; since it is reconverted by hydroxylamine under mild conditions into the δ-dioxime it must have the δ-configuration (IX).

It is remarkable that the β-dioxime is converted by alkali into the anhydride (I): preliminary isomerisation to the γ-dioxime appears scarcely likely and probably the δ-dioxime is first formed, although this could not be established experimentally.



H. WREN.

Action of hydroxylamine on chromones. G. WITTIG and F. BAUGERT (Ber., 1925, **58**, [*B*], 2636—2642).—Chromones generally react extremely slowly with ketonic reagents, but, in this respect, hydroxylamine is exceptional, so that it appears probable that intermediate additive compounds are formed which subsequently become oximated. 2 : 8-Dimethylchromone and 2 : 8-dimethylthiochromone are converted by hydroxylamine in neutral solution into 2 : 8-*dimethylchromoneoxime*, m. p. 145°; by-products are also formed which indicate addition of hydroxylamine to the pyrone ring, but these have not been investigated completely. In alkaline solution, oximation of 2 : 8-dimethylchromone occurs differently; if the warm solution of the reaction product is immediately acidified with dilute mineral acid, 2 : 8-dimethylchromoneoxime is obtained, whereas cautious addition of acetic acid precipitates the *dioxime* of 3-*acetoacetyl-o-cresol*,

$OH{\cdot}C_6H_3Me{\cdot}C(:N{\cdot}OH){\cdot}CH_2{\cdot}CMe{:}N{\cdot}OH$,

m. p. 148—149° (slight decomp.), identical with the product obtained from hydroxylamine and 6-aceto-

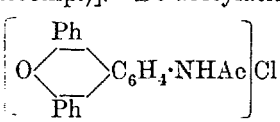
acetyl-*o*-cresol. If the dioxime is warmed with dilute mineral acids, the oximino-group remote from the phenyl radical is hydrolysed, and ring closure follows with production of 2 : 8-dimethylchromoneoxime. Treatment of the dioxime with cold acids yields the monoxime and an isomeric *substance*, $C_{11}H_{16}O_2N$, m. p. 90·5—91°, which is also obtained by the action of alcoholic ammonia on the dioxime or by heating the latter at 160°, and is therefore regarded as 5 : 2′-*hydroxy*-m-*tolyl*-3-*methyl*isooxazole.

Fission of the ring also occurs during the oximation of 2 : 6-dimethylchromone in alkaline solution, whereby an extremely unstable substance, $C_{11}H_{16}O_4N_2$, m. p. 70—73°, is isolated, which passes above its m. p. into the *dioxime* of 3-*acetoacetyl*-*p*-*cresol*, m. p. 122—122·5° (slight decomp.); according to analyses and properties, the compound is regarded as the hydroxylamino-oxime,

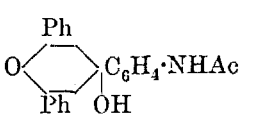
$OH{\cdot}C_6H_3Me{\cdot}C(:N{\cdot}OH){\cdot}CH_2{\cdot}CMe(OH){\cdot}NH{\cdot}OH$.

It is transformed by cold mineral acids into 2 : 6-*dimethylchromoneoxime*, m. p. 184—185°, which is also obtained from the dioxime and hot acids. On the other hand, the dioxime is not converted by cold mineral acid into the expected isooxazole derivative, $C_{11}H_{11}O_2N$, m. p. 53—54°, which is obtained, together with 2 : 6-dimethylchromoneoxime, by heating the dioxime above its m. p. Somewhat unexpectedly, the dioxime is converted by alcoholic ammonia into the hydroxylamino-oxime described above. Prolonged treatment of the dioxime with boiling sodium hydroxide solution leads to the formation of (?) 5 : 6′-*hydroxy*-m-*tolyl*-3-*methyl*isooxdiazine, m. p. 168—169° (slight decomp.) (*dibenzoate*, m. p. 123·5—124°), and (?) 3 : 6′-*hydroxy*-m-*tolyl*-5-*methyl*isooxdiazine, m. p. 185—187° (slight decomp.) (*diacetate*, m. p. 155·5—156°). H. WREN.

Pyrylium compounds. XVI. Triphenylpyrylium salts containing amino-groups. W. DILTHEY and C. BERRES (J. pr. Chem., 1925, [ii], **111**, 340—352; cf. A., 1925, i, 1441).—Condensation of *p*-acetamidobenzylideneacetophenone with acetophenone in acetic anhydride in presence of zinc chloride affords the *zinc chloride* double salt of 4-p-*acetamidophenyl*-2 : 6-*diphenylpyrylium chloride* (I), straw-yellow, m. p. 158°, which, when treated with aqueous pyridine, yields 4-p-*acetamidophenyl*-2 : 6-*diphenylpyranol*, (II), pale yellow, m. p. 188—189° [*perchlorate*, orange-yellow, m. p. 220—225° (decomp.)]. De-acetylation of the above first-named



(I.)



(II.)

condensation product is effected by dissolution in concentrated sulphuric acid, addition of water until turbidity is produced, and subsequent boiling. From the resulting solution, the *monopicrate*, violet-black, decomp. above 250°, the *dipicrate*, brick-red, converted into the monopicrate on recrystallisation, and the *perchlorate*, steel-blue, decomp. 295°, of 4-p-*aminophenyl*-2 : 6-*diphenylpyrylium*, can be precipitated by addition of the appropriate acids. p-*Acetamidostyryl* p-*methoxyphenyl ketone*, pale yellow, m. p. 186—187°, yields *p*-aminostyryl *p*-methoxyphenyl ketone (cf. Pfeiffer, A., 1925, i, 408) when boiled with concentrated alcoholic hydrochloric acid, whilst condensation with *p*-methoxyacetophenone in acetic anhydride, in presence of zinc chloride, affords a *zinc chloride* double salt, which, when treated with alcoholic perchloric acid, yields 4-p-*acetamidophenyl*-2 : 6-*di*-p-*anisylpyrylium perchlorate*, orange-red, decomp. above 250°, or, rapidly heated, m. p. 294°. The corresponding *picrate*, brick-red, m. p. 267° (decomp.), *bromide*, violet, m. p. 196°, and *dihydrochloride*, dark brown, m. p. 205° (decomp.), are described. When heated with concentrated hydrochloric acid at 160°, the last-named salt affords 4-p-*aminophenyl*-2 : 6-*di*-p-*hydroxyphenylpyrylium dihydrochloride*, violet-red, decomp. 240°, from which the corresponding *perchlorate*, reddish-yellow, was prepared. 6-*Phenyl*-4-p-*acetamidophenyl*-2-p-*anisylpyrylium perchlorate*, orange-red, m. p. 143°, is obtained by condensing *p*-acetamidostyryl phenyl ketone with *p*-methoxyacetophenone, or *p*-acetamidostyryl *p*-anisyl ketone with acetophenone, in acetic anhydride in presence of zinc chloride. Boiling with concentrated hydrochloric acid affords 6-*phenyl*-4-p-*aminophenyl*-2-p-*anisylpyrylium dihydrochloride*, violet-red, decomp. when heated, and this, when heated with concentrated hydrochloric acid at 160—170°, yields 6-*phenyl*-4-p-*aminophenyl*-2-p-*hydroxyphenylpyrylium dihydrochloride*, violet-red, decomp. 240°. Crystallisation of the last-named salt from *N*-hydrochloric acid converts it into the corresponding *chloride*, violet with green reflex, decomp. 230°. 6-*Phenyl*-2 : 4-*di*-p-*aminophenylpyrylium picrate*, violet-black, solutions of which in aqueous alcohol have considerable dyeing properties, was prepared analogously.

Whilst *p*-hydroxyphenylpyrylium salts are readily hydrolysed with formation of the corresponding anhydro-bases, the amino-derivatives are considerably more stable, and whilst the action of alkalis appears to lead to the production of violonimines, these could not be isolated in a pure condition, as they appear to possess a facility for polymerisation similar to that exhibited by the fuchsonimines (cf. Baeyer and Villiger, A., 1904, i, 786). F. G. WILLSON.

Degradation of 2 : 2-dichlorothiochromonol. F. ARNDT (Ber., 1925, **58**, [*B*], 2702).—The product obtained by the action of alkali on 2 : 2-dichlorothiochromonol is not 6-thiol-*m*-toluic acid, as recorded previously (A., 1925, i, 1309), but probably 2 : 3-dihydroxythiochromone (cf. Krollpfeiffer, this vol., 166). H. WREN.

1-Methylpyrrolidine from 1-methylpyrrole by catalytic reduction. J. P. WIBAUT (Rec. trav. chim., 1925, **44**, 1101—1105).—By shaking 1-methylpyrrole in acetic acid solution with hydrogen for 41 hrs. under a pressure of 20 cm. of water, successive small quantities of platinic oxide being added as a catalyst, a 74% yield of 1-methylpyrrolidine is obtained. Increasing the temperature of the reaction mixture to 50° has no effect on the reaction velocity.

R. W. WEST.

Existence of the simplest, monomeric dihydroquinolines. W. KÖNIG and R. BUCHHEIM (Ber., 1925, **58**, [*B*], 2868—2870; cf. Meisenheimer and Stotz, this vol., 76).—The compound obtained by the action of chloro- or bromo-acetal on *o*-toluidine (cf. Räth, A., 1924, i, 555, 667) is identified as 4-ethyl-*o*-toluidine. Simple monomeric 1 : 2- or 1 : 4-dihydroquinolines should therefore be deleted from the literature at present. H. WREN.

Synthesis of *s*-homotetrahydro*iso*quinoline. J. VON BRAUN and H. REICH (Ber., 1925, **58**, [*B*], 2765—2767).—Reduction of the lactam of *o*-β-aminoethylphenylacetic acid (von Braun and Reich, A., 1925, i, 1407) by sodium and ethyl alcohol affords a mixture of bases from which *s-homotetrahydroisoquinoline*, $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NH$, b. p. 115°/12 mm., d_4^{19} 1·034, is readily isolated by distillation with steam. The corresponding *hydrochloride*, m. p. 250°, *chloroplatinate*, m. p. 253° (decomp.) after darkening at 230°, *picrate*, m. p. 220°, *methiodide*, m. p. 227°, and *nitroso*-derivative, m. p. 71—72°, are described. o-β′-*Aminoethyl*-β-*phenylethyl alcohol*,

$$NH_2\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH,$$

b. p. about 180°/12 mm., is obtained as by-product; the *di*-p-*nitrobenzoyl* derivative has m. p. 153°. H. WREN.

Configuration of the ammonium ion. W. H. MILLS and E. H. WARREN (J.C.S., 1925, **127**, 2507—2514). The facts hitherto known indicate that the ammonium ion must have either a pyramidal or a tetrahedral configuration. In order to test which of these is correct, 4-phenyl-4′-carbethoxybispiperidinium-1 : 1′-spiran salts

$$\left[\begin{matrix}H\\Ph\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CO_2Et\\H\end{matrix}\right]X$$

have been prepared. These are molecularly asymmetric on the tetrahedral, but not on the pyramidal, configuration. They have now been resolved, and the tetrahedral arrangement is therefore judged to be correct. The *bromide*, m. p. 276—277°, of the *dl*-base was prepared by condensing ethyl di-β-bromoethylacetate with 4-phenylpiperidine. The *iodide* had m. p. 209—210°. The d-*iodide*, m. p. 222—223°, obtained from the d-α-*bromocamphor-π-sulphonate* (m. p. 210—212°) had $[\alpha]_{5780}^{20}$ +8·9° and $[\alpha]_{5461}^{20}$ +9·7° in ethyl alcohol. The d-*bromide*, m. p. 274—275°, had $[\alpha]_{5780}^{20}$ +11·76° and $[\alpha]_{5461}^{20}$ +13·23°, and the l-*bromide*, −11·75° and −13·3°. E. E. WALKER.

Constitution of Fischer and Hepp's phenylpyrrole. G. PLANCHER and E. GHIGI (Gazzetta, 1925, **55**, 757—759).—Direct confirmation is now obtained of the view formerly expressed (A., 1925, i, 597) that the compound prepared by Fischer and Hepp (A., 1886, 1042) by the action of bromobenzene on the potassium derivative of pyrrole is 2- and not 1-phenylpyrrole. T. H. POPE.

Synthesis of carboxylated cryptopyrrolecarboxylic acids etc. H. FISCHER and C. NENITZESCU (Z. physiol. Chem., 1925, **145**, 295—307).—An attempt has been made to investigate the mechanism of Ehrlich's dimethylaminobenzaldehyde reaction (a red coloration which this substance gives with certain pathological constituents of urine) by preparing some of the cryptopyrrole derivatives and synthesising methenes from them. Thus, *bis*-(2 : 4-*dimethyl*-3-*methylmalonic-pyrrole*)-5-*methene*, m. p. 218°, is prepared by condensing the trisodium salt of β-5-carboxy-β-2 : 4-dimethyl-3-pyrrylmethylmalonic acid with formic acid in the presence of perchloric acid. If Ehrlich's reagent is used instead of formic acid, the deep violet (p-*dimethylaminophenyl*)(2 : 4-*dimethylpyrrolene*-3-β-*methylmalonic*)-*methene*, m. p. 190°, is obtained. Ethyl β : 3-carbethoxy-2 : 5-dimethyl-4-pyrrylmethylmalonate is obtained from ethyl 2 : 5-dimethylpyrrole-3-carboxylate and ethyl methoxymethylmalonate. The ester has m. p. 81°, and the acid, 195°. By rapid heating of the acid above its m. p., the corresponding propionic acid is formed, m. p. 178°.

Hæmatic acid has been synthesised by heating together ethyl methoxymethylmalonate, ethyl acetoacetate, acetic anhydride, and zinc chloride, and treatment of the distilled product with hydrocyanic acid, followed by hydrolysis of the resulting nitrile. H. P. MARKS.

Synthesis of ethyl 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylate and its conversion into cryptopyrrole. H. FISCHER and B. WALACH (Ber., 1925, **58**, [*B*], 2818—2822).—The preparation of ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate (cf. A., 1922, i, 758) is considerably simplified by the observation that ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate is hydrolysed by concentrated sulphuric acid at 40° to 5-*carbethoxy*-2 : 4-*dimethylpyrrole*-3-*carboxylic acid*, m. p. 273° (yield 70—95%), which loses carbon dioxide when heated and forms ethyl 2 : 4-dimethylpyrrole-5-carboxylate. Application of the Gattermann synthesis to the latter compound affords ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate, which condenses with malonic acid in the presence of piperidine, yielding 5-*carbethoxy*-2 : 4-*dimethylpyrrole*-3-*acrylic acid*, m. p. 240° (2 : 4 : 5-*trimethylpyrrole*-3-*acrylic acid*, m. p. 203°, and 2 : 4-*dimethyl*-5-*ethylpyrrole*-3-*acrylic acid*, m. p. 205°, are obtained similarly). *Ethyl* 2 : 4-*dimethyl*-3-*vinylpyrrole*-5-*carboxylate*, m. p. 112°, is obtained in 70% yield when the corresponding acrylic acid is heated at 200°/12—15 mm. It is hydrolysed to 2 : 4-*dimethyl*-3-*vinylpyrrole*-5-*carboxylic acid*, m. p. 101—102°, and hydrogenated in the presence of spongy platinum and methyl alcohol to *ethyl* 2 : 4-*dimethyl*-3-*ethylpyrrole*-5-*carboxylate*, m. p. 94°. Catalytic reduction of 2 : 4-dimethyl-3-vinylpyrrole-5-carboxylic acid affords the very unstable 2 : 4-dimethyl-3-ethylpyrrole-5-carboxylic acid, which immediately loses carbon dioxide, yielding 2 : 4-dimethyl-3-ethylpyrrole (cryptopyrrole). Attempts to reduce the unsaturated side-chain by sodium amalgam or aluminium amalgam were unsuccessful. Hydriodic acid does not cause reduction, but displaces the vinyl group with production of 2 : 4-dimethylpyrrole. H. WREN.

Derivatives of 4-aminopyridine. E. KOENIGS, H. FRIEDRICH, and H. JURANY (Ber., 1925, **58**, [*B*], 2571—2576).—The action of methyl iodide on

4-aminopyridine yields 4-aminopyridine methiodide, m. p. 184—185°, which is converted through the methochloride into the chloroplatinate, m. p. 230—232° (decomp.). The substances, m. p. 187—188° and 226—227° (decomp.), have been described previously (A., 1925, i, 1328) by Tschitschibabin and Ossetrova, who consider them to be derived from the tautomeric 1-methyl-4-pyridoneimine; this view is not shared by the authors, mainly on account of the close analogy in behaviour of 4-aminopyridine and 4-dimethylaminopyridine, with which such tautomerism is impossible. 4-Chloropyridine-2 : 6-dicarboxylic acid is converted by methylamine solution at 150° into 4-methylaminopyridine-2 : 6-dicarboxylic acid, m. p. 245—255° (decomp.), and *4-methylaminopyridine*-2 : 6-*dicarboxylmethylamide*, m. p. 269°. The acid is transformed by distillation in a vacuum into 4-methylaminopyridine, m. p. 108—110°, the picrate, m. p. 172°, and chloroplatinate, m. p. 232°, of which are described; Tschitschibabin and Ossetrova (*loc. cit.*) record the respective m. p. 115—118°, 168·5—169°, and 214—215°. *4-Dimethylaminopyridine*, m. p. 114°, obtained by heating 4-dimethylaminopyridine-2 : 6-dicarboxylic acid, functions as a mono-acid base, thus resembling 2- and 4-aminopyridine and differing from the 3-amino-compound; the *chloroplatinate*, m. p. 265° (decomp.) after softening, *chloroaurate*, m. p. 176—178°, *picrate*, m. p. 204°, and somewhat impure *hydrochloride*, m. p. 73°, are described. 4-Chloropyridine-2 : 6-dicarboxylic acid is converted by 4-aminopyridine at 150° into 4 : 4′-*dipyridylamine*-2 : 6-*dicarboxylic acid*,

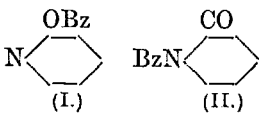
$$C_5H_4N\cdot NH\cdot C_5H_2N(CO_2H)_2,$$

m. p. 255° (decomp.), which is transformed by loss of carbon dioxide into 4 : 4′-*dipyridylamine*, m. p. 138° after softening at 110°; the indefinite m. p. indicates the possibility of the presence of the isomeric pyridoneimine. To limit this possibility, 4-chloropyridine-2 : 6-dicarboxylic acid is converted by 4-aminopyridine-2 : 6-dicarboxylic acid into 4 : 4′-*dipyridylamine*-2 : 6 : 2′ : 6′-*tetracarboxylic acid*, m. p. 272° (decomp.), and the latter is decarboxylated, yielding, however, a base with almost identical properties. The *chloroplatinate* (+H_2O) and *picrate* of the base from the di- and tetra-carboxylic acids have m. p. 260° and (decomp.) above 280°, 168—170°, and 170—174°, respectively. H. WREN.

Acylation of 2-hydroxypyridine. A. E. TSCHITSCHIBABIN and P. G. SZOKOW (Ber., 1925, **58**, [*B*], 2650—2652).—The great instability of the acylated derivatives of 2- and 4-hydroxypyridones has led Meyer (A., 1907, i, 179) to doubt the existence of more than a very limited number of members of this class. 2-*Pyridyl* p-*nitrobenzoate*, m. p. 115—116°, is, however, readily prepared by the action of *p*-nitrobenzoyl chloride on 2-pyridone in the presence of concentrated alkali hydroxide. In the complete absence of moisture, 2-*pyridyl acetate*, b. p. 110—112°/10 mm., is obtained from acetyl chloride and anhydrous sodium 2-pyridone; it is so rapidly decomposed by water or alcohol that treatment of its solutions in these media with chloroplatinic acid affords 2-pyridone chloroplatinate.

Sodium-2-pyridone, obtained by precipitating 2-pyridone from a solution in sodium hydroxide and crystallisation of the precipitate from alcohol, has the composition $C_5H_4ONNa,2H_2O$ (cf. Tschitschibabin and Riazancev, A., 1916, i, 224). H. WREN.

Benzoylation of 2-pyridone. A. E. TSCHITSCHIBABIN and O. P. OPARINA (J. Russ. Phys. Chem. Soc., 1925, **56**, 153—156).—Benzoylation of 2-pyridone under various conditions yields always one and the same benzoylpyridone, which exhibits distinct basic properties and has hence structure (I); the tautomeric form (II) could not be obtained. Meyer's statement that 2-pyridone is incapable of undergoing acylation (A., 1906, i, 107) is thus inaccurate.



(I.) (II.)

Benzoyl-2-pyridone (*2-benzoxypyridine*), obtained by the action of benzoyl chloride in presence of sodium hydroxide, or of benzoic anhydride, on 2-pyridone, by the action of sodium benzoate on 2-iodopyridine, or by the action of benzoic anhydride on pyridine-2-diazotate, has m. p. 42°, b. p. 183—186°/30 mm., and forms a *chloroplatinate*, m. p. 186° (decomp.)

T. H. POPE.

Preparation of indole from o-ω-dinitrostyrene. J. VAN DER LEE (Rec. trav. chim., 1925, **44**, 1089—1092).—It is suggested that *o*-ω-diaminostyrene and *o*-aminophenylacetaldehyde are formed as intermediate products during the reduction of *o*-ω-dinitrostyrene (cf. Nenitzescu, A., 1925, i, 973).

R. W. WEST.

Quinoline derivatives. II. Syntheses of β-2-phenyl-4-quinolylethylamine and β-6-methoxy-2-phenyl-4-quinolylethylamine. H. JOHN [with V. GROSSMANN] (Ber., 1925, **58**, [*B*], 2799—2805; cf. A., 1925, i, 1317).—*γγγ-Trichloro-α-2-phenyl-4-quinolylpropan-β-ol*, $C_9H_5NPh\cdot CH_2\cdot CH(OH)\cdot CCl_3$, m. p. 195°, prepared by heating 2-phenyl-4-methylquinoline with chloral at 118—120°, is converted by potassium hydroxide dissolved in absolute alcohol into β-2-*phenyl-4-quinolylacrylic acid*, m. p. 201° (*hydrochloride*, m. p. 210°; *picrate*; *methyl* ester, m. p. 123°). The unsaturated acid is reduced by hydriodic acid and red phosphorus in glacial acetic acid solution to β-2-*phenyl-4-quinolylpropionic acid*, m. p. 215° (*hydrochloride*, m. p. 189°; *hydriodide*, m. p. 208°; *sulphate*; *picrate*; *methyl* ester, m. p. 63°). The methyl ester and hydrazine hydrate afford β-2-*phenyl-4-quinolylpropionhydrazide*, m. p. 158° (*hydrochloride*), which is converted by nitrous acid into the *azide* and thence by ethyl alcohol into β-2-*phenyl-4-quinolylethylurethane*, m. p. 72°, and by water into *di*-β-2-*phenyl-4-quinolylethylcarbamide*, m. p. 175°. The urethane is hydrolysed by boiling hydrochloric acid to β-2-*phenyl-4-quinolylethylamine*, m. p. 4° (*dihydrochloride*, m. p. 158°; *chloroplatinate*, $C_{17}H_{18}N_2Cl_6Pt$, which does not melt below 270°; *picrate*).

Starting from 6-methoxy-2-phenyl-4-methylquinoline, a precisely similar series of derivatives is prepared, the following being described: *γγγ-trichloro-α-6-methoxy-2-phenyl-4-quinolylpropan-β-ol*, m. p. 222°; β-6-*methoxy-2-phenyl-4-quinolylacrylic acid*,

m. p. 239° (*hydrochloride*; *sulphate*; *picrate*; *methyl* ester, m. p. 140°); β-6-*hydroxy*-2-*phenyl*-4-*quinolylpropionic acid*, m. p. 245° (*hydrochloride*, m. p. 160°; *picrate*); *methyl* β-6-*methoxy*-2-*phenyl*-4-*quinolylpropionate*, m. p. 100°; β-6-*methoxy*-2-*phenyl*-4-*quinolylpropionhydrazide*, m. p. 116°; β-6-*methoxy*-2-*phenyl*-4-*quinolylpropionazide*; β-6-*methoxy*-2-*phenyl*-4-*quinolylethylurethane*, m. p. 125°; β-6-*methoxy*-2-*phenyl*-4-*quinolylethylamine*, m. p. 54° (*dihydrochloride*, m. p. 209°; *chloroplatinate*; *sulphate*; *picrate*). The reactions of the acids and bases with mercuric chloride, potassium chromate, potassium ferrocyanide, and iodine–potassium iodide are described. H. WREN.

Barbituric acids and the picric acid reaction. A. W. DOX (Z. physiol. Chem., 1925, **150**, 118—120).—The picric acid reaction, used by Abderhalden for the detection of diketopiperazines in the breakdown products of protein, is not given by every compound containing a carbonyl group. Barbituric acid, containing three ·CO· groups, gives a characteristic picric acid reaction, but four monoalkyl- and sixteen dialkyl-barbituric acids tested do not react with it, although they contain carbonyl groups. Parabanic acid does not give this reaction. H. D. KAY.

Synthesis of 5-β-hydroxyethylbarbituric acid and its alkyl derivatives. L. H. CRETCHER, J. A. KOCH, and W. H. PITTENGER (J. Amer. Chem. Soc., 1925, **47**, 3083—3085).—β-Chloroethyl vinyl ether (cf. A., 1925, i, 627) condenses with sodium diethyl malonate and sodium diethyl monoalkylmalonates with formation of the corresponding vinyloxyethylmalonates. The latter condense with carbamide and thiocarbamide, with production of 5-β-vinyloxyethylbarbituric acids, which, on hydrolysis with dilute mineral acid, afford acetaldehyde and the corresponding 5-β-hydroxyethylbarbituric acids. The following are described: *diethyl ethyl*-β-*vinyloxyethyl*-, b. p. 151°/18 mm., d_{15}^{15} 1·0264; *diethyl propyl*-β-*vinyloxyethyl*-, b. p. 157°/17 mm., d_{15}^{15} 1·0145; *diethyl butyl*-β-*vinyloxyethyl*-, b. p. 165°/17 mm., d_{15}^{15} 0·9992; and *diethyl bis*-(β-*vinyloxyethyl*)-*malonate*, b. p. 133°/3 mm., d_{15}^{15} 1·0566; 2-*thio*-5-*ethyl*-5-β-*vinyloxyethyl*-, m. p. 136°; 5-*ethyl*-5-β-*vinyloxyethyl*-, m. p. 158°; 5-*butyl*-5-β-*vinyloxyethyl*-, m. p. 141°; 2-*thio*-5-β-*hydroxyethyl*-, m. p. 181° (decomp.); 5-β-*hydroxyethyl*-, m. p. above 300°; 5-*ethyl*-5-β-*hydroxyethyl*-, m. p. 176°; 2-*thio*-5-*ethyl*-5-β-*hydroxyethyl*-, m. p. 143—145°; 5-*propyl*-5-β-*hydroxyethyl*-, m. p. 168°; and 5-*butyl*-5-β-*hydroxyethyl*-*barbituric acid*, m. p. 147°. F. G. WILLSON.

Synthesis of the polypeptide hydantoin: tyrosylalaninehydantoin. II. D. A. HAHN and E. GILMAN (J. Amer. Chem. Soc., 1925, **47**, 2941—2953; cf. A., 1923, i, 487).—The substance previously described as a stereoisomeric form of ethyl 4-*p*-anisylidenehydantoin-3-α-propionate, m. p. 176°, has now been found to be actually *ethyl* 4-p-*anisylidenehydantoin*-1-*acetate*, whilst that described as another isomeride, m. p. 143°, is a mixture (mixed crystals) of the above two compounds, the m. p. of the mixture being now reported as 140—142°. The individual components can be separated from the mixed crystals only by employing very dilute solutions, and on hydrolysis with dilute hydrochloric acid the mixture yields an acid, m. p. 245°, previously reported as 4-*p*-anisylidenehydantoin-3-α-propionic acid, but which actually is probably also a eutectic. The assumption that the ester group entered the hydantoin nucleus in position 3 was based on the observation that ammonia is evolved during the hydrolysis of the polypeptide hydantoin, but it has since been noted that 1-derivatives also yield ammonia when subjected to intense hydrolysis. It is now concluded that the ester groups enter in position 1. When ethyl α-bromopropionate containing the corresponding bromoacetate is condensed with the sodium derivative of anisylidenehydantoin, the ethyl anisylidenehydantoinacetate, m. p. 176°, separates first. The corresponding propionate is formed later, and unites with the acetate immediately to form the mixture of m. p. 140—142°. Condensation of pure ethyl α-bromopropionate with sodium anisylidenehydantoin yields *ethyl* 4-p-*anisylidenehydantoin*-1-α-*propionate*, m. p. 158—158·5°. On hydrolysis, this affords 4-p-*anisylidenehydantoin*-1-α-*propionic acid*, m. p. 255—256° [*potassium* salt, m. p. 280° (decomp.)]. On reduction with hydrogen in alcohol in presence of colloidal palladium, the ester yields two isomeric *ethyl* 4-p-*anisylhydantoin*-1-α-*propionates*, m. p. 117·5—118·5° and 97·5—98·5°, respectively. On hydrolysis with hydrochloric acid, the above isomeride, m. p. 117·5—118·5°, yields 4-p-*anisylhydantoin*-1-α-*propionic acid*, m. p. 160—161°, whilst the ester of lower m. p. affords similarly an isomeric *acid*, m. p. 182—183°. A mixture of the isomeric acids is also obtained by condensing ethyl α-bromopropionate with 4-*p*-anisylhydantoin and hydrolysing the reaction product. Treatment of ethyl 4-*p*-anisylidenehydantoin-1-α-propionate with hydriodic acid affords a mixture, m. p. 168—190°, of two isomeric 4-p-*hydroxybenzylhydantoin*-1-α-*propionic acids*, m. p. 193·5—195° and 187—188·5°, respectively, from which the *ethyl* esters, m. p. 133—138° and 152—155°, were prepared. Hydrolysis of the last-named acids or esters with barium hydroxide yields alanine and tyrosine, whilst similar hydrolysis of the polypeptide hydantoin obtained analogously from ethyl 4-*p*-anisylidenehydantoin-1-acetate affords glycine and tyrosine. F. G. WILLSON.

Absorption spectra of some derivatives of anisylidenehydantoin. E. P. CARR and M. A. DOBBROW (J. Amer. Chem. Soc., 1925, **47**, 2961—2965).—Comparison of the absorption spectra of the substances obtained by condensing different samples of ethyl α-bromopropionate with sodium 4-*p*-anisylidenehydantoin with those of ethyl 4-*p*-anisylidenehydantoin-1-acetate (cf. Johnson and Hahn, A., 1917, i, 475) and ethyl 1-methyl-4-*p*-anisylidenehydantoin-3-acetate (cf. Hahn and Renfrew, A., 1925, i, 581) indicates that the ester group is in all cases attached to the hydantoin nucleus in the 1-position, a result since confirmed by Hahn and Gilman (preceding abstract). The m. p. of mixtures of ethyl 4-anisylidenehydantoin-1-acetate, m. p.

176°, and the corresponding -1-α-propionate, m. p. 158°, form, when plotted, a curve characteristic of substances which form mixed crystals, with a minimum at 140° for the mixture containing 60% of the former ester, in close proximity to the m. p. first quoted (A., 1923, i, 487) for ethyl 4-*p*-anisylidenehydantoin-3-α-propionate (cf. Hahn and Gilman, *loc. cit.*). This mixture melts completely in a range of 2°, whilst the remaining mixtures require ranges of 6—16° for complete liquefaction.

F. G. Willson.

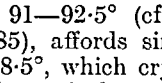
Isomerisation in the hydantoin series induced by the action of hydrogen chloride. D. A. Hahn and E. Gilman (J. Amer. Chem. Soc., 1925, **47**, 2953—2961).—Whilst the existence of isomerides of benzylidene- and anisylidene-hydantoins and their 1-substitution products could not be demonstrated, the corresponding 1 : 3-disubstitution products can be obtained in two isomeric forms. This is explained on the assumption that the former compounds can undergo keto-enol tautomerisation, by which the double linking responsible for stereoisomerism may be saturated. In the following cases examined, the isomeride of higher m. p. is obtained from that of lower m. p. by treatment with alcoholic hydrogen chloride. The reverse change could be effected only by the action of aqueous-alcoholic alkali in one case, probably owing to the instability of the compounds examined in presence of alkali.

When treated with hot alcoholic hydrogen chloride, ethyl 1-methyl-4-anisylidene-3-acetate, m. p. 107—108° (cf. A., 1925, i, 581), is converted into an *isomeride*, m. p. 127—128°. 1 : 3-Dimethyl-4-anisylidenehydantoin, m. p. 91—92·5° (cf. Johnson and Nicolet, A., 1912, i, 585), affords similarly an *isomeride*, m. p. 127·5—128·5°, which crystallises either in long, colourless needles or in large, yellow prisms, the latter being converted into the colourless form by recrystallisation from alcoholic hydrochloric acid. Treatment of the isomeride of higher m. p. with 0·2 mol. of alkali in aqueous-alcoholic solution gave a small yield of the other isomeride. Partial isomerisation appears to be effected by heating either isomeride at 135—150°. Both isomerides yield 1 : 3-*dimethyl*-4-*anisylhydantoin*, m. p. 78·5°, on reduction. *Methyl* 3-*methyl*-4-*benzylidenehydantoin*-1-*acetate* exists in two isomeric forms, m. p. 66·5—68° and 101—102·5°, respectively. *Methyl* 4-*anisylidenehydantoin*-1-*acetate*, long needles, m. p. 183—184°, which change in contact with the mother-liquor into compact prisms of the same m. p., was prepared from the corresponding ethyl ester (cf. Johnson and Hahn, A., 1917, i, 475) by hydrolysis and re-esterification. When treated with methyl iodide and potassium hydroxide in alcoholic solution, it yields *methyl* 3-*methyl*-4-*anisylidenehydantoin*-1-*acetate*, m. p. 84—85°, which is converted into an *isomeride*, m. p. 129·5—131°, when treated with alcoholic hydrogen chloride. *Methyl* 4-*anisylidenehydantoin*-1-*propionate*, m. p. 163—164°, obtained from the corresponding ethyl ester (cf. preceding abstract), affords, on methylation, *methyl* 3-*methyl*-4-*anisylidene*-1-*propionate*, m. p. 103—104°, converted similarly into the *isomeride*, m. p. 142—143°.

F. G. Willson.

Methylated piperazines. E. Abderhalden and R. Haas (Z. physiol. Chem., 1925, **149**, 94—99).—From 2 : 5-dimethylpiperazine ("lycetol") the dihydriodide of 1 : 2 : 4 : 5-tetramethylpiperazine has been prepared by direct methylation with methyl iodide in methyl alcohol. From this substance by treatment with cold 4*N*-alkali the monohydriodide is obtained. The removal of a further molecule of hydriodic acid is accomplished by shaking with silver sulphate. The tetramethylated piperazine is a syrup, which becomes partly crystalline on long keeping. The dihydriodide of 1 : 1 : 2 : 4 : 4 : 5-hexamethylpiperazine may be prepared in good yield by long boiling of the dimethyl compound with methyl iodide. The corresponding hexamethylpiperazinium hydroxide, m. p. 224°, is obtained by treatment with silver sulphate and the calculated quantity of barium hydroxide. 2 : 5-Dimethylpiperazine may also be methylated by methyl sulphate in presence of alkali. The dichloride of the hexamethyl compound is prepared by acidifying the reaction mixture with hydrochloric acid, precipitating the mercury salt with mercuric chloride, decomposing the crystalline precipitate with hydrogen sulphide, and evaporating the mercury-free filtrate almost to dryness. The dichloride is then crystallised from its alcoholic solution.

H. D. Kay.

Desmotropic forms of diketopiperazines. E. Abderhalden and E. Schwab (Z. physiol. Chem., 1925, **149**, 100—103).—A new *form* of glycine anhydride has been isolated from a reaction mixture of ordinary glycine anhydride and tyrosine which had been heated with glycerol at 180°. It gives a strong xanthoproteic reaction and reduces cold permanganate at once. It is considered to have the formula  . By treating it with diazomethane, the dimethyl ether may be obtained. Glycine anhydride heated alone with glycerol appears to give the same unsaturated desmotropic modification.

H. D. Kay.

***o*-Hydroxyazo [pyrazolone] dye.** O. Kaltwasser, H. Kirchhoff, and H. Oehrn.—See B., 1926, 7.

Pyrazolone azo dyes. British Dyestuffs Corp., Ltd., K. H. Saunders, and H. Goodwin.—See B., 1926, 7.

Velocity of decomposition of heterocyclic diazonium salts. I. Diazonium salts of the pyrazole and pyrazolone series. J. Reilly and D. Madden (J.C.S., 1925, **127**, 2936—2940).—Solutions of the diazonium chlorides derived from *m*- and *o*-nitroaniline, 4-aminopyrazole, 4-aminoantipyrine, and 4-amino-3 : 5-dimethylpyrazole, maintained at 100° in a special apparatus, showed a stability increasing in the order given, the time for half decomposition varying from 10 to 1020 min. The diazonium sulphates of both 4-aminoantipyrine and 4-amino-3 : 5-dimethylpyrazole decompose much more rapidly than the corresponding chlorides.

B. W. Anderson.

Microchemical reactions for the identification of *p*-hydroxyphenylethylamine (tyramine) and 4-β-aminoethylglyoxaline (histamine). L. VAN ITALLIE and A. J. STEENHAUER (Mikrochem., 1925, **3**, 65—67).—A 1% solution of tyramine hydrochloride gives pale yellow needles and prisms with picric acid, pale yellow prisms and hexagonal tablets with chloroplatinic acid, large brownish-violet dichroic prisms in stellate aggregates with sodium iodide and chloroplatinic acid, large orange-red prisms in stellate aggregates with potassium bismuth iodide and hydrochloric acid, and oily drops which soon crystallise in warty or stellate aggregates with phosphotungstic acid. A 1% solution of histamine phosphate gives a crop of pale yellow, feathery needles with picric acid, large yellow prisms with chloroplatinic acid, brownish-black prisms in diamond-shaped aggregates with sodium iodide and chloroplatinic acid, small orange-red prisms with potassium bismuth iodide, and a finely-divided white precipitate, which slowly changes into prisms and diamond-shaped crystals, with silicotungstic acid. A. R. POWELL.

Triazole-*o*-dicarboxylic acids analogous to phthalic acid. A. BERETTA (Gazzetta, 1925, **55**, 788—792).—2-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid may be obtained in good yield by oxidising either 5-amino-2-phenyl-1 : 3-benztriazole or 5-amino-2-phenyl-6-methyl-1:3-benztriazole in alkaline solution by means of potassium permanganate. In presence of zinc chloride, the anhydride of this acid condenses with resorcinol to give the corresponding *triazolefluorescein*, NPh$\langle$ N·C·C:C$_{12}$H$_8$O$_3$ / N·C·CO $\rangle$ >O, a reddish-yellow, amorphous compound giving, in presence of alkali, solutions which are deep red when concentrated and exhibit pronounced yellowish-green fluorescence even when highly dilute. Triazolefluorescein combines with bromine (4 atoms) to give the bright red *triazole-eosin*, $C_{22}H_9O_5N_3Br_4$, the sodium derivative of which dyes wool and silk brilliant red. 2-Phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic anhydride condenses also with diethyl-*m*-aminophenol to give the deep red rhodamine similar to ordinary rhodamine.

For the preparation of 5-amino-1-phenylaziminobenzene, better results are obtained if the corresponding nitro-compound, suspended in aqueous alcohol, is heated with zinc dust in presence of calcium chloride, than if Zincke and Petermann's method of reduction (A., 1901, i, 104) is employed. Oxidation of this amino-compound by means of potassium permanganate in alkaline solution furnishes a new method for preparing 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid. T. H. POPE.

Hydroxy-derivatives of 1 : 2 : 4-triazole. H. J. BACKER and C. H. K. MULDER (Rec. trav. chim., 1925, **44**, 1113—1117).—By ferric chloride oxidation of the appropriate semicarbazones the following compounds were obtained: 3-*hydroxy*-5-p-*methoxyphenyl*-2-*methyl*-1 : 2 : 4-*triazole*, m. p. 223·5°; 3-*hydroxy*-5-*methylenedioxyphenyl*-2-*methyl*-1 : 2 : 4-*triazole*, m. p. 273°, from *piperonal*-2-*methylsemicarbazone*, m. p. 226°; 3-*hydroxy*-2 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 234·5°; 3-*hydroxy*-4 : 5-*diphenyl*-1 : 2 : 4-*triazole*, m. p. 260—261°, from *benzylidene*-3-*phenylsemicarbazone*, m. p. 177°. On nitration, 3-hydroxy-5-phenyl-2-methyl-1 : 2 : 4-triazole gave 3-*hydroxy*-5-p-*nitrophenyl*-2-*methyl*-1 : 2 : 4-*triazole*.

R. W. WEST.

Degradation of uric acid-glycol ethers by alkali hydroxide. H. BILTZ and H. KLEIN (Ber., 1925, **58**, [*B*], 2740—2747; cf. Biltz and Max, A., 1921, i, 893, 895).—The smooth conversion of uric acid–glycol dimethyl ether (4 : 5-dimethoxy-4 : 5-dihydrouric acid) into allantoin by potassium hydroxide appears to be exceptional. Tetramethyluric acid–glycol dimethyl ether is transformed by barium hydroxide solution into tetramethylallantoin, but the yield is very poor, whereas 1- and 7-methyluric acid–glycol dimethyl ethers are unexpectedly resistant towards alkali hydroxide and after protracted action yield ill-defined products from which a homogeneous material could not be isolated.

The action of more concentrated alkali hydroxide on the glycol ethers of 3 : 7- and 3 : 9-dimethyluric acids followed by acidification assumes an unexpected course, since cyanic acid is lost and a substituted hydantoin is produced. It appears essential for the "cyanic acid degradation" that the pyrimidine ring of the uric acid should contain an alkyl group in position 3. The effect of the alkali hydroxide appears to consist essentially in opening the ring between positions 1 and 6; loss of methylamine, cyanic acid, and carbon dioxide takes place after acidification. 3 : 7-Dimethyluric acid–glycol diethyl ether is converted by 40% potassium hydroxide solution into 5-*ethoxy*-1-*methylhydantoin*, m. p. 99·5—100·5°. 3 : 7-Dimethyluric acid–glycol dimethyl ether affords 5-*methoxy*-1-*methylhydantoin*, m. p. 118°, but 5-methoxy-3-methylhydantoin could not be obtained from 3 : 9-dimethyluric acid–glycol dimethyl ether.

1 : 3 : 7-Trimethyluric acid–glycol dimethyl ether loses methylamine when boiled with 1—1·5% potassium hydroxide solution and, after acidification, yields a non-crystalline product which is reduced by hydriodic acid to 1-methylhydantoin, showing thus that fission of the pyrimidine ring has occurred. Treatment of the glycol with 30% potassium hydroxide at the atmospheric temperature affords a crystalline *compound*, m. p. 123—124°, regarded as 4-s-*dimethylcarbamido*-5-*methoxy*-1-*methyl*-Δ^3-*glyoxal*-2-*one*, NMe·CH(OMe) / CO———N $\rangle$ C·NMe·CO·NHMe. The corresponding *perchlorate* and *hydrochloride*, decomp. 190°, are described. The compound is reduced by hydriodic acid to a *polyiodide*, which is converted by the successive action of sulphur dioxide, lead carbonate, and hydrogen sulphide into the *compound*, $C_5H_6ON_2S$, subliming at 350°. 1 : 3 : 7-Trimethyluric acid–glycol dimethyl ether is not affected by solutions of ammonia or methylamine at the atmospheric temperature, but, at 100°, is transformed into 4-methylimino-5-methoxy-1-methylhydantoylamide, m. p. 254° (cf. Biltz and Damm, A., 1914, i, 1096), and 4-*methylimino*-5-*methoxy*-1-*methylhydantoylmethylamide*, m. p. 270°

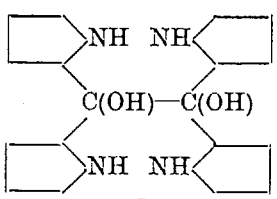
(decomp.), respectively. With ethylamine a similar change occurs, but the products could not be caused to crystallise. H. WREN.

Dye formed by the action of ethyl oxalate on magnesium pyrryl bromide. T. N. GODNEV and N. A. NARYSCHKIN (Ber., 1925, **58**, [*B*], 2703—2705).—Ethyl oxalate is converted by magnesium 2-pyrryl bromide into tetra-2-pyrrylethylene glycol, which becomes dehydrated to the *dye*

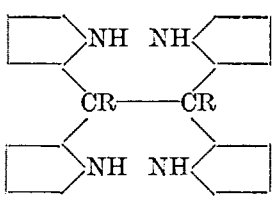
$C_4H_4N{\cdot}C(:NC_4H_3){\cdot}C(:NC_4H_3){\cdot}NC_4H_4$;

the corresponding *dihydrochloride* is described. H. WREN.

Structural formula of chlorophyll and hæmin in relation to the synthesis of complex pyrrole derivatives. T. GODNEV (Astrachan Mediz. J., 1922, [2—3], pp. 14; from Chem. Zentr., 1925, II, 401).—The correctness of the Willstätter formula for chlorophyll may be tested by comparing compounds of similar but simpler structure with the degradation products of chlorophyll. The synthesis of the nucleus of the Willstätter formula, tetrapyrrylcthane (Fischer and Eismayer, A., 1914, i, 993), may be investigated in the following ways. (1) Tetra-2-pyrrylethylene glycol (I) is prepared from magnesium pyrryl bromide and ethyl oxalate.



(I.)



(II.)

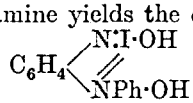
From it, tetrapyrrylethane is formed, analogously to the behaviour of diphenyl-2-pyrrylcarbinol (Tschelincev, Tronov, and Terentiev, A., 1915, i, 990). (2) In the last reaction, ethyl oxalate may be replaced by hexabromoethane. (3) Tetra-2-pyrrylethylene glycol may be obtained by reduction of di-2-pyrryl ketone. (4) Compound (II) may be prepared from magnesium pyrryl bromide and glyoxal or 1 : 2-diketones, similarly to the formation of diphenyldipyrrylmethane from benzophenone and magnesium pyrryl bromide. (5) In the last reaction, glyoxal may be replaced by *s*-tetrabromoethane and the 1 : 2-diketone by the corresponding tetrahalogen derivative (see preceding abstract). G. W. ROBINSON.

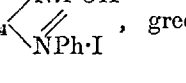
Nitro-derivative of di-iminazolyl, $C_6H_5O_{10}N_7$. K. LEHMSTEDT.—See B., 1926, 7.

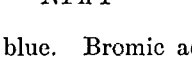
2-*m*-Xylidino-5-ethoxy-4 : 5-dihydrothiazole. V. K. NIMKAR and F. L. PYMAN (J.C.S., 1925, **127**, 2746).—The base obtained by Marckwald (A., 1892, 1330) by the action of strong sulphuric acid on acetalyl-*m*-xylylthiocarbamide has now been prepared in a pure state and shown to be 2-*m*-xylidino-5-ethoxy-4 : 5-dihydrothiazole, m. p. 102—103°; picrate, m. p. 152—154°. B. W. ANDERSON.

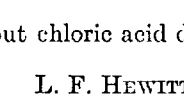
Thiazoles. VII. Behaviour of *o*-aminophenylmercaptan with aldehydes, ketones, and *gem*-dihalides. Synthesis of benzthiazoles. M. T. BOGERT and A. STULL (J. Amer. Chem. Soc., 1925, **47**, 3078—3083).—Condensation of *o*-aminothiophenol hydrochloride with formaldehyde affords benzthiazole, b. p. 230—231° (cf. Claasz, A., 1912, i, 513; 1916, i, 669). Condensation of the aminothiophenol, or its zinc salt, with benzaldehyde yields similarly 2-phenylbenzthiazole, formation of 2-phenylbenzthiazoline not being observed. The thiazole is also obtained when benzylidene chloride is substituted for benzaldehyde in the above condensation, whilst vanillin, piperonal, and furfuraldehyde afford similarly 2-p-*hydroxy*-m-*methoxyphenylbenzthiazole*, pale yellow, m. p. 175·5°, 2-m : p-*methylenedioxyphenylbenzthiazole*, m. p. 125°, and 2-α-*furfurylbenzthiazole*, m. p. 105°, respectively. Attempts to condense the aminothiophenol with acetone, Michler's ketone, and benzophenone chloride were unsuccessful. These results confirm the original observations of Hofmann (A., 1880, 386) and are at variance with those of Claasz (*loc. cit.*). F. G. WILLSON.

Heterocyclic compounds containing quinquevalent iodine or bromine. G. HUGEL (Compt. rend., 1925, **182**, 65—67).—Aqueous solutions of equimolecular amounts of iodic acid and *o*-phenylenediamine when mixed give *piaziodonium hydroxide*, $C_6H_4\langle{}^{N}_{N}\rangle I{\cdot}OH$, black, which with hydriodic acid gives the *hydriodide*, black amorphous, and this when warmed changes to *piaziodonium iodide*, green crystals, which on boiling is transformed into 2 : 3-diaminophenazine derivatives. 2 : 3-Diaminophenazine reacts with iodic acid, yielding the corresponding *iodonium hydroxide*, $C_6H_4\langle{}^{N}_{N}\rangle C_6H_2\langle{}^{N}_{N}\rangle I{\cdot}OH$. *o*-Aminodiphenylamine yields the *compound*,



which gives the *monoiodide*, 

, green, and the *di-iodide*, 

, blue. Bromic acid reacts with *o*-aminodiphenylamine, yielding the *compound*, 

, green, but chloric acid does not react in this manner. L. F. HEWITT.

Sterilisation of tropacocaine hydrochloride. S. MATSUNAMI.—See B., 1926, 75.

Instability of atropine sulphate. J. BODNAR and J. FERENCZY (Arch. Pharm., 1925, **263**, 566—570).—From certain commercial preparations of atropine sulphate, chloroaurates were obtained having m. p. 127° or lower, instead of the usual 135—137°. The impure chloroaurate was produced only after the aqueous solution of the atropine sulphate had been heated. In these conditions, it is found, atropine is hydrolysed to tropine and tropic acid. Only the

sulphate behaves in this way; the chloride, nitrate, and phosphate are stable. W. A. SILVESTER.

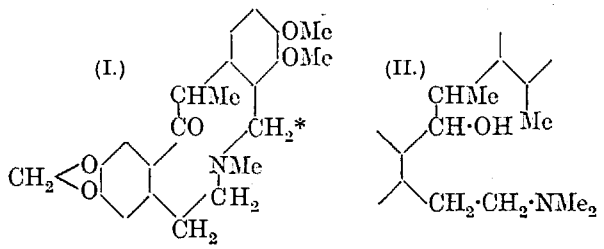
Constitutions of corycavidine and corycavamine. F. VON BRUCHHAUSEN (Arch. Pharm., 1925, **263**, 570—602).—Corycavidine, separated from corycavine as its more soluble hydrochloride, has the empirical formula $C_{22}H_{25}O_5N$ (m. p. 211—212°, $[\alpha]_D^{20}$ +210·8°); its nitrogen atom forms part of a monocyclic methylimino-group, whilst of its oxygen atoms four are combined as one methylenedioxy-group and two methoxy-groups (cf. Gadamer, A., 1902, i, 306). The function of the fifth oxygen atom, hitherto undetermined, is apparently not alcoholic, because the alkaloid is unaffected by hot acetyl chloride. Boiling acetic anhydride converts the base chiefly into an optically inactive form, m. p. 193—194° (cf. Gadamer, *loc. cit.*), but in part also into an N(?)-*acetyl* derivative, m. p. 212°, together with a little quaternary nitrogen compound, coloured red. These results are ambiguous, offering no direct evidence of the presence of either a tetrahydroquinoline or a 10-membered ring. Moreover, phosphorus oxychloride, which quantitatively isomerises corycavine (Gadamer and von Bruchhausen, Arch. Pharm., 1922, **260**, 97), has here no action at 130°, and at 160° destructive decomposition takes place. No interaction takes place with hydroxylamine or semicarbazide.

When the alkaloid is treated with methyl sulphate, the *methosulphate* (m. p. 220—222°, weakly dextrorotatory) is formed. The *methiodide* is weakly lævorotatory. The methosulphate is reduced by treatment in boiling dilute acid solution with sodium amalgam to *tetrahydromethylcorycavidine*, $C_{23}H_{31}O_5N$, an oil ($[\alpha]_D^{20}$ +39·9°; *hydrochloride*, m. p. 190°; *chloroplatinate*, m. p. 164—165°; *picrate*, m. p. 174—176°). As for a ring scission only two hydrogen atoms are needed, this result suggests reduction also of a carbonyl group. This tetrahydro-compound, when treated with hot dilute hydrochloric acid (or with acetyl chloride), yields an optically inactive, unsaturated base, *anhydrotetrahydromethylcorycavidine*, an oil (*dibromide*, m. p. 213—214°; *hydrochloride*, m. p. 233—235°; *nitrate*), together with a small proportion of a dihydric *phenol*, m. p. 130—133°, apparently formed by scission of the methylenedioxy-group. When the acetate of the anhydro-base is oxidised in ice-cold solution by potassium permanganate the following products are isolated: (i) 3 : 4-*dimethoxy*-2-*methylacetophenone* (*methylacetoveratrone*), m. p. 70—71° (*semicarbazone*, m. p. 235—236°), the constitution of which was determined by synthesis (see below); (ii) 5 : 6-dimethoxy-*o*-toluic acid (methylveratric acid), m. p. 183°, sublimes (Kempf) at 75°. This acid was also obtained, together with iodoform, when (i) was oxidised with sodium hydroxide and iodine, and has been described by Perkin (J.C.S., 1918, **113**, 762, and earlier reference given there, where the m. p. is given as 177°); (iii) a second *acid*, sparingly soluble in ether, m. p. 248°, containing no nitrogen, and probably produced by oxidation of the methylamino-chain; (iv) *N*-methylhydrastinine, which was not isolated as such, but was treated with methyl iodide and trimethylhydrastylammonium iodide, m. p. 264°, so obtained; (v) an amino-*acid*, $CH_2O_2{:}C_6H_2{<}\begin{matrix}CO\text{—}O\\CH_2{\cdot}CH_2\end{matrix}{>}NHMe_2$, the *mercuric* double salt (m. p. 202°), and *chloroaurate* of which are described.

In attempting the reproduction of the methylacetoveratrone, it was found that the hydroxymethylene group in ψ-meconine cannot be reduced. The synthesis was eventually carried out with 2 : 3-dimethoxytoluene as a starting point. This, treated by the Friedel–Crafts process with acetyl chloride, directly affords the required compound, substitution taking place exclusively in the 6-position. On oxidation with alkaline permanganate, the acid (ii, above) is obtained from both the synthetic and natural products, together with much of what appears to be the α-ketonic *acid*,

$$C_6H_2Me(OMe)_2{\cdot}CO{\cdot}CO_2H,$$

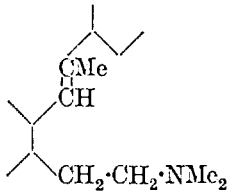
m. p. 130—133°. The above results, in spite of some discrepancies, considered in the light of earlier work in this field (Gadamer and von Bruchhausen, A., 1922, i, 675 etc.), suggest that corycavidine has the structure (I), the tetrahydromethyl and anhydrotetrahydromethyl derivatives having the constitutions indicated by (II) and (III), respectively. The conversion of (II) into (III) is considered to be analogous to that of toluylene hydrate into stilbene.

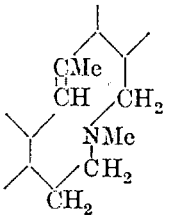


It is difficult to bring all the evidence into line with the above formula. For example, when the alkaloid is treated with ethyl chloroformate (Gadamer and Knoch, A., 1921, i, 579) it affords a *urethane*, m. p. 91° (the analogous *derivative* of inactive corycavidine has m. p. 129°), which contains chlorine. This chlorine is reactive and the compound resembles in this respect benzyl chloride, so that this urethane is presumably produced by scission between the nitrogen atom and the carbon denoted by a * in the formula above (I). On the other hand, the formation of the methine (Gadamer, 1902, *loc. cit.*) is readily explained and the following affords a further demonstration of the validity of the formula.

The proposed ketonic 10-membered ring structure, whilst suggesting how it is that corycavidine is not readily isomerised, suggests that its reduction product, a secondary alcohol, should readily change in this way. *Dihydrocorycavidine* (m. p. 147—148°, $[\alpha]_D^{20}$ −44·3°), obtained by treating the alkaloid, in dilute sulphuric acid solution, with sodium amalgam, is, in fact, converted by hot acetyl chloride into the *iso*-compound (an oil, the *hydrochloride* and *hydriodide*, m. p. 153°, are described). This yields an optically inactive anhydro-base, namely, *anhydrodihydroisocorycavidine* (m. p. 160—161°), which is found to be identical with *des*-N-*methyl*-4-*methyltetrahydroberberine*, the latter compound being prepared for comparison by boiling 4-methyltetra-

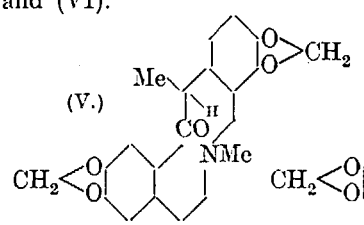
hydroberberine methochloride (Freund and Fleischer, A., 1915, i, 982) with methyl-alcoholic potassium hydroxide. Both compounds have therefore the constitution (IV).

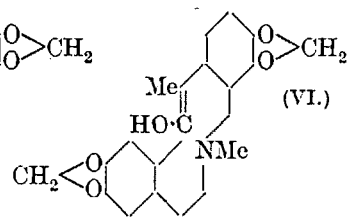
(III.) 

(IV.) 

In the isolation of corycavidine, Gadamer separated a small quantity of another alkaloid, m. p. 191°. This, after purification *via* the hydrochloride, has m. p. 193—194°, and proves to be optically inactive corycavidine (methine, m. p. 141·5°, urethane, m. p. 129°, cf. above). It may have been formed in the extraction process.

When corycavamine (m. p. 149°; Gadamer, 1902, *loc. cit.*), which is isomeric with corycavine ($C_{21}H_{21}O_5N$, Gadamer and von Bruchhausen, A., 1922, i, 675), is heated at 155° in hydrogen, it is converted into the latter base (m. p. 153°). It is therefore considered to be the ketone of which corycavine is the enol, (V) and (VI).

(V.) 

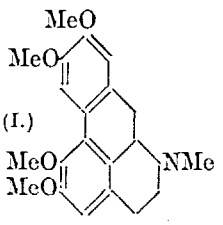
(VI.) 

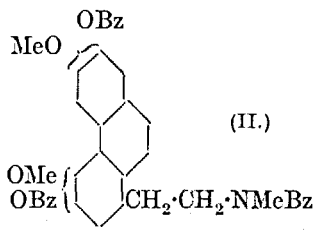
W. A. SILVESTER.

Alkaloids of *Corydalis cava*: corybulbine and *iso*corybulbine. [Synthesis of the methyl ethyl ether of nor-*m*-hemipinic acid.] F. VON BRUCHHAUSEN and K. SAWAY (Arch. Pharm., 1925, **263**, 602—605).—Späth and Dobrowsky (A., 1925, i, 1085) have anticipated the authors in their work in this field; they therefore publish the following notes on their independent synthesis of the ethylimide of the methyl ethyl ether of nor-*m*-hemipinic acid. 3-Methoxy-4-ethoxytoluene, when condensed with acetyl chloride by the Friedel–Crafts method, yields *4-methoxy-5-ethoxy-2-methylacetophenone* (b. p. 156—160°/11 mm.; *oxime*, m. p. 99—100°; *semicarbazone*, m. p. 185—186°). This is oxidised by potassium permanganate in alkaline solution to a mixture of *4-methoxy-5-ethoxy-2-methylbenzoylformic acid* (m. p. 75—77°; *methyl* ester, m. p. 108—109°) and *4-methoxy-5-ethoxy-2-methylbenzoic acid* (*5-methoxy-4-ethoxy-o-toluic acid*; m. p. 180—183°; *methyl* ester, m. p. 64—65°). The acids are separated by fractional extraction of their ethereal solution with sodium hydroxide, the first acid being first extracted. The second acid is obtained from the first by further oxidation with hydrogen peroxide, and when again oxidised with alkaline permanganate it yields the *methyl ethyl ether* of *nor*-m-*hemipinic acid* (*4-methoxy-5-ethoxyphthalic acid*) (m. p. 184—185°), which is separated as its sparingly soluble *barium* salt. The ethylimide of this acid has the m. p. given by Späth and Dobrowsky (*loc. cit.*), viz., 205°.

W. A. SILVESTER.

Constitution of boldine. K. WARNAT (Ber., 1925, **58**, [*B*], 2768—2773).—Boldine was isolated from the South American tree, *Pneumus Boldus*, by Bourgoin and Verne in 1872, but, apart from an investigation by Merck (Jahresber., 1922, p. 110), who assigned to it the composition $C_{19}H_{24}O_4N$, it does not appear to have been examined further. Boldine contains two methoxyl groups and is converted by hydriodic acid into *norboldine*, a very unstable base which gives a characteristic *hydriodide*, m. p. 249—250°. It is converted by diazomethane into *boldine dimethyl ether*, m. p. 117—118° (*hydriodide*, m. p. 243°), which is transformed by hydriodic acid into norboldine. Analysis of these derivatives establishes the composition $C_{19}H_{21}O_4N$ for boldine. The alkaloid is converted by benzoyl chloride in alkaline solution into *tribenzoylboldine* (II), m. p. 173°, in which the third benzoyl group must be attached to nitrogen, since the product is optically inactive and does not react with methyl iodide as does the dimethyl ether. It is therefore probable that the nitrogen atom in boldine is tertiary and that benzoylation is rendered possible by fission of the ring, whereby the asymmetric carbon atom loses its asymmetry. In addition, *dibenzoylboldine*, m. p. (indef.) 124—127°, is formed in small amount. The assumption just made is confirmed by the Hofmann degradation of boldine dimethyl ether, to which the

(I.) 

(II.) 

constitution (I) is therefore assigned (for position of methoxyl groups, see later). Dimethylboldine and methyl iodide readily yield a *methiodide*, $C_{22}H_{28}O_4NI$, m. p. 221°, which is converted by potassium hydroxide into the oily, optically inactive, *boldinedimethylmethine*; the *methiodide*, $C_{23}H_{30}O_4NI$, m. p. 276—280° after darkening, of the latter substance is converted by successive treatment with silver oxide and potassium hydroxide into (?)2 : 3 : 5 : 6-*tetramethoxy-8-vinylphenanthrene* and trimethylamine. The hydrocarbon is oxidised by potassium permanganate in the presence of aqueous acetone to (?)2 : 3 : 5 : 6-*tetramethoxyphenanthrene-8-carboxylic acid*, m. p. 213—214°, and when distilled with zinc dust gives in very small yield a hydrocarbon which is probably ethylphenanthrene (cf. Pschorr, A., 1906, i, 820). Further confirmation of the presence of the phenanthrene nucleus in boldine is found in the production of benzene-1 : 2 : 3 : 4-tetracarboxylic acid when boldinedimethylmethine, its methiodide, or tetramethoxyvinylphenanthrene is oxidised by concentrated nitric acid.

The exclusive production of oxalic acid when

boldine is oxidised by permanganate in alkaline solution appears to indicate that the two hydroxyl groups are attached to different nuclei. Oxidation of the dimethyl ether does not throw any further light on this question. Nevertheless, it appears probable from the recorded constants of glaucine (cf. Pschorr, Stählin, and Silberbach, A., 1904, i, 611; Gadamer, A., 1911, i, 483) that this substance is identical with boldine dimethyl ether (whence the position of the methoxyl group, *v.s.*). The experimental comparison of the two compounds has not yet been made. H. WREN.

Morphine in opium. E. MACHIGUCHI and S. SHIRONO.—See B., 1926, 27.

Microchemical analysis. IV. Anthraquinone-β-sulphonic acid as a reagent for alkaloids. L. ROSENTHALER (Mikrochem., 1925, **3**, 80—83).—Anthraquinone-β-sulphonic acid is a general reagent for alkaloids, with which it forms more or less insoluble salts, generally amorphous. Among the crystalline precipitates produced by the addition of a solid alkaloid or alkaloidal salt to a 10% solution of the acid are the following: aniline, oily drops slowly changing to bundles of needles; antipyrine, oily drops becoming stellate aggregates of needles; atropine, amorphous precipitate changing to bundles of needles; hydrastinine, first drops, then a microcrystalline precipitate, and finally four-sided, strongly polarising leaflets; nicotine, first amorphous, then warty masses; novocaine, first orange-red droplets, then needles, and the alkaloids of the quinine group a white, microcrystalline precipitate. If solid cinchonine sulphate is added to a 10% solution of anthraquinone-β-sulphonic acid, bubbles first form round the crystals of the alkaloid salt, which is gradually converted into a spherical mass of needle-shaped crystals. Salts of quinine, cinchonidine, and quinidine exhibit the bubble phenomenon, but no crystallisation ensues. A. R. POWELL.

Electrometric titration of alkaloids and reaction of alkaloid salts. I. M. KOLTHOFF.—See B., 1926, 74.

Preparation of tertiary arsines by the Friedel–Crafts reaction. A. F. HUNT and E. E. TURNER (J.C.S., 1925, **127**, 2667—2671).—Phenylmethylchloroarsine condenses with mesitylene to give *phenylmesitylmethylarsine*, b. p. 164°/17 mm., from which *phenylmesitylmethylarsonium iodide*, m. p. 187°, and *phenylmesitylbenzylmethylarsonium bromide*, m. p. 180°, were obtained. A similar condensation with toluene yielded *phenyl*-p-*tolylmethylarsine*, b. p. 165°/12 mm., which with methyl iodide formed *phenyl*-p-*tolyldimethylarsonium iodide*, m. p. 93°. With bromobenzene, the condensation yielded p-*bromodiphenylmethylarsine*, from which the *benzobromide* and p-*bromodiphenyldimethylarsonium iodide*, m. p. 87°, were prepared. The constitution of these compounds was confirmed by independent syntheses. p-*Bromophenylarsenious oxide*, m. p. 259—261°; p-*bromophenyldichloroarsine*; p-*bromophenylmethyliodoarsine*, m. p. 36·5°; p-*chlorophenyldichloroarsine*, b. p. 277°; p-*chlorophenylarsenious oxide*, m. p. 198°; and *di*-p-*chlorophenylchloroarsine*, m. p. 51°, were also prepared. B. W. ANDERSON.

Resolution of an asymmetric arsenic compound into its optically active form. W. H. MILLS and R. RAPER (J.C.S., 1925, **127**, 2479—2483).—p-*Carboxyphenylmethylethylarsine sulphide* has been resolved into its optically active enantiomorphs, thus confirming the fact that arsenic can function as a centre of asymmetry. The substance is a much stronger acid than the corresponding oxygen compound and forms stable alkaloid salts; the *dl*-acid melts at 183° and the optically active acids melt at 175—177°. The *l*-acid obtained from the brucine salt has in ethyl alcohol $[\alpha]^{20}_{5780}$ −19·1° and $[\alpha]^{20}_{5461}$ −21·6°, and the *d*-acid obtained from the morphine salt has in the same solvent $[\alpha]^{20}_{5780}$ +18·7°, $[\alpha]^{20}_{5461}$ +22·2°, and $[\alpha]^{20}_{4359}$ +39·4°. The following substances are also described: p-*tolylmethyliodoarsine*, b. p. 163—165°/12 mm., m. p. 29°; p-*tolylmethylethylarsine*, b. p. 117°/15 mm.

E. E. WALKER.

Trypanocidal action and chemical constitution. II. Arylamides of 4-aminophenylarsinic acid. H. KING and W. O. MURCH (J.C.S., 1925, **127**, 2632—2651).—A series of *p*-substituted *m*-nitrobenzoic acids and their corresponding acid chlorides has been prepared, including 3-*nitro*-4-*ethoxybenzoic acid*, m. p. 201°; 3-*nitro*-4-*ethoxybenzoyl chloride*, m. p. 82°; 3-*nitro*-4-*ethylcarbonatobenzoic acid*, m. p. 164° (from 4-*ethylcarbonatobenzoic acid*, m. p. 154—156°), and 3-*nitro*-4-*anisoyl chloride*, m. p. 52·5—53·5°. By introducing the acid chlorides into 4-aminophenylarsinic acid by modifications of the Schotten–Baumann method with subsequent reduction of the nitro-groups, some twenty-five substituted aminoarsinic acids were formed. Permanent trypanocidal properties were shown by the *aminoanisoyl-*, *aminochlorobenzoyl-*, *diaminobenzoyl-*, *diaminotoluoyl-*, and *diaminochlorobenzoyl-aminophenylarsinic acids*. When the amino-group of aminoanisoyl-4-aminophenylarsinic acid was substituted with acetyl and other radicals, the trypanocidal action was lost. The following were prepared: 3 : 3′-*dinitrobenzoyl-*, 3′ : 5′-*dinitrobenzoyl-*, 3′-*nitro*-4′-*toluoyl-*, 3′-*amino*-4′-*toluoyl-*, 3 : 3′-*dinitro*-4′-*toluoyl-*, 3′-*nitro*-4′-*anisoyl-*, 3′-*acetamido*-4′-*anisoyl-*, 3′-*carbethoxyamino*-4′-*anisoyl-*, 3″-*nitro*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*amino*-4″-*anisoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*nitrobenzoyl*-3′-*amino*-4′-*anisoyl-*, 3″-*aminobenzoyl*-3′-*amino*-4′-*anisoyl-*, 3′-*nitro*-4′-*ethoxybenzoyl-*, 3′-*amino*-4′-*ethoxybenzoyl-*, 4′-*chloro*-3′-*nitrobenzoyl-*, 4′-*chloro*-3 : 3′-*dinitrobenzoyl-*, 3′-*nitro*-4′-*ethylcarbonatobenzoyl-*, 3′-*nitro*-4′-*hydroxybenzoyl-*, 3′-*amino*-4′-*hydroxybenzoyl-*, 3′-*acetamido*-4′-*acetoxybenzoyl-*, and 3′-*acetamido*-4′-*hydroxybenzoyl*-4-*aminophenylarsinic acids*. 3′-*Amino*-4′-*hydroxybenzoyl*-4-*aminoarsenobenzene* and 3-*acetamido*-4-*acetoxyphenylarsinic acid* were also obtained. In the nitration of *para*-substituted benzoic acids, it was found that the relative directive powers for *ortho*-substitution of a nitro-group may be written OH, NMe_2>Me, OMe, OEt>F, Cl, Br, $O{\cdot}CO_2Et$.

B. W. ANDERSON.

Arsenical derivatives of thiophen. III. C. FINZI (Gazzetta, 1925, **55**, 824—834).—The methods

of synthesis previously employed (A., 1916, i, 94, 95) serve also for the preparation of halogenated thiophen-2-arsinic acids. Thus, the action of arsenic trichloride on 2-bromo- and 2-iodo-thiophen 5-mercurichloride (cf. Steinkopf and Bauermeister, A., 1914, i, 427) yields 2-bromo- and 2-iodo-5-thienyldichloroarsine, and these, when oxidised by means of hydrogen peroxide in presence of sodium hydroxide, give, respectively, crystalline *5-bromothiophen-2-arsinic acid*, $C_4H_2BrS\cdot AsO(OH)_2$, and *5-iodothiophen-2-arsinic acid*, which remain unfused at 300°, and when heated with magnesia mixture give the reaction of the primary arsinic acids. The bromo-acid is not attacked by concentrated nitric acid, but is partly decomposed, although not nitrated, by a mixture of sulphuric and nitric acids. This mixture, however, converts the iodo-acid into 3(or 4)-*nitro*-5-*iodothiophen*-2-*arsinic acid*, $NO_2\cdot C_4HIS\cdot AsO(OH)_2$, m. p. 302°.

Reduction of the above compounds by means of hypophosphorous acid (cf. Bart, A., 1922, i, 1202) yields the following derivatives. 2 : 2′-*Arsenothiophen*, $C_4H_3S\cdot As{:}As\cdot C_4H_3S$, a canary-yellow, amorphous compound, begins to soften below 100° and gradually decomposes. 5 : 5′-*Dinitro*-2 : 2′-*arsenothiophen*, greenish-yellow and amorphous, turns brown at 150° and explodes violently at 170—178°. 5 : 5′-*Dibromo*-2 : 2′-*arsenothiophen* softens at 130° and melts with frothing at about 170°. 5 : 5′-*Di-iodo*-2 : 2′-*arsenothiophen*, a yellow, amorphous substance, softens at 135° and is almost completely fused at 175°. *Dinitro*-5 : 5′-*di-iodo*-2 : 2′-*arsenothiophen* softens at 120° and decomposes with intense charring at about 140°.

Tri-2-thienylarsine (cf. Steinkopf, A., 1917, i, 303) may be readily obtained by the action of metallic sodium on an ethereal solution of 2-bromothiophen and arsenic trichloride. T. H. Pope.

Trypanocidal action and chemical constitution. III. Arsinic acids containing the glyoxaline nucleus. I. E. Balaban and H. King J.C.S., 1925, **127**, 2701—2714).—The preparation of *glyoxaline*-4(or 5)-*carboxy*-o-*nitroanilide*, m. p. 229° (*nitrate*, m. p. 196°, decomp.; *hydrochloride*), and *glyoxaline*-4(or 5)-*carboxy*-p-*nitroanilide* (with 2 mols. of acetic acid, m. p. 307°; *hydrochloride*, m. p. 265°, decomp.) was carried out and by reduction of these compounds *glyoxaline*-4(or 5)-*carboxy*-o-*aminoanilide*, m. p. 270° (*chlorostannate*; *dihydrochloride*, decomp. 310°; *dipicrate*, m. p. 242°, decomp.), and *glyoxaline* 4(or 5)-*carboxy*-p-*aminoanilide*, m. p. 228° (*dihydrochloride*, blackens at 290°; *picrate*, decomp. 266°), were obtained. Treatment of glyoxalinecarboxy-o-aminoanilide dihydrochloride with nitrous acid yields a sparingly soluble *diazoimide*, m. p. 196°, which will detect nitrous acid at a dilution of 1 in 6400. From the *p*-aminoanilide was prepared *glyoxaline*-4′(or 5′)-*carboxy*-p-*aminophenylarsinic acid* (*hydrochloride*; *magnesium*, *calcium*, and *sodium* salts), and both this and *glyoxaline*-4′(or 5′)-*carboxy*-p-*amino*-3-*aminophenylarsinic acid* (*diazoimide*; *magnesium* and *calcium* salts) showed permanent trypanocidal activity; the latter acid was prepared by reduction of *glyoxaline*-4′(or 5′)-*carboxy*-p-*amino*-3-*nitrophenylarsinic acid* (*magnesium*, *calcium*, *barium*, and *lithium* salts). Unsuccessful attempts were made to introduce the arsinic acid group into 2-m-*aminophenylglyoxaline* (*monohydrate*, m. p. 203°; *dihydrochloride monohydrate*, decomp. 282°; *monopicrate*, decomp. 218°) and into 2-p-*aminophenylglyoxaline* (*dihydrochloride*; *monopicrate*, decomp. 238°). 2-p-*Nitrophenyl*-1-*methylglyoxaline*, m. p. 116·5° (*chloroaurate*, m. p. 226°; *hydrochloride*; *nitrate*, decomp. 180°; *picrate*, decomp. 212°), was obtained in poor yields, and the following were also prepared in the course of the investigation: 2-o-*aminophenylglyoxaline*, m. p. 137° (*dihydrochloride*, m. p. 234—236°; *monopicrate*, m. p. 212°); 4-p-*aminophenylglyoxaline*, m. p. 98° (*chlorostannate*; *dihydrochloride*; *dipicrate*, m. p. 240°, decomp.); *glyoxaline*-4(or 5)-*phenyl*-p-*arsinic acid*, m. p. >310° (*magnesium* and *calcium* salts); 4-o-*aminophenylglyoxaline*, m. p. 131° (*dihydrochloride monohydrate*, decomp. 256°; *dipicrate*, decomp. about 200°; normal *tartrate*, m. p. 95—97°; *di*-d-*camphor*-10-*sulphonate*, m. p. 198—200°); 2-*phenyl*-1-*methylglyoxaline*, b. p. 175°/15 mm. (*methochloride*, m. p. 272°; *picrate*, m. p. 133°; *chloroaurate*, m. p. 189°; *nitrate*, m. p. about 100°; *hydrochloride*; *hydrogen oxalate*, m. p. 135°). B. W. Anderson.

Thiazoles. X. Synthesis of some 1-phenylbenzthiazolearsinic acids. M. T. Bogert and H. B. Corbitt (Proc. Nat. Acad. Sci., 1925, **11**, 768—772).—1-*Phenylbenzthiazole*-5-*arsinic acid*, unmelted at 310°, is obtained in 5·4% yield by Bart's reaction from 5-amino-1-phenylbenzthiazole, copper-bronze being the best catalyst. The isomeric 4′-*arsinic acid*, unmelted at 302°, prepared similarly from 1-*p*-aminophenylbenzthiazole (yield 26%), gives 5(?)-*nitro*-1-*phenylbenzthiazole*-4′-*arsinic acid* when treated with mixed acid at 40—45°. The corresponding *amino*-derivative, obtained by reduction of the nitro-compound with ferrous sulphate and alkali, couples with β-naphthol to give a cherry-red *dye*. The amine has trypanocidal properties and is free from the powerful action on the nervous system associated with other quinquevalent arsenic compounds. 1-*p*-Hydroxyphenylbenzthiazole, nitrated and reduced, gives an *amine*, which is converted by Bart's reaction into a 1-p-*hydroxyphenylbenzthiazolearsinic acid*. C. Hollins.

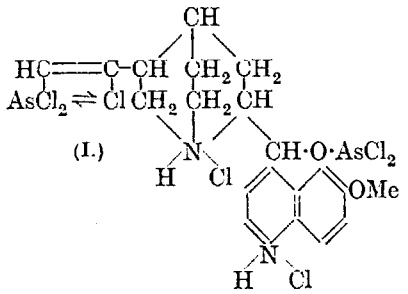
Neosalvarsan and sulpharsphenamine. E. Elvove.—See B., 1926, 27.

Diphenylaminechloroarsine [chlorophenarsazine]. W. L. Tanner.—See B., 1926, 76.

Arsinophenylcinchoninic acid (arsinocinchophen) and derivatives. II. H. O. Calvery, C. R. Noller, and R. Adams (J. Amer. Chem. Soc., 1925, **47**, 3058—3060; cf. A., 1925, i, 706).—5-Nitroisatin, m. p. 254—255° (cf. Baeyer, A., 1879, 937; D.R.-P. 221259), condenses with acetophenone in boiling aqueous alcoholic potassium hydroxide solution, with formation of 6-*nitro*-2-*phenylquinoline*-4-*carboxylic acid* (*nitrocinchophen*), yellow, m. p. 350—355° after darkening, as the *potassium* salt. This is reduced by stannous chloride and hydrochloric acid to 6-amino-2-phenylquinoline-4-carboxylic acid, orange, m. p. 259—260° (decomp.) after sintering at 240° (cf. D.R.-P. 287804), and this, when diazotised and treated with arsenious oxide, is converted into 6-*arsino*-2-*phenylquinoline*-4-*carboxylic acid* (*arsino*-

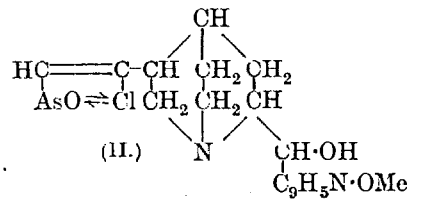
cinchophen), m. p. not below 360°. On reduction with sodium hyposulphite, the latter yields 2 : 2′-*diphenyl*-6 : 6′-*arsenoquinoline*-4 : 4′-*dicarboxylic acid*, red, m. p. not below 300°. Both the arsino- and the arseno-derivatives are trypanocides, but too toxic for ordinary use. F. G. WILLSON.

Action of arsenic trichloride on dehydroquinine, quinine, and dihydroquinine. F. X. ERBEN, E. PHILIPPI, and N. SCHNIDERSCHITZ [with F. SPORER and E. DIAMONT] (Ber., 1925, **58**, [*B*], 2854—2859).—The action of arsenic trichloride on dehydroquinine in the presence of chloroform at 150° yields a *substance* (I.) which is very sensitive towards



(I.)

moisture and is transformed by ammonium carbonate solution into *chloroarsinosoquinine* (II). The constitution assigned to substance (I) depends on the observation that six of the seven chlorine atoms are

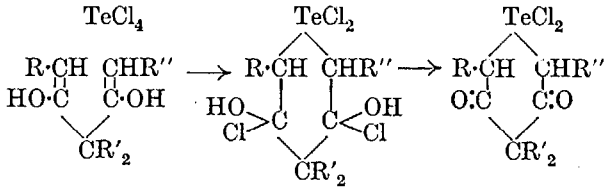


(II.)

removed by the action of cold silver nitrate solution, whereas the seventh remains attached to the molecule. Further, quinine and dihydroquinine are transformed by arsenic trichloride into *compounds*, $C_{20}H_{25}O_2N_2Cl_4As$ and $C_{20}H_{27}O_2N_2Cl_4As$, which are converted by ammonium carbonate solution into the arsenious *esters*, $C_{20}H_{23}O_3N_2As$ and $C_{20}H_{25}O_3N_2As$, which contain the arsenic atom united to the secondary hydroxy-group, –CH·O·As:O. The presence of a free hydroxy-group in substance (II) and, consequently, the attachment of arsenic to the vinyl group, is established by the production of a *benzoyl* derivative, $C_{27}H_{26}O_4N_2ClAs$. H. WREN.

Interactions of tellurium tetrachloride and monoketones. G. T. MORGAN and O. C. ELVINS (J.C.S., 1925, **127**, 2625—2632).—Tellurium tetrachloride undergoes condensation with many monoketones which are capable of enolisation, forming either a tellurium bisketone dichloride or a tellurium ketone trichloride. Thus *tellurium bisacetone dichloride*, m. p. 126—128°; *tellurium methyl ethyl ketone trichloride*, m. p. 101·5°; *tellurium bismethyl* n-*propyl ketone dichloride*, m. p. 92—93°; *tellurium bismethyl* iso*propyl ketone dichloride*, m. p. 90° after softening at 85°; *tellurium bismethyl* n-*butyl ketone dichloride*, m. p. 62°; *tellurium bismethyl* iso*butyl ketone dichloride*, m. p. 95°; *tellurium diethyl ketone trichloride*, m. p. 78°; and *tellurium di*-n-*propyl ketone trichloride*, m. p. 70°, have been prepared. The condensation with pinacolin yielded both *tellurium pinacolin trichloride*, m. p. 115°, and *tellurium bispinacolin dichloride*, m. p. 192°; with diisopropyl ketone, no condensation took place. By using mixed ketones containing aromatic radicals, *tellurium phenyl ethyl ketone trichloride*, m. p. 115°; *tellurium phenyl* n-*propyl ketone trichloride*, m. p. 129°; and *tellurium phenyl benzyl ketone trichloride*, m. p. 143°, were also obtained. B. W. ANDERSON.

Production of *cyclo*telluripentanedione dichlorides. G. T. MORGAN [with F. J. CORBY, O. C. ELVINS, E. JONES, R. E. KELLETT, and C. J. A. TAYLOR] (J.C.S., 1925, **127**, 2611—2625).—The condensation occurring between tellurium tetrachloride and β-diketones yields cyclic products due to two-fold terminal enolisation :



and also noncyclic products due to simple median enolisation of the diketone, the course of the reaction depending on the nature of R, R′, and R″ in the above formulæ. From n-*propylpropionylacetone*, b. p. 210° (*copper* derivative, m. p. 178°, decomp.), was obtained 2-*methyl*-4-n-*propyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, blackens at 150°, readily reduced to 2-*methyl*-4-n-*propyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 102°. Similarly, 3-iso*propylpropionylacetone*, b. p. 195°, gave 2-*methyl*-4-iso*propyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, blackens at 173°, which on reduction yielded 2-*methyl*-4-iso*propyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 127°. 4-*Benzyl*-2-*methyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 168°, was obtained from 3-*benzylpropionylacetone*, b. p. 185°/20 mm. (*copper* derivative, m. p. 182°), and the dichloride yielded the corresponding 4-*benzyl*-2-*methyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 124° (decomp.). 3-iso*Butylacetylacetone*, b. p. 94°/10 mm. (*copper* derivative, m. p. 158°), was prepared, and from it 4-iso*butyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 142°, which gave 4-iso*butyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 150°. In a similar manner, 2-*benzyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, 2-*benzyl*cyclo*telluropentane*-3 : 5-*dione* (decomp. 159°), 2-n-*decyl*cyclo*telluripentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 89°, and 2-n-*decyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 99° (decomp.), were obtained. 3-Phenylpropionylacetone yielded no *cyclo*telluri-derivatives. From 3-sec.-*butylacetylacetone*, b. p. 109—111°/13 mm., were formed 4-sec.-*butyl*cyclo*telluri-pentane*-3 : 5-*dione*-1 : 1-*dichloride*, m. p. 169°, and 4-sec.-*butyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 145°; and from dl-sec.-*amylacetylacetone*, b. p. 116°/15 mm. (*copper* derivative, m. p. 120°), 4-sec.-*amyl*cyclo*telluri-pentane*-3 : 5-*dione*-*dichloride*, m. p. 162°, and 4-sec.-*amyl*cyclo*telluropentane*-3 : 5-*dione*, m. p. 139°, were obtained. The condensation of tellurium tetra-

chloride with 3-sec.-*amyldipropionylmethane*, b. p. 137°/15 mm. (*copper* derivative, m. p. 105°), yielded only oily products. B. W. ANDERSON.

Naturally occurring porphyrins. XVII. Transformation of uroporphyrin into coproporphyrin, and certain derivatives of these porphyrins. H. FISCHER and J. HILGER (Z. physiol. Chem., 1925, **149**, 65—70).—By heating dry uroporphyrin at 180° in an atmosphere of nitrogen, decarboxylation occurs, and coproporphyrin is formed in 60% yield. Uroporphyrin is probably an ætioporphyrin, of the formula $C_{40}H_{38}O_{16}N_4$, containing thirty-two carbon atoms in the nucleus with, in addition, eight carboxyl groups. A new *porphyrin* giving a crystalline *copper* salt is obtained by the action of fuming nitric acid on the methyl ester of uroporphyrin. In similar conditions, coproporphyrin methyl ester yields a dinitro-derivative. Crystalline *cadmium* and *manganese* salts of coproporphyrin methyl ester have been prepared. H. D. KAY.

Formation of protein complexes with hydroxides of tervalent metals. De-proteinisation by means of alums. L. C. MAILLARD and H. WUNSCHENDORFF (Compt. rend., 1925, **181**, 941—942; cf. A., 1925, i, 1346).—Potassium alums of aluminium, chromium, and iron precipitate proteins quantitatively from biological fluids on addition of alkali. Thus, to a solution containing serum 2 c.c., water 5 c.c., and 5% solution of potassium aluminium alum 25 c.c., 0·5*N*-sodium hydroxide is added until the hydrogen-ion concentration reaches p_H 7, and the volume is made up to 50 c.c. The filtrate is protein-free, but contains the original amount of ammonia, carbamide, and uric acid. L. F. HEWITT.

General properties of proteins. M. L. ANSON and A. E. MIRSKY (J. Gen. Physiol., 1925, **9**, 169—179).—Theoretical, with no new experimental evidence. It is concluded that: (1) hæmoglobin, when denatured, is probably depolymerised to hæmochromogen, and that in other proteins denaturation probably consists in depolymerisation, native proteins, therefore, being considered as aggregates of denatured proteins; (2) the globins and histones are to be regarded as denatured proteins rather than as a distinct class; (3) a non-polar group is uncovered when a protein is denatured; and (4) proteins are highly specific only in the native form. The factors affecting the equilibrium between native and denatured protein are discussed. C. P. STEWART.

Crystallisation and specific rotation of ovalbumin and an attempt to crystallise lactalbumin. C. W. CHAPMAN (Canadian Chem. Met., 1925, **9**, 268—270).—Crystallisation of ovalbumin by the method of Hopkins occurs only between p_H 4·7 and 5·4. It is uncertain at p_H above 5·1, the best yield being obtained between p_H 4·7 and 5·1, *i.e.*, near the isoelectric point of the protein. Within this p_H range, recrystallisation yields a product almost wholly crystalline and with a constant specific rotation, $[\alpha]_D$+30·68°. Lactalbumin prepared by various methods did not crystallise when submitted to the process used for ovalbumin. C. P. STEWART.

Tryptophan-content of proteins; determination of tryptophan. J. TILLMANS and A. ALT (Biochem. Z., 1925, **164**, 135—162).—The colorimetric method of Fürth and Nobel (A., 1921, i, 74) for the determination of tryptophan in proteins gives very high results. The colour obtained with pure tryptophan solutions is bluish-violet and with proteins reddish-violet. Comparison is therefore difficult and the use of blue glass filters gives incorrect results. The methods of May and Rose (A., 1923, i, 160) and of Folin and Looney (A., 1922, ii, 539) give more trustworthy results, but are tedious. A new method based on the protein reaction with formaldehyde and sulphuric acid is elaborated which is much simpler, allows of ready comparison of colours, and is carried out directly without hydrolysis of the proteins. The tryptophan contents of a large number of proteins are tabulated. The tryptophan content of the protein of cow's and goat's milk is about the same, but is smaller than that of human milk. The tryptophan content of three types of cheese did not change during the ripening process. By means of this method, it is shown that the Fritzmann reaction (A., 1899, ii, 54) for the detection of nitrate in milk is a specific tryptophan reaction. The myosin from horse-flesh has almost the same tryptophan content as that from beef. Wheat protein contains more tryptophan than rye protein. Zein is devoid of tryptophan. Adulteration of wheat flour by rye flour can therefore be detected by determination of the tryptophan content of the alcohol-soluble proteins, which for wheat should not be below 0·8%. P. W. CLUTTERBUCK.

Determination of halogens and sulphur in organic substances. O. WAGNER.—See B., 1926, 75.

Separation of ethyl alcohol from acetaldehyde or acetone. G. GORR and J. WAGNER (Biochem. Z., 1925, **161**, 488—491).—The liquid is boiled under a reflux condenser for 5 hrs. with freshly prepared mercuric oxide. The alcohol can now be distilled off and determined. H. I. COOMBS.

Gasometric method for the determination of acetic anhydride. E. L. WHITFORD (J. Amer. Chem. Soc., 1925, **47**, 2939—2940; cf. this vol., 146).—Anhydrous oxalic acid is added in excess to pyridine which has been dried by treatment with fused sodium hydroxide, barium oxide, and calcium carbide, and the mixture then saturated with dry carbon monoxide and dioxide. The weighed sample of acetic anhydride is added, and the gases evolved are collected over water saturated previously with carbon monoxide and dioxide. The amount of acetic anhydride present in the sample is deduced from the volume of gas generated: $C_2H_2O_4+Ac_2O=CO+CO_2+2HO\cdot Ac$. F. G. WILLSON.

Accurate general iodometric method for the determination of the carbonyl group in organic compounds. E. G. R. ARDAGH and J. G. WILLIAMS (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 73—74, and J. Amer. Chem. Soc., 1925, **47**, 2983—2988).—The method described consists in converting the aldehyde or ketone into a phenylhydrazone and determining the excess of phenylhydrazine iodo-

metrically. In a 100-c.c. glass-stoppered flask are placed 20 c.c. of 0·5*M*-phenylhydrazine hydrochloride, 20 c.c. of a solution of disodium phosphate slightly weaker than 0·5*M*, and sufficient carbonyl compound to react with about half of the phenylhydrazine. The volume is made up to 100 c.c. with saturated sodium chloride solution, the air removed with nitrogen, and the whole kept at the ordinary temperature (or if necessary on the water-bath) for 30 min. until the reaction is completed. If a solid hydrazone separates it is quickly filtered off. Twenty-five c.c. of this solution are shaken with 4—5 c.c. of light petroleum in a 100-c.c. separating funnel (air removed with nitrogen) for 2 min. and 2 min. allowed for separation. Ten c.c. of the aqueous layer are run into a stoppered Erlenmeyer flask, air being replaced by nitrogen, and the solution is made just acid to methyl-orange. Sufficient 0·1*N*-iodine is run in to give a 5 c.c. excess and the mixture kept for 5 min. Starch solution is added and 3—4 c.c. excess of 0·1*N*-sodium thiosulphate run in. The contents are now shaken with 5 c.c. of ether to extract iodine from the drops of iodobenzene and a final titration is made with 0·1*N*-iodine. The volumes of the remainder of the aqueous and ethereal solutions are then determined. A control is made under similar conditions on the phenylhydrazine alone. The correction to be applied is usually quite small. Distilled water boiled and cooled in an atmosphere of nitrogen is used throughout. The method described is superior to that of Benedikt and Strache (A., 1893, i, 560) using Fehling's solution for the determination of the excess of phenylhydrazine. J. S. Carter.

Determination of cystine and cysteine. Y. Okuda (J. Dept. Agric. Kyusha Univ., 1925, **1**, 163—196).—Cysteine, in the absence of cystine and certain other amino-acids, may be accurately determined in acid solution containing bromide by titration with a standard solution of bromate, 1 mol. of cysteine being oxidised to cysteic acid by six atoms of the liberated bromine. Another method, not vitiated by the presence of cystine etc., is to titrate the acid cysteine solution in presence of iodide with standard iodate solution. Definite conditions, however, must be employed and corrections made from a temperature curve. This method may be applied to the determination of cystine by first reducing this compound to cysteine under regulated conditions. There is no appreciable decomposition of cystine during acid hydrolysis of proteins, but the amount precipitable as phosphotungstate decreases rapidly, as part of the cystine is transformed into an isomeride the phosphotungstate of which is soluble. A series of determinations of the cystine content of proteins using the above iodine method and Folin and Looney's method (A., 1922, ii, 539) showed that the latter is untrustworthy. The cystine present in urine may be determined by the iodine method after removing coagulable protein and thiocyanate.
B. W. Anderson.

Biochemistry.

Thiocyanates and cellular respiration. N. Tarugi (Annali Chim. Appl., 1925, **15**, 416—426).—A discussion of this question, the influence of the thiocyanic group on cellular respiration being regarded as analogous to that of the thiol group (cf. A., 1903, ii, 460; 1904, ii, 220; 1905, i, 176). T. H. Pope.

Carbon dioxide excreted in one minute by one cm. of nerve fibre. G. H. Parker (J. Gen. Physiol., 1925, **9**, 191—195).—One cm. of nerve-fibre from the lateral-line nerve of the dogfish was estimated to excrete an average of $4{\cdot}2\times10^{-8}$ mg. of carbon dioxide per min. C. P. Stewart.

Tissue respiration. O. Warburg (Biochem. Z., 1925, **163**, 252).—A comment on publications by Dixon and Thurlow (A., 1920, i, 1213) and Ahlgren ("Zur Kenntnis der tierischen Gewebsoxydation," 1925). E. C. Smith.

Spirometer method of studying continuously the gaseous metabolism of man during and after exercise. K. Furusawa (Proc. Roy. Soc., 1926, **B**, **99**, 148—154).—A new method, including a specially designed apparatus, is described for studying continuously the rapidly altering gaseous metabolism of man, during and after muscular exercise.
W. O. Kermack.

Muscular exercise, lactic acid, and supply and utilisation of oxygen. XIII. Gaseous exchanges of restricted muscular exercise in man. K. Furusawa (Proc. Roy. Soc., 1926, **B**, **99**, 155—166).—The gaseous metabolism occurring during exercise, involving only a comparatively small portion of the total musculature of the human body, shows certain differences as compared with exercise involving practically the whole musculature. The lactic acid formed in the exercised muscle may pass into the blood-stream and hence to the other muscles of the body. In this way, the large magnitude of the "oxygen debt" observed is rendered possible.
W. O. Kermack.

Muscular exercise, lactic acid, and supply and utilisation of oxygen. XIV. Relation in man between oxygen intake during exercise and lactic acid content of the muscles. C. N. H. Long (Proc. Roy. Soc., 1926, **B**, **99**, 167—172).—During moderate muscular exercise in man, the concentration of lactic acid in the muscle as measured by its concentration in the blood plasma, with which it is in equilibrium, is proportional to the square root of the rate of oxidation of lactic acid, as measured by the rate of oxygen intake, when a steady state has been established. This result agrees with that previously obtained for isolated muscle, and it indicates that the

controlling reaction in the re-synthesis of glycogen from lactic acid in the muscle is a bimolecular one.
W. O. KERMACK.

Molecular concentration in internal fluids of *Ascidia mentula*, Müll. M. DUVAL and M. PRENANT (Compt. rend., 1926, **182**, 96—98).—The blood of *Ascidia mentula*, Müll., has p_H 7·1, a f. p. (—2·08°) lower than that of the surrounding sea-water (—1·98°), and a higher content of sodium chloride (3·47%) than the sea-water (3·3%).
L. F. HEWITT.

Body fluids of the honey-bee larva. II. Constituents of the blood and their osmotic effect. G. H. BISHOP, A. P. BRIGGS, and E. RONZONI (J. Biol. Chem., 1925, **66**, 77—88).—As compared with mammalian blood, the blood of the honey-bee larva has a high content of sugar (which falls during pupation); also of fats, amino-acids, potassium, calcium, magnesium, and phosphorus; the proteins, sodium, chlorine, and total salts are low. The depression of the f. p. of larval blood was 0·86° during feeding and 0·75° after pupation; the high values are chiefly due to the large amount of amino-acids, and the difference in the two periods to the above-mentioned reduction of sugar on pupation. Since, on adjusting a synthetic solution of inorganic salts, in similar concentrations, to the p_H of the blood, calcium phosphate was precipitated, it is assumed that, in the blood, part of the calcium is in the form of undissociated compounds of calcium carbonate with amino-acids. C. R. HARINGTON.

Conservation of red corpuscles *in vitro* and selective sensitivity to poisons. O. LAVES (Biochem. Z., 1925, **161**, 416—443).—A solution is recommended in which blood-corpuscles may be kept for some time without hæmolysis. It consists of 2/3 isotonic salt solution (containing 0·9% of sodium chloride; 0·098% of potassium chloride; 0·098% of calcium chloride; 0·049% of sodium hydrogen carbonate) and 1/3 isotonic (9·15%) sucrose solution. The hæmolytic action of morphine, methyl- and ethyl-morphine, quinine, and codeine in solutions containing various anions was investigated. H. I. COOMBS.

Reaction of potassium ferricyanide with blood pigment. M. NICLOUX and J. ROCHE (Compt. rend., 1925, **181**, 823—826).—On treatment of oxyhæmoglobin and carboxyhæmoglobin with potassium ferricyanide in alkaline solution methæmoglobin is formed and oxygen and carbon monoxide, respectively, are liberated in proportions indicating that methæmoglobin contains half the amount of oxygen present in oxyhæmoglobin (cf A., 1925, i, 993). L. F. HEWITT.

Hæmoglobinogenous pigments. J. OBERZIMMER and L. WALKER (Virchow's Archiv, 1924, **252**, 33—38; from Chem. Zentr., 1925, II, 310).—By dissolving liver or spleen containing hæmosiderin in 60% potassium hydroxide and subsequently diluting with water, a precipitate consisting principally of ferric hydroxide together with some organic matter is obtained. In amount, it is roughly proportional to the hæmosiderin present. Ferric hydroxide is deposited in living tissues, where it may be adsorbed by protein and lipoid substances. In acid, dying tissues it becomes reduced to ferrous hydroxide, which then becomes diffused as ferrous hydrogen carbonate, from which ferric hydroxide is again formed in the presence of air. Ferric oxide or hæmosiderin is precipitated in large amounts in the superficial portions of fragments of liver containing hæmosiderin.
G. W. ROBINSON.

Inorganic elements associated with oxyhæmoglobin in horse blood. A. DESGREZ and J. MEUNIER (Compt. rend., 1925, **181**, 1029—1031; cf. A., 1923, i, 409).—Oxyhæmoglobin was obtained from horse blood by defibrination, separation of the red cells at a low temperature after centrifuging, hæmolysis by water at 35°, crystallisation by addition of 25% of ethyl alcohol and cooling to a low temperature, filtration, drying, and recrystallisation in the same manner. After the second recrystallisation, the hæmoglobin dissolved only partly in 25% alcohol, leaving a brown, amorphous residue; the soluble matter was precipitated by addition of more ethyl alcohol. The various fractions were burnt in a hydrogen flame and the flame was examined spectrographically. A considerable amount of potassium together with iron, lithium, calcium, sodium, and traces of manganese were detected in the first crystalline crop of hæmoglobin. In the second crop of crystals, the potassium had decreased considerably in quantity, whilst the amounts of calcium and iron were unchanged. In the insoluble portion of the third crop, lithium, iron, and sodium were detected, but no potassium or calcium. In the portion of the third crop precipitated by alcohol, calcium but no lithium or sodium was detected. L. F. HEWITT.

Tartarylhæmin. S. HAJDU (Biochem. Z., 1925, **163**, 233—240).—By the action of tartaric acid in methyl alcohol on hæmoglobin, a dark brown, crystalline product, m. p. 250—300° (decomp.), containing C 64·93, H 5·10, N 9·79, Fe 9·77%, has been obtained. By analogy with formylhæmin, this substance is considered to be *tartarylhæmin*,

$$[C_{34}H_{31}O_4N_4MeFeO]_4.$$

E. C. SMITH.

Ultrafiltration of serum. B. BRUKNER and P. UHLENBRUCK (Z. Biol., 1925, **83**, 586—592).—The rate of filtration through a Zsigmondy ultra-filter is increased by stirring. A magnetically-operated stirrer is briefly described. The size of the pores in a filter is reduced by prolonged subjection to high pressures, with consequent reduction of the speed of filtration. On this account, the accurate fractionation of proteins by ultrafiltration is very difficult.
H. P. MARKS.

Physico-chemical properties of certain serum constituents. F. VLÈS and A. DE COULON (Compt. rend., 1925, **181**, 1189—1191).—Human serum is subjected to cataphoresis at various hydrogen-ion concentrations and treated with a mixture of equal parts of ethyl alcohol and acetone. In this manner, flakes and a powdery precipitate are obtained. In the case of healthy men the flakes have two distinct isoelectric points, one in the neighbourhood of p_H 5·5—6·5 and another at p_H 11—12. The points

in the case of women vary with their physical condition. In acute infections and cancer, the flakes obtained have different isoelectric points and in some cases only one point is observed. L. F. HEWITT.

So-called anion-deficit in blood-serum. Determination of the dissociation constant and concentration of an unknown acid present in serum. R. MOND and H. NETTER (Pflüger's Archiv, 1925, **207**, 515—522; from Chem. Zentr., 1925, II, 315; cf. A., 1924, i, 114).—The alkali of blood at normal reaction is not combined with serum proteins. The deficit of anionic and osmotically active substances in the serum necessitates the assumption of the existence of a hitherto unknown acid. The presence in the ultrafiltrate from ox-serum of an acid, or mixture of acids, of dissociation constant $10^{-3\cdot5}$ and concentration 1/70—1/120*N*, was indicated by electrometric titration. G. W. ROBINSON.

Activity of sodium in serum. L. MICHAELIS and S. KAWAI (Biochem. Z., 1925, **163**, 1—7).—The determination of sodium ion in serum by means of a sodium amalgam electrode gives the same value as the determination of total sodium by the Kramer and Gittleman method (A., 1925, i, 180). It is concluded that serum proteins have no effect on the ionisation of sodium. E. C. SMITH.

Thiocyanate content of human serum. H. SCHREIBER (Biochem. Z., 1925, **163**, 241—251).—In women and non-smoking men, the thiocyanate content varies between 0·025 and 0·04 mg.% of the serum. Smoking causes an increase to three times this value. Administration of thiocyanates causes an increase to thirty times the normal value, the level then remaining constant while administration continues. On cessation of treatment, the normal level is attained only after 2—3 weeks. Variations from the normal cannot otherwise be correlated with the condition of the subject. E. C. SMITH.

The *pK′* of the Henderson-Hasselbalch equation for blood-serum. G. E. CULLEN, H. R. KEELER, and H. W. ROBINSON (J. Biol. Chem., 1925, **66**, 301—322).—The average value of the term *pK′* of the Henderson-Hasselbalch equation, determined by observation on the blood-serum from fifteen miscellaneous pathological cases, was 6·095 at 38° and 6·183 at 20°, the temperature coefficient being therefore −0·005 per 1°; similar values were obtained from normal dog's blood-serum; the constancy of the figures derived from the various cases with differing protein and salt contents indicates that variations in the latter have no measurable effect on the value of *pK′*. The temperature coefficient of $[BHCO_3]$ is −0·1 millimol. per 1° at constant $[H_2CO_3]$ and −0·14 millimol. per 1° at constant p_H. C. R. HARINGTON.

Charcoals from colloids. R. EHRENBERG (Biochem. Z., 1925, **161**, 339—347).—Blood etc. from animals and diseased human beings was converted into charcoals and the adsorptive power of these measured. H. I. COOMBS.

Simple colorimetric method for the determination, and a contribution to the physiology, of the sugar of the blood. I. B. GLASSMANN (Z. physiol. Chem., 1925, **150**, 16—43).—If excess of resorcinol is added to a solution of dextrose in presence of 20% hydrochloric acid, and boiled for an hour, a yellow solution is obtained, the colour of which, at temperatures above 60°, is a linear function of the dextrose content of the original solution. A method of blood-sugar determination, based on this principle, yields results which are not interfered with by any of the other reducing substances present in blood. Using this method, 45% of blood samples taken from normal, fasting individuals were found to contain no dextrose. The "hypoglycæmic" syndrome following injection of insulin is not due to a lowering of the blood-sugar, but to the production of a toxin which may be neutralised by dextrose. The sugar of the blood is not identical with ordinary dextrose. H. D. KAY.

Carbohydrate utilisation. I. Rate of disappearance of dextrose from the blood. V. DU VIGNEAUD and W. G. KARR (J. Biol. Chem., 1925, **66**, 281—300).—Rabbits which have fasted for some days show an exaggerated response to administration of dextrose in that the blood-sugar reaches a higher concentration and takes longer to return to the normal level. Administration of fat 18 hrs. previous to the test exaggerates this effect still further, but administration of dextrose, and still more of protein, at the same point increases the tolerance of the animal; a similar increased tolerance is induced by injection of adrenaline and by daily administration of sodium hydrogen carbonate, but insulin has the reverse effect, and morphine, although it raises the blood-sugar to the same extent as adrenaline, has no effect in improving the tolerance of the fasting rabbit. C. R. HARINGTON.

Normal variations of the inorganic phosphate of blood. R. E. HAVARD and G. A. REAY (Biochem. J., 1925, **19**, 882—887).—There is a rise of inorganic phosphate during sleep even by day. The seasonal variation in average normal blood was observed to be from 2·9 mg. of phosphorus per 100 c.c. in January to 4·0 mg. per 100 c.c. in August. The best normal results of the inorganic phosphate of the blood are obtained early in the day when the subject is seated. A micro-adaptation of Briggs' method was employed in this investigation. S. S. ZILVA.

Acid-combining power of the blood of healthy and diseased children. J. CSAPÓ and G. MIHALOVICS (Biochem. Z., 1925, **161**, 459—464).—The acid-combining power of blood and plasma (cf. A., 1925, i, 188) was investigated. In healthy children, the blood has twice the combining power of the plasma, and the combining power varies with the red corpuscle content. In anæmia and icterus the value is low. H. I. COOMBS.

Quantitative changes in blood-sugar and blood lactic acid in canine anaphylaxis. M. MCCULLOUGH and F. I. O'NEILL (J. Infect. Dis., 1925, **37**, 225).—Canine anaphylactic shock is accompanied by a rapid rise in the sugar content of the blood,

reaching a maximum in 20 min. of nearly twice the normal value. After the first 15 min. the curve thus obtained is identical with the blood-sugar curve obtained by intravenous injection of a quantity of dextrose equivalent to the estimated glycogen content of the liver. The lactic acid increases during anaphylactic shock, the maximum of twice the normal value being reached within 30 min.

CHEMICAL ABSTRACTS.

Toxicity of serum left in contact with starch. A. LUMIÈRE and H. COUTURIER (Compt. rend., 1926, **182**, 89—91).—The toxicity of serum left in contact with starch is due to a finely-divided suspension which does not turn blue with iodine and which is removed by long centrifuging. L. F. HEWITT.

Immunological properties of alcohol-soluble vegetable proteins. IX. Biological reactions of vegetable proteins. J. H. LEWIS and H. G. WELLS (J. Biol. Chem., 1925, **66**, 37—48).—Complement fixation and anaphylactic tests indicate a close relationship between the alcohol-soluble proteins from the different species of the wheat family on the one hand, and between those from several species of maize on the other, but no inter-relationship between the two groups. C. R. HARINGTON.

Antigenic properties of hæmoglobin. W. ENGELHARDT (Biochem. Z., 1925, **163**, 187—196).—The addition to rabbit serum of dog's hæmoglobin to which the animals have previously been immunised results in the formation of a precipitate in which the hæmoglobin may be determined and thus serve as an index of the amount of antibody in the serum. The values vary between 0·02 mg. and 0·07 mg. of hæmoglobin per 0·1 c.c. of serum. Variation in the method of preparation and repeated crystallisation of the hæmoglobin have very little effect on its action on the immune serum. Heating at 70° for 30 min. has no effect on the power of the immune serum to precipitate hæmoglobin. The action of the immune serum is not rigidly specific, since a small quantity of sheep-hæmoglobin is precipitated.

E. C. SMITH.

Conversion products of the pigments of flesh and blood. VII. Muscle pigment and MacMunn's myohæmatin. O. SCHUMM (Z. physiol. Chem., 1925, **149**, 111—149).—The differences observed by Mörner and Günther between the spectrum of a freshly-prepared aqueous extract of muscle (myochrome solution) and that of an oxyhæmoglobin solution are confirmed. In the muscle of pigeons immediately after death, besides myochrome there is a small quantity of a pigment which gives a similar spectrum to hæmochromogen, with a well-marked absorption band about 550 μμ. MacMunn's "dominant band of myohæmatin" is also visible if sections of suitable thickness are employed, but in water extracts the pigment has only been detected if the muscle was kept ½—1 hr. before extracting. The complete spectrum of the pigment, for which the name *myochromogen* is suggested, consists in a very dark, symmetrical band at 549·5 μμ and a weaker one at about 519μμ. The altered position of the bands distinguishes the spectrum from that of hæmochromogen. Myochromogen can be converted into myatin (supposed), but the myochromogen spectrum reappears in alkaline solution when hydrazine hydrate is added. The identity of myatin and MacMunn's myohæmatin is not considered proved. Myatin in the presence of much myochrome, oxyhæmoglobin, or methæmoglobin can easily be overlooked, but small quantities incapable of recognition in the spectrum can easily be detected by conversion into myochromogen. It is concluded that muscle from pigeons immediately after death contains very little free myatin or myochromogen, but these are found in increasing quantities in aqueous extracts prepared some time after death. No proof has been found of the presence of myatin or myochromogen in quantity in the living muscle of dogs or pigeons. MacMunn's idea that fresh muscle (breast) of the pigeon contains only or almost only myohæmatin, is erroneous. Myochromogen is found together with other pigments in the flesh juices obtained by the Struve-MacMunn "ether method." The extracts from flesh after leaving it to decompose at 37° or 50° over long periods contain a pigment like hæmochromogen, which gives a spectrum like myochromogen and (for the present) cannot be distinguished from it. Pyridine extracts from the fresh muscle of pigeons give the same hæmochromogen reaction with hydrazine as is given by α-hæmatin. No definite proof has been found of the presence of coprohæmatin in the fresh muscle of pigeons or of calves. A. COULTHARD.

New porphyrin. H. M. FOX (Nature, 1926, **117**, 49—50).—Although the hæmatin of hæmoglobin and that of chlorocruorin both contain iron, the former has a different porphyrin from the latter, the axes of the bands of the two porphyrins obtained by Nencki's method being, respectively, 593, 549, and 613, 553 μμ in dilute (1 : 3) hydrochloric acid. When a modification of Laidlaw's procedure for the preparation of porphyrin was employed, the porphyrin from chlorocruorohæmatin, which is soluble in chloroform, gives bands situated considerably on the red side of those from ooporphyrin or porphyrin from hæmin. A. A. ELDRIDGE.

Ageing process. R. EHRENBERG (Biochem. Z., 1925, **164**, 175—182).—Comparative analysis of human livers and brains of the same and different ages appear to give periodicity with age in the values obtained for the alcohol–ether extract (% dry weight), for the total nitrogen and phosphorus of the extract and of the residue, and for the content of the hydrolysed extract in ammonia, monoamino-nitrogen, melanoidin, total nitrogen of diamino-acids and cystine, arginine, cystine, histidine, and lysine. Similar results are obtained in the comparative analysis of six batches of whole mice of age 0, ½, 1, 3, 8, and 24 months, the material of the mice of the same age being mixed to equalise individual variations. Comparative values are obtained also for the liver, brain, and kidney of a female rabbit and the corresponding organs of its litters of age six weeks and six months.

P. W. CLUTTERBUCK.

Chemical topography of the brain. I. Lipins and total nitrogen of the human cortex. H. GORODISSKAY (Biochem. Z., 1925, **164**, 446—480).—The chemical differences between functionally different areas are most marked with regard to cholesterol content, and also the content in alcohol-extractable lipins (cerebrosides and saturated phospholipins), total nitrogen, and the phosphorus of the unsaturated phosphatides. The richest in lipins and total nitrogen is the motor area (ascending frontal gyrus), the poorest is the anterior association centre (frontal pole), occupying an intermediate position are the psycho-sensorial areas (cuneus and ascending parietal gyrus). Corresponding areas of the right and left hemispheres differ considerably in constitution. Above the age of fifty, cholesterol increases and total nitrogen and the phosphorus of the unsaturated phosphatides decrease. Alterations due to sex and age are most pronounced at the occipital pole. E. C. SMITH.

Hydrogen-ion concentration and oxidation-reduction potential of the cell-interior before and after fertilisation and cleavage. Micro-injection study on marine eggs. J. NEEDHAM and D. M. NEEDHAM (Proc. Roy. Soc., 1926, **B**, **99**, 173—198).—Both the p_H and r_H (reduction potential) of certain marine eggs, studied by the method of micro-injection of indicators, show a remarkable constancy, the former being in the neighbourhood of 6·6 and the latter varying from 19 to 22, and both remain constant during fertilisation and also during the initial cell divisions. Asphyxia has no influence on the values found, and although during cytolysis the p_H decreases to between 4 and 5, the r_H does not appear to change. The results do not agree with those obtained by the method of vital staining.
W. O. KERMACK.

Physiology of plain muscle. IV. Lactic acid content of plain muscle under various conditions. C. L. EVANS (Biochem. J., 1925, **19**, 1115—1127).—Lactic acid is present in small amount in "resting" plain muscle (0·03—0·08%; the larger amounts in mammalian tissue). It increases when the muscle is made to contract, but the maximum is never so high as in skeletal muscle from the same species. Treatment which in skeletal muscle produces rigor raises the lactic acid content in plain muscle. When placed in solutions of phosphates, the lactic acid production is much greater when the p_H of the solution is 9 than when it is 4·5. The rate of lactic acid formation in disodium hydrogen phosphate solutions is accelerated by the presence of arsenates. The rate of acid production is much the same in 0·8% sodium hydrogen carbonate solution as in disodium hydrogen phosphate solution. Lactic acid rapidly accumulates in plain muscle under anaërobic conditions, but scarcely at all in the presence of oxygen. The glycogen content of plain muscle is small. The lactacidogen content of the muscle of the tortoise stomach (autumn) corresponds with about 0·15% of lactic acid.
S. S. ZILVA.

Liver function. I. Determination of bile acids and pigments in duodenal contents. C. W. MCCLURE, E. VANCE, and M. C. GREENE (Boston Med. Surg. J., 1925, **192**, 431—433).—The bile acids are determined colorimetrically by means of furfuraldehyde and sulphuric acid, and the pigments similarly with sodium sulphite and glacial acetic acid. Optimal conditions are given, but neither reaction is specific. CHEMICAL ABSTRACTS.

Elementary composition of hair. Z. STARY (Z. physiol. Chem., 1925, **150**, 202—204).—Human hair which has been previously washed and extracted with alcohol and ether, then treated with pepsin and trypsin to remove any traces of hydrolysable protein, washed and dried, has a very constant carbon, hydrogen, and nitrogen content. There is little difference between men's and women's hair. Average figures are C 50·3, H 6·6, N 16·3%. H. D. KAY.

Keratin substances of human skin. H. MENSCHEL (Arch. exp. Path. Pharm., 1925, **110**, 1—45).—Human nail swells almost equally (25—35%) in water and various acids, but alkalis, especially potassium hydroxide, and the alkali hydrogen sulphides, produce a much increased swelling. Ammonium and calcium hydroxides have only a feeble effect. Similarly, hair is rendered more extensible and less tenacious by the action of alkalis, due to the swelling of the keratin constituents. If the alkali is washed out, the hair returns almost to its original condition. Tanning agents, especially formaldehyde, render hair brittle.

In alkalis skin loses its elasticity, due to the swelling of the keratin constituents. Acids, however, which have little or no action on the keratin constituents, cause rapid swelling and peptisation of the albumoses contained in the reticular layer, and the skin assumes a glassy appearance. H. P. MARKS.

I. Colour reaction for disulphides. II. Sulphydryl reaction of skin. E. WALKER (Biochem. J., 1925, **19**, 1082—1084, 1085—1087).—I. To the solution to be tested a few drops of 5% aqueous sodium nitroprusside are added, followed by 3—5 drops of 10% aqueous potassium cyanide. If the disulphide is present in high concentration, the colour, a deep magenta, develops immediately; if present in low concentration, there is a delay of a few minutes. The concentration 1 : 10000 is about the limit of sensitivity of the reaction. Sulphydryl compounds give an instantaneous colour. A few illustrations of the applicability of the colour test are given.

II. No evidence could be obtained that the nitroprusside reaction of skin is due to the presence of glutathione (A., 1925, i, 180). It is suggested that the reaction is due to the presence of a substance similar to or identical with the thermostable sulphydryl constituent of muscle. The skin rapidly loses its sulphydryl reaction under the influence of allyl thiocarbimide. S. S. ZILVA.

Spermine. H. W. DUDLEY and O. ROSENHEIM (Biochem. J., 1925, **19**, 1034—1036).—Spermine is identical with musculamine, neuridine, and gerontine, bases which have been obtained from calf's muscle, human brain, and dog's liver, respectively, by earlier workers. The yields of spermine obtained from various animal tissues and yeast are tabulated. It is absent from bull's semen, ox blood, cow's milk, and hen's egg. Spermine cannot replace vitamin-*B* or the

antincuritic vitamin (as tested on pigeons). Spermine phosphate does not function as a co-enzyme in alcoholic fermentation. S. S. ZILVA.

Oils from sharks and rays. A. ROGERS.—See B., 1926, 19.

Solubility of tertiary calcium phosphate in cerebrospinal fluid. L. E. HOLT, jun. [with I. GITTLEMAN] (J. Biol. Chem., 1925, **66**, 23—28; cf. A., 1925, i, 1209).—The reduction in the calcium and phosphorus concentration in human cerebrospinal fluid brought about by prolonged shaking in contact with tertiary calcium phosphate indicates that, as in the case of blood-serum, the fluid is normally supersaturated with this salt to the extent of at least 200%. The true solubility product in cerebrospinal fluid is less than 10^{-28}, being thus much lower than in serum. It is suggested that the lack of agreement between the observed ratios of the diffusible ions of the serum to those of the cerebrospinal fluid with the ratios demanded by the Donnan equilibrium may be due to the fact that the latter theory is concerned, not with stoicheiometric ionic concentrations, but with ionic activities, and that in serum, owing to the relatively high concentration of multivalent protein ions, the activity coefficients, particularly of the multivalent inorganic ions, will be much reduced.
C. R. HARINGTON.

Properties and origin of lymph. XI. Influence of specific lymphagogues on the activity of the liver, detected by acetone formation. Y. ABE (Biochem. Z., 1925, **165**, 312—322).—When the surviving liver of rats and guinea-pigs is perfused with blood containing butyric acid, addition of lymphagogues (leech extract, peptone, extract of crab's muscle) causes considerable increase in acetone formation. This favours the view that lymphagogues stimulate the activity of the liver cells.
P. W. CLUTTERBUCK.

Influence of certain salts on the yield and composition of milk. A. T. R. MATTICK and N. C. WRIGHT (Biochem. J., 1925, **19**, 915—920).—Calcium chloride, ammonium chloride, sodium hydrogen carbonate, or disodium hydrogen phosphate when administered to cows does not alter the plasma calcium content, nor does such treatment alter the composition of the milk. The administration of ammonium chloride (16 oz.) causes an almost complete suppression of the milk yield, accompanied in its later stages by a temporary increase in the concentration of the constituents of the milk. S. S. ZILVA.

Variation of the amount of nitrogenous material, particularly urea, in the saliva. A. DESGREZ, R. MOOG, and (MME.) L. GABRIEL (Compt. rend., 1925, **181**, 755—757).—Normal saliva contains from 59 to 197 mg. of urea per litre. When the secretion is stimulated, mechanically or chemically (citric acid), the urea content varies from 23 to 164 mg./litre, whilst with people suffering from uræmia the stimulated secretion contains from 330 to 1140 mg./litre. In uræmia, the ratio of nitrogen in the form of urea to total nitrogen in the saliva is about 0·27, compared with 0·16 for normal people. In all cases, the urea is destroyed by enzymic action if the saliva is kept.
W. HUME-ROTHERY.

Menotoxin. K. KLAUS (Biochem. Z., 1925, **163**, 41—50).—Choline in sweat is not derived from the breakdown of phosphatides in the glands, but is secreted in the free form. On the first day of menstruation and on the preceding day women excrete nearly fifty times as much choline in the sweat than in the intermediate period. E. C. SMITH.

Presence of rare elements in the food and excretions of man. R. BERG (Biochem. Z., 1925, **165**, 461—462).—Foodstuffs often contain traces of manganese, zinc, nickel, cobalt, copper, and lead. Silicic and titanic acids are always detectable in urine.
P. W. CLUTTERBUCK.

Arsenic content of urine. I and II. I. BANG (Biochem. Z., 1925, **165**, 364—376, 377—410).—I. A modification of the author's method (this vol., 39) is found to be satisfactory for the determination of arsenic in urine, the limits being $\pm$0·05 mg. As per litre. The detection by the method of a small amount of arsenic in normal urine is not due to the presence of traces of substances which by using up iodine titrate as arsenic, since Ramberg's micro-method gives the same results. In order to decide whether arsenic is lost during the determination as volatile organic compounds, known amounts of cacodylic acid, atoxyl, and salvarsan were determined both in aqueous solution and in urine. Providing the salvarsan is dried to constant weight, all three substances were determined with the same accuracy as inorganic arsenic. Arsenic in the urine of a large number of hospital patients on the same diet was determined. In 16% of the cases, no arsenic was present; in 43%, 0·01—0·06 mg. As per litre; in 33%, 0·07—0·20; in 8%, 0·21—0·69. In four cases, the physiological variation in urinary arsenic over periods of 4—6 days was from 0 to 0·23 mg. As per litre.

II. Existing knowledge of the arsenic content of a large number of food materials is summarised and greatly amplified by further determination. Arsenic administered by mouth to man and animals quickly appears in the urine and to a greater extent than was previously supposed, the amount excreted varying directly with the dose. The rate at which it leaves the organism varies greatly in different individuals. A considerable amount of arsenic is retained and appears to be absorbed by various organs, chiefly the liver and kidney, and is then very slowly excreted. In acute poisoning, the liver, intestine, and kidney are chiefly affected, but in chronic poisoning chiefly the nervous system. The arsenic content of bone was investigated in one case only, but the quantity found was much greater than expected.
P. W. CLUTTERBUCK.

Concentration of chlorides in glomerular urine of frogs. J. T. WEARN and A. N. RICHARDS (J. Biol. Chem., 1925, **66**, 247—273).—By means of the nephelometric method of Richards and Wells (A., 1904, ii, 287), the concentration of chlorides has been determined in the fluid withdrawn directly from the Bowman capsule of the frog's kidney (cf. Amer. J.

Physiol., 1924, **71**, 209). Amounts of chlorine of the order of 0·005 mg. could be determined with an average error of ±2·3%. Comparison of the figures so obtained with simultaneous determinations of the chlorides in the bladder urine indicates that the concentration of the latter is always much lower than that in the glomerular fluid; this affords direct evidence that chlorides are reabsorbed during passage of the urine through the renal tubules; this condition obtains even when the concentration of chlorides in the blood-plasma has been doubled by injection of sodium chloride. The chloride concentration in the glomerular fluid was constantly higher than that in the blood-plasma; the glomerular fluid is therefore not derived from the blood-plasma by a simple process of filtration; it is pointed out that the Donnan equilibrium must play a part in the distribution of ions between plasma and glomerular fluid, and this may account in part for the observed differences.

C. R. HARINGTON.

Melanogen. P. SACCARDI (Atti R. Accad. Lincei, 1925, [vi], **2**, 346—349).—An unstable melanogen has been isolated, by means of its diazo-derivative, from the melanotic urine of rabbits injected with pyrrole. The properties of the melanogen diazo-compound are quite different from those of bisdiazopyrrole, indicating that the pyrrole does not pass unchanged into the urine. The chemical behaviour of the melanogen suggests that it is possibly a polymerised hydroxy-derivative of pyrrole, the oxidation of the pyrrole occurring in the system, and not as a result of the action of enzymes in the urine.

F. G. TRYHORN.

Production of volatile fatty acids in the intestinal tract of calves fed whole milk or cereal gruel. L. C. NORRIS (Cornell Agric. Exp. Sta. Mem., 1925, **90**, 1—32).—Acetic and propionic acids in approximately equal proportions, and very slight traces of butyric acid, were found in the fæces of growing calves; ethyl alcohol, and occasional small quantities of propyl alcohol, were also present. A much greater excretion of acid was observed with the cereal gruel diet than with whole milk.

CHEMICAL ABSTRACTS.

Influence of ethyl ι-hydroxystearate on acidosis. R. WEST and E. M. BENEDICT (J. Biol. Chem., 1925, **66**, 139—144).—The substitution of ethyl ι-hydroxystearate for an equivalent amount of fat, in the diet of normal individuals suffering from artificial fat acidosis, caused a marked fall in the excretion of acetone. This may indicate that the physiological oxidation of this compound involves the intermediate formation of a fatty acid with an odd number of carbon atoms, which, in its further oxidation, would not give rise to acetoacetic acid.

C. R. HARINGTON.

Amyloid. F. PAVLICA (Biol. Listy, 1924, **10**, 256—264; from Chem. Zentr., 1925, II, 318).—The origin of amyloid is attributed to proteins which occur in chronic suppuration, and to the accumulation of sulphuric acid, which appears to be the actual cause of the pathological condition, together with the inability of the tissue to eliminate the accumulated sulphur.

G. W. ROBINSON.

Iron in anæmia. C. S. WILLIAMSON and H. N. ETS (Arch. Intern. Med., 1925, **36**, 333—354).—In the case of rats and dogs, iron lactate given by the mouth, or iron citrate given subcutaneously or intravenously, neither increased the hæmoglobin content of the blood above the normal nor accelerated the return to the normal of artificially reduced hæmoglobin values.

CHEMICAL ABSTRACTS.

Naturally-occurring porphyrins. XVIII. Chemical findings in a case of porphyrinuria. H. FISCHER, H. HILMER, F. LINDER, and B. PÜTZER (Z. physiol. Chem., 1925, **150**, 44—101).—A *post-mortem* examination of a congenital porphyrinic was made, and porphyrins were found in most of the organs. Uroporphyrin was isolated with some difficulty from the bones. In the bone marrow, both copro- and uro-porphyrin were found, the former in larger quantity than the latter, but in the long bones freed from the marrow no definite evidence of the presence of coproporphyrin was obtained. Copper salts of porphyrins were found in various parts of the body. The bile contained large amounts of coproporphyrin. In the blood was found coproporphyrin, but no uroporphyrin. The intestine contained no uroporphyrin, but large quantities of coproporphyrin, which agrees with the *pre-mortem* findings of no uroporphyrin in the fæces. Along with coproporphyrin the spleen contained two other pigments, possibly hitherto undescribed, one of which is volatile. Uroporphyrin was found also in the liver and kidney. The musculature contained pigments in small amounts only. These consisted of coproporphyrin and Kämmerer's porphyrin, but no coprohæmin. The bone marrow appears to be the principal seat of porphyrin formation. Probably normal hæmin is here transformed into Kämmerer's porphyrin, and then into coproporphyrin and uroporphyrin. The relation of these new findings to the physiology and pathology of blood pigments is discussed.

H. D. KAY.

Isolation of methylated guanidines from urine in parathyroid tetany. J. KÜHNAU (Arch. exp. Path. Pharm., 1925, **110**, 76—88).—In two cases of parathyroid tetany, a much increased excretion of methylated guanidines was observed. They consisted of methyl- and dimethyl-guanidines and when injected into mice produced typical fatal symptoms.

H. P. MARKS.

Wild silk-moth, *Dictyoploca japonica*, Moore. I. Chemical development in growth. O. SHINODA (Mem. Coll. Sci. Kyōtō, 1925, *A*, **9**, 225—235).—Caterpillars (*Dictyoploca japonica*) fed on chestnut leaves have a constant chemical composition until becoming pupæ, when the ash content, moisture content, chitin content, and aqueous extract decrease sharply and the total nitrogen content and ether extract increase. When the pupæ become moths the ether extract decreases, whilst the aqueous extract increases.

L. F. HEWITT.

Metamorphosis of insects. II. Apparatus for investigation of the gaseous metabolism of small animals. J. HELLER (Biochem. Z., 1925, **165**, 411—419).—The apparatus is described and used for determination of the gaseous metabolism of pupating caterpillars. The oxygen utilisation is, during the restless stage, about 60 c.c./24 hrs., during the next three days falling to 40 c.c., and, after movement stops, decreasing fairly rapidly to 10 c.c.

P. W. CLUTTERBUCK.

Effect of addition of ternary foodstuffs to milk on nitrogen retention during growth. E. F. TERROINE and A. M. MENDLER (Compt. rend., 1925, **181**, 1176—1179).—Young pigs fed on whole milk show a higher proportional nitrogen retention than those fed on skimmed milk, those fed on whole milk with added cream higher still, and those fed on whole milk with added carbohydrates the highest of all. These effects are intensified if the diets be continued for several weeks. L. F. HEWITT.

Nutritive value of wheat. I. Effect of variation of sodium in a wheat ration. G. A. OLSON and J. L. ST. JOHN (J. Agric. Res., 1925, **31**, 365—375).—Normal growth and reproduction were not obtained when rats were fed on a basal diet of 100 g. of ground wheat, 10 g. of wheat gluten, and 5 g. of butter fat. The addition of sodium hydrogen carbonate to this diet had its greatest effect when the percentage of sodium in the ration was raised to 0·53; percentages of sodium in the diet greater than 0·785 were detrimental. H. J. CHANNON.

Rôle of cystine and mineral elements in nutrition. E. WOODS (J. Biol. Chem., 1925, **66**, 57—61).—Rats which have been stunted in growth by a deficiency of cystine in their food recover completely on restoration to a normal diet. Whereas whole-milk powder alone is not an adequate diet for rats over long periods, it can be made so by the addition of whole wheat, probably owing to the mineral constituents of the latter.

C. R. HARINGTON.

Effect of zirconium, titanium, and manganese salts on nutrition. C. RICHET, GARDNER, and GOODBODY (Compt. rend., 1925, **181**, 1105—1106).—Administration of daily doses of 0·1 g. per kg. of zirconium or titanium citrates has no physiological effects on dogs. The same daily dose of manganese citrate has a slightly harmful effect, and the same dose every fourth day a slightly beneficial effect on the nutrition of dogs. L. F. HEWITT.

Nitrogen and mineral balances in infants receiving cow's or goat's milk. A. L. DANIELS and G. STEARNS (Amer. J. Dis. Children, 1925, **20**, 359—366).—Goat's milk leads to a larger urinary excretion of phosphate than cow's milk, and to a considerably smaller retention of nitrogen.

CHEMICAL ABSTRACTS.

Metabolism of the suckling. J. ELLINGHAUS, E. MÜLLER, and H. STEUDEL (Z. physiol. Chem., 1925, **150**, 133—148).—The nitrogen metabolism of three healthy human infants of about the same age and weight fed for six-day periods on (1) human milk, (2) cow's milk mixture, (3) human milk, has been followed using Folin's methods, or modifications of these, both for the analysis of the ingesta and of the excreta. The results agree well with those of older investigations using macro-methods. The relatively large excretion of uric acid by infants may be correlated with the relatively larger amount and greater activity of their glandular tissue as compared with adults. Infants also excrete more ammonia nitrogen per kg. than do adults, thereby conserving the fixed base which is necessary for growth. It is concluded that six days is an insufficiently long time to leave between the experimental periods. The metabolism of infants and that of adults is not widely dissimilar considering the amounts and activities of corresponding tissues.

H. D. KAY.

Effect of mineral content of food on fat content of body. K. ONOHARA (Biochem. Z., 1925, **163**, 61—66).—Administration to rats of 0·1 g. of calcium chloride, 0·2 g. of magnesium chloride, or 0·2 g. of sodium chloride *per diem* for 3 weeks results in an increase of body fat of approximately 1% compared with animals not so treated. Only two out of five animals survived treatment with 0·05 g. of potassium chloride *per diem* for the same period.

E. C. SMITH.

Soft pork. I. Formation of fat in the pig. N. R. ELLIS and O. G. HANKINS (J. Biol. Chem., 1925, **66**, 101—122).—The hardening of the fat of pigs as they reach maturity involves a rise in m. p. and a decrease in refractive index and iodine number, the latter being chiefly due to a decrease in the linoleic acid, since the percentage of oleic acid remains almost constant. The general effect is due to an increase in the rate of deposition of fat, which means (with a diet moderately low in fat) that progressively more of the deposited fat is synthesised in the body and less derived directly from the fat of the food.

C. R. HARINGTON.

Intermediate carbohydrate metabolism. X. Glycolysis. T. BRUGSCH and H. HORSTERS (Biochem. Z., 1925, **164**, 191—198).—The authors are unable to detect any glycolytic enzyme in the washed or unwashed dried liver or muscle preparations, and the liver and muscle glycogenase of these preparations is not inhibited by insulin. P. W. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XI. The hexosediphosphatase of muscle and liver and the product of fission, hexosemonophosphoric acid. T. BRUGSCH, M. CAHEN, and H. HORSTERS (Biochem. Z., 1925, **164**, 199—206).—Dried preparations of muscle and liver of rabbits and dogs contain a hexosediphosphatase which converts hexosediphosphoric acid into a dextrorotatory hexosemonophosphoric acid differing from that obtained from yeast by Robison and possessing a different rotation from that of Neuberg's acid. This acid gives a strong Selivanov reaction and may be determined by the method of Pinoff and Gude (A., 1914, ii, 499). Fresh muscle contains also an α-hexosediphosphatase which converts the hexosediphosphoric acid into phosphoric acid and lævulose, the latter being used for glycogen synthesis. Fresh muscle also contains a

hexosemonophosphatase which converts the hexosemonophosphoric acid into phosphoric acid and a *d*-hexose which undergoes glycolysis, giving lactic acid. P. W. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XIII. Formation of lactic acid in the liver from acetic, tartaric, malonic, and succinic acids. S. NARITA (Biochem. Z., 1925, **164**, 247—256).—Acetic acid does not give rise to lactic acid in the liver either under normal conditions or in pancreatic diabetes, whereas malonic, *l*-tartaric, and succinic acids give lactic acid under both conditions. P. C. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XIV. Action of insulin on muscle dehydrogenases. S. NARITA (Biochem. Z., 1925, **164**, 257—270).—Insulin is an activator of lactic acid dehydrogenase of washed muscle. The washed muscle of animals treated *in vivo* with insulin shows a dehydrogenase action in presence of galactose, dextrose, lævulose, *d*-fructose-diphosphoric acid, and benzaldehyde, but it is probable that these substances act rather as substrata than as activators. P. W. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XV. Muscle dehydrogenases. Y. HARADA (Biochem. Z., 1925, **164**, 271—278).—Lactic acid dehydrogenase of fresh muscle has an optimum action in a concentration of $M/10$—$M/2$-lactate, and washed muscle (poor in coenzyme) of M—$2M$. The optimum for succinic acid dehydrogenase is M—$M/10$, and is not influenced by washing or by higher concentrations of succinic acid. Malic acid inhibits lactic acid dehydrogenase. Dried muscle contains both dehydrogenases, the succinic acid oxydase being more active. Since malic acid inhibits lactic acid dehydrogenase also in dried muscle, it is concluded that malic acid is probably not decarboxylated to lactic acid.
P. W. CLUTTERBUCK.

Physiology of glands. LXXXIII. Formation of carbohydrates from fat and its dependence on the liver. V. CALVO-CRIADO (Biochem. Z., 1925, **164**, 76—96).—Addition of fat to the food of rats, which had been rendered carbohydrate-free by feeding for several days on flesh, Witte's peptone, and thyroid tablets with subsequent injection of phloridzin, causes an increased urinary dextrose excretion, the urinary nitrogen remaining constant or even diminishing, whilst the D/N ratio greatly increased. The sugar thus appearing must have been formed from fat. By the addition of a trace of sucrose to the food, the excretion of dextrose is still further increased, quite out of proportion to the amount added. P. W. CLUTTERBUCK.

Condensation products of ethyl acetoacetate. II. Oxidation and possible relationship to antiketogenesis in the animal body. E. S. WEST (J. Biol. Chem., 1925, **66**, 63—75).—Condensation products of ethyl acetoacetate with aldehydes (*e.g.*, ethyl benzylidenebisacetoacetate) are much more readily oxidised *in vitro* than ethyl acetoacetate itself; dextrose condenses with ethyl acetoacetate in presence of zinc chloride to give a compound which reduces Fehling's solution in the cold. These results support the theory of Shaffer and Friedemann (A., 1924, i, 1369) regarding the mechanism of the antiketolytic action of dextrose. It is shown that the facts that in the oxidation of acetoacetic acid the α-carbon atom is the point of attack, and that the substitution of a more strongly positive group for one of the hydrogen atoms attached to this carbon yields a more readily oxidisable compound, are in accordance with the electronic relationships involved.
C. R. HARINGTON.

Effect of various carbohydrates on the ketosis of starvation in human subjects. M. W. GOLDBLATT (Biochem. J., 1925, **19**, 948—957).—When administered during starvation ketosis, dextrose, lævulose, sucrose, and maltose have an antiketogenetic action, whilst galactose, mannose, lactose, and glycerol are inert. The rise in respiratory quotient following the injection of a sugar has been shown to occur some time after the maximum blood-sugar is reached. The maximum antiketogenetic action of the sugar, as evidenced by a negative nitroprusside reaction in the urine, has been shown to occur during the period of fall in blood-sugar. Evidence of some deficiency in storage power and oxidation of carbohydrates after starvation is produced. S. S. ZILVA.

Distribution of phosphorus and fat in the resting and fatigued muscle of the cat; partition of phosphorus in the blood. D. P. CUTHBERTSON (Biochem. J., 1925, **19**, 896—910).—In the fatigued muscle there was practically no change in either the total P_2O_5 or the total amount of inorganic plus lactacidogen P_2O_5. There was, however, an increase in the inorganic P_2O_5 of the stimulated muscle, the maximum increase observed being 34%. A decrease in the inorganic P_2O_5 of resting muscles remaining *in situ* during the stimulation (maximum noted was 11%) was also recorded. Little or no effect on the organic acid-soluble P_2O_5 other than lactacidogen was observed. A consistent but small increase (1—2%) in the total acid-soluble fraction was established. There was no alteration in the phosphatide P_2O_5. The effect of fatigue on the phosphorus compounds of the blood was as follows. There was an increase in the inorganic P_2O_5 (100% after 50 minutes' stimulation), in the total acid-soluble P_2O_5 (12—37%), and a decrease in the organic acid-soluble P_2O_5 (17—36%). There was an increase of 4—5% in the water content after stimulation of a muscle for 45 min. The phosphorus-containing proteins of skeletal muscle belong to the nucleoprotein group.
S. S. ZILVA.

Metabolism of arginine and histidine. II. Arginine and histidine as precursors of purines. C. P. STEWART (Biochem. J., 1925, **19**, 1101—1110).—On a diet deficient in histidine and arginine, young rats lose weight, and their allantoin excretion, but not the total nitrogen excretion, falls almost to half the normal value. Restoration of histidine to the diet is followed by resumption of growth and by increased allantoin excretion. The restoration of arginine to

the deficient is, however, not followed either by appreciable growth or by increased allantoin excretion, but by a cessation of both the fall in weight and the allantoin excretion. It is concluded that histidine functions as a precursor of purines in the animal body and that arginine and histidine are not completely interchangeable. Adult rats can live for 28 days without loss of weight or decrease in the allantoin excretion on a diet containing only traces of histidine and arginine. S. S. ZILVA.

Fate in the animal body of phenylsuccinic acid and β-phenylhexoic acid. P. W. CLUTTERBUCK and H. S. RAPER (Biochem. J., 1925, **19**, 911—914).—β-Phenylhexoic acid administered subcutaneously in the dog as the sodium salt is excreted partly unchanged and partly as a glycuronate; 45% of the acid is recovered in this way. No phenylsuccinic acid can be detected as an oxidation product. As it is also shown that phenylsuccinic acid is not easily oxidised in the body, it is concluded that β-phenylhexoic acid does not undergo γ-oxidation. S. S. ZILVA.

Iodine metabolism. W. H. VEIL and A. STURM (Deut. Arch. Klin. Med., 1925, **147**, 166—223; from Chem. Zentr., 1925, II, 1187—1188).—The average iodine content in human blood in late summer and autumn is 0·0128 mg.%, and in winter 0·0083 mg.%. The organic iodine is 65% of the total. The partition of iodine between plasma and corpuscles corresponds approximately with their relative volumes. The iodine of the blood originates principally in the thyroid. Oral administration of 0·5 g. of potassium iodide produced very little effect on the iodine content of the blood after 24 hrs. Up to 68% of the iodine was recovered in the urine. In one case, a decrease in organic iodine in blood occurred after administration of iodine in inorganic form. Resorption of iodine after administration of thyreoidin is similar to that of potassium iodide, except that, owing to digestion, part of the organic iodine is changed to inorganic forms. Absorption takes place partly as organic iodine. Elimination of iodine in the urine takes place more slowly than in the case of administration of potassium iodide. In the urine containing the greatest amount of iodine, 33% of the iodine was in organic form. In untreated goitre, hyperiodæmia was observed. During menstruation, pregnancy, and childbed, marked hyperiodæmia was observed. Stimulation of the sympathic system by means of adrenaline resulted in four cases in a temporary hyperiodæmia followed by hypoiodæmia. In fever, there was no hyperiodæmia corresponding with the sympathicotonic stage, but an actual hypoiodæmia, due probably to increased demand by the tissues and increased excretion of iodine in the urine. G. W. ROBINSON.

Metabolism under reduced atmospheric pressure. II. Behaviour of blood and of liver. W. LAUBENDER (Biochem. Z., 1925, **165**, 427—442).—With normal guinea-pigs, starvation for 48 hrs. and continued subnormal feeding lead to an increase of the residual nitrogen of the liver, the peptone-nitrogen being greatly increased, the urea- and amino-nitrogen only slightly. The residual-nitrogen values are not altered by an oxygen-lack corresponding with a pressure of 430—380 mm., but are increased under pressures of 330—230 mm. up to 15·9—18·8% and in starving animals up to 12·1—14·5%. This increase is due chiefly to an increase of amino- and urea-nitrogen. During oxygen-lack only slight changes occur in sugar and residual nitrogen content of blood. P. W. CLUTTERBUCK.

Effect of radium on metabolism. J. ROSENBLOOM (J. Metabol. Res., 1923, **4**, 75—88).—Intravenous injection of 0·1 mg. of radium in dogs produced an increase in the nitrogen, total sulphur, and neutral sulphur excretion, but not in that of creatinine and uric acid. Local application in carcinoma produced retention of nitrogen, sulphur, calcium, magnesium, and phosphorus. The analytical picture of the urine was normal. CHEMICAL ABSTRACTS.

Biological action of *X*-rays of different wave-lengths. A. DAUVILLIER (Compt. rend., 1925, **181**, 1130—1132).—A criticism of the conclusions of Dognon (Thesis; Strasbourg, 1925), who examined the action of rays of wave-lengths 0·22, 0·70, and 1·54 Å. on the eggs of *Ascaris*, and deduced that the absorption of equal amounts of energy resulted in very different biological action. It is shown, on the contrary, that the results indicate equality of biological action for equal energy absorbed, a conclusion supported by a study of the literature, and from general considerations. S. I. LEVY.

Absorption of electrolytes in small intestine. Z. MALKIEVICZ (Bull. Intern. Acad. Polonaise, 1925, **B**, 259—275).—The absorption of sodium, potassium, and calcium chlorides was studied by introducing isotonic solutions of these salts (0·78% NaCl) into the small intestine of a dog through fistulæ, and later measuring and analysing the unabsorbed residue. The sodium chloride (and calcium chloride) solution is rapidly absorbed, but at the same time potassium and calcium ions pass into the intestine, so that the unabsorbed residue contains all three ions. In the case of potassium chloride, the passage of sodium into the intestine, accompanying the absorption of the potassium, is so considerable that the total volume of fluid in the intestine may actually increase. Ringer's solution and a mixture of the potassium and calcium chloride solutions are uniformly absorbed, but in a mixture of the sodium and potassium chloride solutions, whilst the potassium is rapidly absorbed, sodium either passes into the intestine, or is only slowly absorbed. In general, absorption is accompanied by a readjustment in the concentrations of the ions, tending to bring them into closer conformity with the concentrations in the blood. In all cases, there is a passage of carbonate ions into the intestine, with consequent increase in alkalinity. H. P. MARKS.

Influence of pregnancy on lipins of blood. M. TYLER and F. P. UNDERHILL (J. Biol. Chem., 1925, **66**, 1—14).—During pregnancy, the total cholesterol and lecithin of the whole blood progressively increase in amount from the third month until term; the increase is maintained during the first two weeks *post partum*. The proportion of lecithin to cholesterol is not changed from the normal, but cholesterol esters

form a higher proportion of the total cholesterol than in non-pregnant women. C. R. HARINGTON.

Action of choline and of a choline ester on the blood pressure after removal of the suprarenal glands. S. GLAUBACH and E. P. PICK (Arch. exp. Path. Pharm., 1925, **110**, 212—224).—"Cholazyl" (a preparation described as chloroacetylcholine chloride urea) is ten times as effective in reducing the blood pressure in decerebrate cats as is choline. After atropine, both drugs raise the blood pressure, cholazyl being some five times the more active. Extirpation of the suprarenal glands weakens or destroys the latter effect of the ester, but not of choline.
R. K. CANNAN.

Diuretic action of theobromine derivatives. H. VIETH and E. LEUBE (Biochem. Z., 1925, **163**, 13—26).—The diuretic action of theobromine and theophylline substituted in the 1-position by acyl, alkyl, and carbalkoxyl groups has been investigated. Of these only acetyltheobromine shows a greater diuretic power than theobromine. The diuretic action of purine derivatives is increased by simultaneous administration of salicylates, more particularly of calcium salicylate, but these cause increased heart-rate, whereas theobromine has no action on the heart. Cinnamoyl-, carbomethoxy-, and nitro-theobromine are irritant and cause albuminuria, although the latter is a very active diuretic.
E. C. SMITH.

Toxicity of hexosediphosphoric acid. N. ABELLES (Biochem. Z., 1925, **163**, 226—229).—Intraperitoneal injection of 0·46 g. of hexosediphosphoric acid as the sodium salt proves fatal to 100-g. rats. The symptoms are those of phosphate poisoning. The toxicity of hexosediphosphoric acid is to that of phosphoric acid (referred to P_2O_5) as 2 : 3, but there is no evidence of detoxication of phosphoric acid in the organism *via* hexosediphosphoric acid.
E. C. SMITH.

Toxicity of arsenic under reduced atmospheric pressure. E. ISELIN (Arch. exp. Path. Pharm., 1925, **110**, 66—75).—The lethal dose for rabbits of atoxyl and of sodium cacodylate is lowered when the animals are kept under reduced pressure. This is not due to increased retention of the arsenic. Methods of determining arsenic in urine, fæces, and liver are described. H. P. MARKS.

Nitrogen metabolism in lead poisoning. A. TSCHERKESS (Arch. exp. Path. Pharm., 1925, **110**, 174—197).—In sub-acute poisoning there is an intensified nitrogen metabolism. In chronic poisoning two periods may be distinguished. In the first, there is increased nitrogen metabolism. This is followed by a decrease and general distortion of the protein metabolism, suggesting an attempted compensation for an impaired function of the oxidation mechanisms by diminished intake and metabolism.
R. K. CANNAN.

Cholesterol in lead poisoning. KRETSCHMER and FRIEDER (Biochem. Z., 1925, **164**, 44—46).—The cholesterol content of the serum is reduced and that of the whole blood is increased by lead poisoning. P. W. CLUTTERBUCK.

Transmineralisation in poisoning by mercuric chloride. H. STRAUB and K. GOLLWITZER-MEIER (Deut. med. Woch., 1925, **51**, 642—645; from Chem. Zentr., 1925, II, 323).—In the anuric stage of mercuric chloride poisoning there is an increase in the content of nitrogen and salts in the blood corresponding to a retention of these constituents. During recovery, *i.e.*, when the kidneys are again functioning, the nitrogen and sodium chloride balances are markedly negative. The elimination of the debris of toxically degraded tissues and the migration of sodium, chloride, and hydrogen carbonate ions (transmineralisation) from the blood to the tissue in the anuric stage and to the urine in the polyuric stage is not so much the consequence of the pathological condition of the kidneys as of general protoplasmic injury.
G. W. ROBINSON.

Intravenous silver therapy. VI. Bactericidal action of injections of ionised silver salts. K. VON NEERGAARD (Arch. exp. Path. Pharm., 1925, **110**, 103—120; cf. A., 1925, i, 1212, 1357; this vol., 92).—A discussion of the therapeutic action of colloidal and ionised silver preparations. The maximum silver concentration attainable in the body-fluids by administration of ionisable salts is more than sufficient for bactericidal purposes, but the bactericidal dose lies very close to the tolerance limit of the animal. The latter may be raised slightly by repeated injections, whilst a combination of silver with certain toxic dyes may achieve some diminution of the former. The doses of silver preparations normally employed are too small to be of therapeutic value. H. P. MARKS.

[Non-]detoxicating effect of dextrose in guanidine poisoning. J. BAKUCZ (Arch. exp. Path. Pharm., 1925, **110**, 121—128).—Although the convulsive symptoms following an injection of guanidine are accompanied by a fall in the blood-sugar, they are not relieved by administration of dextrose. H. P. MARKS.

Metabolism of the liver in chloroform and phosphorus poisoning. R. HURTHLE (Arch. exp. Path. Pharm., 1925, **110**, 153—173).—The accumulation of acetoacetic acid in the perfusion of the rat's liver with this substance was greater in the case of the poisoned animal than in the normal, and was accompanied by an increase in β-hydroxybutyric acid. Both in the normal and in the poisoned liver, the addition of acetoacetic acid to the perfusate led to a considerable production of β-hydroxybutyric acid, whilst addition of the latter gave similar yields of acetoacetic acid. The poisoning would seem to be associated with a diminished capacity to decompose acetoacetic acid together with a possible increase in the metabolism of the unknown precursors of β-hydroxybutyric acid. R. K. CANNAN.

Narcotic and toxic effects of halogen derivatives of hydrocarbons. J. MÜLLER.—See B., 1926, 75.

Influence of narcotics on surface tension. E. CZANIK (Biochem. Z., 1925, **165**, 443—460).—The surface tension of aqueous solutions against air,

paraffin oil, or nitrobenzene is decreased by a number of alkaloids (both stimulating and inhibiting), chloral hydrate, phenol, etc., the amount of decrease increasing with increasing concentration and being much greater against paraffin oil and nitrobenzene than against air. The various pharmacological actions of these substances cannot therefore be attributed simply to an effect on surface tension.

P. W. CLUTTERBUCK.

Intoxication by sulphonal. Localisation of the sulphonal and hæmatoporphyrin. R. FABRE and H. SIMONNET (Bull. Soc. Chim. biol., 1925, **7**, 1129—1130).—A rabbit which had received 1 g. of sulphonal per day for 12 days was killed, and the following quantities of sulphonal were recovered from the various organs: brain and cord, 0·057 g.; liver, 0·043 g.; kidneys, 0·018 g.; muscle (24 g.), 0·015 g.; blood (7·5 g.), 0·009 g.; spleen, 0·007 g. Hæmatoporphyrin was definitely detected only in the bile, the urine, and, in very small amounts, in the blood.

C. P. STEWART.

Comparative actions of several local anæsthetics on the heart and intestine. F. LASCH (Arch. exp. Path. Pharm., 1925, **110**, 142—152).—In a series of six local anæsthetics (cocaine and substitutes) no relation was found between the activity on the frog's skin, the isolated frog's heart, and the surviving rat's intestine.

R. K. CANNAN.

Influence of lecithins on the action of drugs. VI. D. M. LAWROW (Bioehem. Z., 1925, **161**, 257—274).—If lecithins be injected subcutaneously or intraperitoneally into dogs or rabbits, daily, during a week before an injection of morphia, the effect of the latter is distinctly diminished. This diminution is also evident if the lecithin be injected just after the dose of morphia.

H. I. COOMBS.

Is enzyme action colloido-chemical? (Investigation with pepsin.) H. W. VAN URK (Biochem. Z., 1925, **165**, 358—363).—The changes of viscosity of pepsin solutions with changes of concentration of hydrochloric acid and of various salts may be explained in terms of changes of dissociation. No viscosity difference is caused by anions up to a salt concentration of $M/2$.

P. W. CLUTTERBUCK.

Kinetics of enzyme action. G. E. BRIGGS (Biochem. J., 1925, **19**, 1037—1038).—Theoretical.

S. S. ZILVA.

Do spring-waters containing carbon dioxide and hydrogen carbonates activate amylases? M. LOEPER and A. MOUGEOT (Compt. rend. Soc. Biol., 1925, **92**, 569—571; from Chem. Zentr., 1925, II, 1173).—Spring-waters containing carbon dioxide and hydrogen carbonates have no amylolytic action, but strongly activate the amylase of saliva and pancreatic juice. The effect is not due to the alkali present, since a solution of a hydrogen carbonate does not behave in this way. Removal of carbon dioxide by boiling does not destroy the activating effect. This excludes also the possibility of the action being due to a biological factor. The effect cannot be due to radioactivity nor to the influence of p_H, since the latter is considerably changed on boiling.

G. W. ROBINSON.

Spring-waters containing hydrogen carbonates and the activity of invertase from beer yeast. A. MOUGEOT and V. AUBERTOT (Compt. rend. Soc. Biol., 1925, **92**, 1504—1506; from Chem. Zentr., 1925, II, 1173; cf. preceding abstract).—The effect of spring-waters on invertase depends simply on the p_H of the solution.

G. W. ROBINSON.

Variations of phosphorus-containing lipins during liver autolysis. C. ARTOM (Bull. Soc. Chim. biol., 1925, **7**, 1099—1128).—In the liver of normal dogs the fatty acids are present chiefly as phosphatide, and vary only within narrow limits. The chloroform-soluble phosphorus can be divided into three fractions: (1) true phosphatide phosphorus, (2) "carnithin" phosphorus, and (3) acetone-soluble phosphorus. Since the ratio of phosphatide fatty acid to phosphatide phosphorus is almost 18, almost all the phosphatides are to be classed as lecithins or cephalins. During antiseptic autolysis, the phosphatide content of the liver gradually diminishes, more rapidly in the case of dogs killed during digestion or after administration of hydrochloric acid than in the case of fasting dogs, more slowly than usual when an excess of fat has been added to the liver tissue. Since the ratio of phosphatide fatty acid to phosphatide phosphorus usually varies little during autolysis, it seems that there is a complete cleavage of the molecule with liberation of the whole of the fatty acid. Sometimes, however, the ratio is appreciably decreased, indicating an incomplete cleavage, and experimental addition of fat usually leads to a slight increase in the ratio. The "carnithin" phosphorus diminishes more rapidly than that of the phosphatides. The acetone-soluble phosphorus, on the other hand, increases both in absolute amount and relatively to the total chloroform-soluble phosphorus.

C. P. STEWART.

Diastase. II and IIIa. V. SYNIEVSKI (Bull. Intern. Acad. Polonaise, 1925, **A**, 47—50, 51—54).—See this vol., 93.

Enzyme extracted from seeds of *Rhamnus*, rhamnodiastase. M. BRIDEL and C. CHARAUX (Compt. rend., 1925, **181**, 925—926).—It is suggested that the enzyme extracted from seeds of *Rhamnus utilis*, *R. frangula*, etc., which hydrolyses various complex glucosides without breaking down the polysaccharides (A., 1911, i, 391; 1924, i, 659; 1925, i, 336), be named *rhamnodiastase*. A modified method for its preparation is described.

L. F. HEWITT.

Glucosides in plants hydrolysed by rhamnodiastase. M. BRIDEL and C. CHARAUX (Compt. rend., 1925, **181**, 1167—1168).—The effect of rhamnodiastase (cf. preceding abstract) on the rotatory power and reducing power of aqueous extracts of twelve plants has been examined. This provides a method of investigation of the carbohydrates contained in plant glucosides.

L. F. HEWITT.

Fate of invertase in the normal and immune organism. A. SAMISSLOV (Biochem. Z., 1925, **164**, 110—116).—The rate of disappearance from the blood-stream of invertase after its injection into normal rabbits or rabbits which had received preliminary injection of yeast autolysate, is measured. Invertase added to blood of normal or immunised rabbits *in vitro* does not disappear appreciably in 6 hrs. The injected invertase is neither destroyed nor adsorbed by the corpuscles, but is adsorbed by the cells of various organs, *e.g.*, in immunised animals the liver adsorbs 50—60% of the invertase, whilst in normal animals only 20—30%.

P. W. CLUTTERBUCK.

Effect of radioactive radiations and X-rays on enzymes. IV. Effect of radiations from radium emanation on solutions of invertase. R. G. HUSSEY and W. R. THOMPSON (J. Gen. Physiol., 1925, **9**, 211—215; cf. A., 1923, i, 871; J. Gen. Physiol., 1923—4, **6**, 1, 7).—The inactivation of invertase by β-radiation from radium emanation can be explained quantitatively on the same basis as that of trypsin and pepsin previously reported. Within limits, the rate of inactivation is inversely proportional to the volume of the solution.

C. P. STEWART.

Maltase from barley malt. H. PRINGSHEIM and J. LEIBOWITZ (Biochem. Z., 1925, **161**, 456—458).—A sample of maltase is described which is apparently different from formerly known samples, in that it has not the usual sensitivity to acidity. It is active between p_H 3 and 7·5 and has its optimum between p_H 4·5 and 5. H. I. COOMBS.

Enzymic cleavage of cellulose. P. KARRER, P. SCHUBERT, and W. WEHRLI.—See B., 1926, 44.

Action of emulsin on amygdalin. L. ROSENTHALER (Arch. Pharm., 1925, **263**, 563—566).—When this hydrolysis is followed quantitatively, the amounts of hydrocyanic acid and dextrose formed being determined, results are obtained that agree only with the supposition that the primary products are dextrose and mandelonitrile glucoside, the latter being then hydrolysed itself (cf. Auld, J.C.S., 1908, **93**, 1276). There is no indication that gentiobiose is a direct scission product, but a little is possibly formed. W. A. SILVESTER.

Perhydridase of milk. B. SBARSKY (Biochem. Z., 1925, **164**, 442—443).—A reply to Hopkins and Dixon (A., 1925, i, 1506). E. C. SMITH.

Toxic action of hydrocyanic acid on laccase and its relationship to the reaction of the solution. P. FLEURY (Compt. rend. Soc. Biol., 1925, **92**, 596—598; from Chem. Zentr., 1925, II, 1172).—Hydrocyanic acid solution (0·67 mg. per litre) reduces the activity of laccase to 60%. The original activity is restored if the hydrocyanic acid is removed by a stream of air. Hydrocyanic acid acts as a negative catalyst; its effect is not directly proportional to concentration, but shows a logarithmic relationship. The maximum toxicity is shown at the optimum p_H for the action of the enzyme.

G. W. ROBINSON.

Significance of metallic salts in the action of blood lipases. L. E. WALBUM and K. BERTHELSEN (Z. Immunit., 1925, I, **42**, 467—476; from Chem. Zentr., 1925, II, 307).—The effect of metallic salts in increasing lipolysis by blood lipase, as also their effect on the formation of agglutinins and amboceptors and on the action of bactericidal substances, depends to some extent on the atomic numbers in the individual chemical groups. The effect generally increases with decrease in the atomic number.

G. W. ROBINSON.

Action of urethanes on serum lipase. P. RONA and A. LASNITZKI (Biochem. Z., 1925, **163**, 197—225).—At low concentrations of urethane, the inhibitory action on serum lipase is directly proportional to the concentration. At concentrations of 0·1*M* and above, the inhibition follows the adsorption isothermal. Methyl-, ethyl-, and propyl-urethanes show increasing inhibition, but do not exactly obey Traube's law. *iso*Propylurethane behaves anomalously, being strongly inhibitory at low concentrations. Inhibition increases with decreasing concentration of the lipase, hence the active surface of the latter must increase on dilution. The inhibitory action of urethane on lipase is reversible. E. C. SMITH.

Effect of different preparations of the quinine group on the enzymic functions of the organism. V. Effect of concentration of the substrate on the hydrolysis of triacetin by pancreatic lipase. J. A. SMORODINCEV and V. A. DANILOV (Biochem. Z., 1925, **164**, 394—400; cf. this vol., 94).—Quinine hydrochloride accelerates the hydrolysis of 0·5—1% solutions of triacetin by pancreatic lipase. No effect is shown in 3—5% solutions until the third hour, when a retarding effect is manifested. The velocity of hydrolysis in presence or absence of quinine is independent of the initial concentration of triacetin, and follows the course of a unimolecular reaction. The constant of this reaction is less for higher concentrations of triacetin than for lower.

E. C. SMITH.

Nature of so-called serum antipepsin. W. MOZOLOVSKI and H. HILAROVICZ (Biochem. Z., 1925, **164**, 295—311).—The inhibitory action of serum on peptic digestion, and the phenomena explained by adsorption of pepsin by a serum antipepsin, can be fully accounted for by the change in p_H brought about by the addition of the serum. E. C. SMITH.

Buffers in the study of proteases. III. Influence of buffers on the p_H during the digestion of caseinogen by the method of Gross. J. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1925, **7**, 1154—1157).—The presence of buffers does not cause any alteration in p_H during the digestion of caseinogen by pepsin.

C. P. STEWART.

Effect of radiations from a mercury arc in quartz on enzymes. I. Effect of ultra-violet radiation on pepsin. R. G. HUSSEY and W. R. THOMPSON (J. Gen. Physiol., 1925, **9**, 217—219).—Pepsin in solution is inactivated by the radiations from a mercury arc in quartz, the effective radiations,

apparently, being those in the ultra-violet region. The reaction appears to be unimolecular.
C. P. STEWART.

Tryptic digestion with low concentrations of enzymes. III. R. EHRENBERG (Biochem. Z., 1925, **161**, 348—360).—Further evidence is brought forward to support the author's view that enzyme action changes during its course, quantitatively and qualitatively, and the nature of the substrate affects this change. Evidence is also brought to show that a mere change of enzyme concentration qualitatively affects the course of hydrolysis (cf. A., 1925, i, 202). H. I. COOMBS.

Tyrosinase, its action on phenols, tyrosine, and other amino-acids. R. A. MCCANCE (Biochem. J., 1925, **19**, 1022—1031).—Quinol, which is spontaneously oxidised by atmospheric oxygen, reduces methylene-blue only extremely slowly. It reduces dinitrobenzene. In the presence of an amino-acid, however, quinol and pyrocatechol both reduce methylene-blue freely. After complete reduction of the methylene-blue the amino-nitrogen content of the amino-acid is unaltered, and there is no increase in ammonia. *p*-Cresol does not reduce methylene-blue, but does so very slowly in the presence of glycine. The spontaneous oxidation of all the phenols examined was not affected by *M*/500-potassium cyanide, although this treatment inhibits both the aërobic and anaërobic action of tyrosinase. Tyrosine, being both an amino-acid and a phenol, reduces methylene-blue slowly. Tyrosinase catalyses the reduction of methylene-blue by a solution of p_H 8 of *p*-cresol and glycine. The action of tyrosinase on tyrosine depends on the fact that the compound is an amino-acid and a phenol. Additive compounds have been prepared from pyrocatechol and diethylamine (2 : 1 mol.), m. p. 78—79°; resorcinol and diethylamine (2 : 1), m. p. 115°; benzoquinone and *p*-cresol (1 : 2), orange-red, m. p. 63·5°. This compound is not identical with the compound formed by the *p*-cresol–tyrosinase system. S. S. ZILVA.

Formation of acetylmethylcarbinol and βγ-butylene glycol in metabolism of yeast. A. J. KLUYVER, H. J. L. DONKER, and F. V'T. HOOFT (Biochem. Z., 1925, **161**, 361—378).—A method is described for detecting the above compounds in presence of large amounts of impurities. The first-named compound is converted into diacetyl (which can be distilled off and identified) by ferric chloride, and then the second compound can also be oxidised to diacetyl by means of bromine. If suitable hydrogen acceptors are added to fermenting dextrose solutions, both acetylmethylcarbinol and βγ-butylene glycol are formed from the accumulated acetaldehyde. When air is blown through a fermenting sugar solution the oxygen also acts as a hydrogen acceptor.
H. I. COOMBS.

Occurrence of an amino-acid containing sulphur in the alcoholic extract of yeast. S. ODAKE (Biochem. Z., 1925, **161**, 446—455).—From the mother-liquors of adenylthiomethylpentose (cf. A., 1925, i, 338), obtained from the alcoholic extraction of 6000 kg. of yeast, 0·6 g. of a sulphur-containing *amino-acid*, $C_5H_{11}O_2NS$, m. p. 272—273°, was obtained. The aqueous solution had $[\alpha]_D^{16}$ −11·77°, and except for a small variation in this value, the compound has the same properties as that described by Müller (A., 1923, i, 869, 963) from the products of hydrolysis of caseinogen and egg-albumin. The properties and reactions of the acid are described and the *copper* salt and *naphthylcarbimide* derivative, m. p. 187° (uncorr.), were also prepared. H. I. COOMBS.

Volutin in yeast cells. M. GLAUBITZ.—See B., 1926, 25.

Laboratory pure culture apparatus. F. M. HILDEBRANDT.—See this vol., 142.

Endo's medium for *Bacillus coli*. N. M. HARRIS.—See B., 1926, 78.

Salt action. X. Influence of electrolytes on the viability and electrophoretic migration of *Bacillus coli*. H. J. SHAUGHNESSY and K. I. CRISWELL (J. Gen. Physiol., 1925, **9**, 123—136).—Electrophoretic charge is highest in distilled water adjusted to p_H 6·0 or p_H 8·0; in the presence of salts, p_H 8·0 is somewhat more favourable to electrophoretic charge (although much less so to viability) than p_H 6·0. At p_H 11·0, electrophoretic charge is only slightly decreased, but at p_H 2·0 it may even be reversed. Sodium chloride solutions, in concentrations ranging from 0·0145 to 0·725*M*, were somewhat toxic and tended to decrease electrophoretic charge; calcium chloride in similar concentrations was more toxic; Locke–Ringer solution was slightly toxic (although less so than pure salt solutions) and depressed the migration velocity at all p_H values. It is concluded that the parallelism between viability and electrophoretic charge is not a close one, and that the two effects seem, on the whole, to follow different laws. C. P. STEWART.

Behaviour of pyrimidine derivatives in organisms. II. Action of *Bacillus coli* on uracil and cytosine. A. HAHN and L. SCHÄFER (Z. Biol., 1925, **83**, 511—514).—Cytosine is deaminated by *Bacillus coli*, as by yeast (A., 1923, i, 1269). The uracil formed is not further attacked. H. P. MARKS.

***Bacillus pyocyaneus*. Relation of its metabolism to intramolecular respiration.** O. ACKLIN (Biochem. Z., 1925, **164**, 312—370).—*Bacillus pyocyaneus* is capable of vigorous growth on artificial media containing sodium nitrate and sodium lactate as sole source of nitrogen and carbon, respectively. The reaction becomes more alkaline owing to formation of ammonia from nitrate. Growth can take place from p_H 5·6 to 9·2, the optimum being from p_H 6·4 to 8·1. The reaction of maximum denitrification lies between p_H 7·4 and 9·0. At p_H 6·4 very little denitrification takes place. The character of the source of nitrogen is the determining factor in growth and pigmentation. Of the sources of nitrogen investigated, nitrate, ammonia, and peptone, the last gives maximum growth. In cultures with ammonium salts as the source of nitrogen, pigmentation is absent. The assimilatory reactions consist largely in the formation of ammonia and pyruvic acid, from which alanine and proteins are synthesised. The dissimilatory reactions consist in the breakdown

of pyruvic acid to carbon dioxide, acetaldehyde, alcohol, and acetic acid. In peptone–lactic acid media no utilisation of lactic acid occurs. The intracellular respiration, determined colorimetrically by addition of nitroanthraquinone, is at a maximum in 1-day cultures, whereas in most media the maximum rate of growth occurs between the first and third days. The presence of 0·00005*M*-manganese chloride inhibits growth and reduction in nitrate–lactic acid media. The virulence of the organism is unaltered by 5—10 days' growth on synthetic media, no influence of the nature of the source of nitrogen being observed. The toxicity of sterile cultures is, however, dependent on the source of nitrogen, cultures grown in ammonium chloride media being less toxic than those grown in nitrate media. E. C. SMITH.

Lipochromes present in certain bacteria. V. READER (Biochem. J., 1925, **19**, 1039—1046).—*Sarcina aurantiaca* contains two lipochromes, carotin and lycopin, the latter predominating. The pigment is formed to the same extent whether the organism is grown in the dark or in diffuse light. Direct sunlight impedes growth and prevents the development of colour. Although growth is much more vigorous at 20° than at 37°, pigment formation per mg. of growth is the same whether in light or dark. *Streptothrix corallinus* contains an unknown lipochrome for which the name "coralin" is suggested. The maximum coloration of this pigment appears at 18°. Above 27°, only traces of colour are produced. Growth of this organism is vigorous from 22° to 37° and direct sunlight has no decolorising effect on it. Neither of the above organisms contains appreciable quantities of vitamin-*A*. Yeast contains traces of carotin. *Streptothrix corallinus* contains no cholesterols or phytosterols.

S. S. ZILVA.

Utilisation of thiocarbamide by *Aspergillus niger*. A. RIPPEL (Biochem. Z., 1925, **165**, 473—474).—*Aspergillus niger* oxidises cystine to a much greater extent (40%) than thiocarbamide (4%).

P. W. CLUTTERBUCK.

Chemical composition of the sporangial wall of *Myxomycetes*. A. KIESEL (Z. physiol. Chem., 1925, **150**, 102—117).—The wall substance contains 3·63% of nitrogen, 3·98% of ether-soluble substances, and 2·84% of ash. It contains 50% of complex carbohydrate insoluble in water, which by acid hydrolysis yields, in part, dextrose. Whilst some 27% of the cell-wall material is resistant to 66% sulphuric acid, by heating with alkali to 160—180°, 98—99% goes into solution. In the insoluble portion, neither cellulose nor chitin can be detected. The nitrogen-free polysaccharides may be separated completely from nitrogenous substances by heating on the water-bath with 8% sodium hydroxide, when the former do not go into solution. On longer heating a part of the carbohydrate is gradually destroyed. The name "myxoglucosan" is given to the polysaccharide which is resistant to the action of 8% sodium hydroxide. Previous treatment of the wall substance with 2% hydrochloric acid largely diminishes the yield of polysaccharide insoluble in sodium hydroxide. It is probable that there is protein in the wall material, since a portion of the nitrogen insoluble in hydrochloric acid appears to be soluble in pepsin solutions. No definite protein colour reactions were observed. H. D. KAY.

Effect of p_H on the availability of iron for *Chlorella* sp. E. F. HOPKINS and F. B. WANN (J. Gen. Physiol., 1925, **9**, 205—210).—In a phosphate buffered nutrient solution the acid limit for growth of *Chlorella* Sp. was p_H 3·4; the optimum p_H 5·7; and the alkaline limit p_H 6·1. When special precautions—omission of calcium from the medium and addition of sodium citrate—were taken to prevent removal of iron by precipitation or adsorption at the more alkaline reactions, growth was maximal at p_H 7·5.

C. P. STEWART.

Penetration of carbon dioxide into living protoplasm. W. J. V. OSTERHOUT and M. J. DORCAS (J. Gen. Physiol., 1925, **9**, 255—267; cf. A., 1925, i, 1355).—Little or no carbon dioxide enters normal cells of *Valonia macrophysa* except in the form of undissociated molecules. Whenever the interior of a cell is more acid than the surrounding medium (excess of base being the same in both) the internal concentration of total carbon dioxide at equilibrium may be expected to be less than the external. C. P. STEWART.

Accumulation of brilliant-cresyl-blue in the sap of living cells of *Nitella* in the presence of ammonia. M. IRWIN (J. Gen. Physiol., 1925, **9**, 235—253).—When living cells of *Nitella* are placed in a solution of brilliant-cresyl-blue containing ammonium chloride, the rate of accumulation of the dye in the sap is less than when ammonium chloride is absent, this decrease occurring without any increase in the p_H of the cell sap. Since the decrease in the rate of accumulation of the dye takes place only when ammonia is present in the sap, and not when the ammonia is confined to the external solution, it is interpreted as being due to competition between the ammonia and the dye for certain substances in the cell. C. P. STEWART.

Protoplasm. Composition of the plasmodium of *Reticularia lycoperdon*. A. KIESEL (Z. physiol. Chem., 1925, **150**, 149—176).—The plasmodium gave the following figures (on the dry weight): fat, 17·85; lecithin, 4·67; cholesterol, 0·58; reducing sugar, 2·74; non-reducing, soluble carbohydrate (not glycogen), 5·32; glycogen, 15·24; difficultly hydrolysable polysaccharide, 1·78; nitrogenous extractives, 12·00; protein (partly nucleoprotein), 20·65; "plastin," 8·42; nucleic acid, 3·68; fat of lecitho-protein (?), 1·20; unknown residue, 5·87%. H. D. KAY.

Cholesterol-synthesising function of the spleen: influence of internal secretion of the spleen on cholesterol in muscle. J. E. ABELOUS and L. C. SOULA (Compt. rend., 1926, **182**, 98—100).—In normal dogs there is more cholesterol in venous than in arterial blood, but this is not the case in the posterior limb when the trunk of the crural and sciatic nerves is severed. When the peripheral ends of the severed nerves are subjected to galvanic stimu-

lation, the venous blood cholesterol content is increased by the tetanus produced. In the splenectomised dog stimulation of the severed nerves does not produce this increase unless an extract of spleen is injected into the opposite saphenous vein. That the influence of the spleen is not direct secretion of cholesterol is shown by the fact that in the above experiments no increase in cholesterol content of the blood in the vein leading directly from the spleen is observed. L. F. HEWITT.

Properties and composition of oocytin. II. G. W. CLARK and P. W. SHARP (J. Biol. Chem., 1925, **66**, 123—131).—Oocytin has been prepared by a method similar to that previously described (A., 1918, i, 463) from the blood of all mammalian species so far investigated, and also, in much greater yield, from that of the fowl and the turkey; the latter result suggests that it may be derived from the nuclear material of the red cells; it could not be obtained from an abdominal transudate, but was isolated in undiminished yield from serum which had been kept for 15 months at 4°. The activity of the oocytin, measured by the fertilisation membrane formation in sea-urchin's eggs activated with strontium chloride, was greatest in those preparations derived from adult male animals. Similar membrane formation was observed with nucleic acids from yeast, thymus, and salmon sperm, but these substances were much less active than oocytin. C. R. HARINGTON.

Active principles of pituitary extract. H. H. KNAUS (J. Pharm. Exp. Ther., 1925, **26**, 337—346).—When given intravenously, pituitary extract equivalent to 0·01 mg. of fresh posterior lobe per kg. was required to produce an appreciable rise in the blood pressure of the pithed cat, and 0·004 mg. to show an effect on the uterus. With intra-arterial administration, the minimal doses were 0·6 and 0·01 mg. per kg., respectively. These results and those of intramuscular injection are explained by the assumption that there are separate pressor and oxytocic principles in pituitary extract and that the pressor substance is rapidly destroyed by passing through the arterioles. C. P. STEWART.

Mineral metabolism of the lymph following injections of *l*- and *d*-adrenaline, pituitrin, and pilocarpine. W. F. PETERSEN and T. P. HUGHES (J. Biol. Chem., 1925, **66**, 229—246).—Injections into dogs of natural adrenaline and synthetic *l*- and *d*-adrenaline have almost identical effects on the inorganic salts of the lymph; in general, there is observed a preliminary increase and subsequent fluctuation in the concentration of calcium, and a preliminary fall and subsequent rise in that of phosphate; variations in the other inorganic ions are somewhat irregular; following injections of pituitary extract there is an immediate rise in the concentration of phosphate and of sodium and a slight rise in the calcium; pilocarpine causes an increase in the phosphates, and, if the dog has previously been treated with calcium lactate, an increase in the calcium. It is thought that the alterations observed are the result of the action of the drugs directly on the tissues, rather than on the autonomic nervous system. C. R. HARINGTON.

Biocatalysts concerned in carbohydrate metabolism. III. H. VON EULER and K. MYRBÄCK (Z. physiol. Chem., 1925, **150**, 1—15).—Pancreatic insulin cannot replace the co-zymase of yeast. The formation of hexosediphosphate by chopped muscle, without oxygenation, is not greatly increased by pancreatic insulin. H. D. KAY.

Pancreatic hormone. H. LANGECKER and W. WIECHOWSKI (Klin. Woch., 1925, **4**, 1339—1343; from Chem. Zentr., 1925, II, 1180).—By the methods in use for extracting the pancreatic hormone, substances can be extracted from other organs which have a similar effect on blood-sugar, but their mode of action differs from that of the pancreatic product. Such substances may be also present in the active fraction isolated from the pancreas by existing methods. Using a new method, which consists in salting out the raw insulin with potassium lactate, and after redissolving in water, precipitating with *N*-hydrochloric acid, an active fraction was obtained from the pancreas, but not from other organs. The preparation thus obtained is 2—5 times as active as the preparations hitherto available and must contain the pancreatic hormone free from other substances of similar action. The substance is uncrystallisable and appears to be an albumose rich in sulphur. G. W. ROBINSON.

Measurement of the action of insulin. H. LANGECKER and W. STROSS (Biochem. Z., 1925, **161**, 295—336).—The action of insulin is dealt with statistically, about 200 rabbits being used in many experiments. The average blood-sugar value for 224 rabbits, starved for 24 hrs., was 96 mg.%; 47 rabbits which had never previously had insulin gave 99 mg.%. The mean value necessary to bring about convulsions was 28 mg.%. Whilst different rabbits show great variations in their sensitivity to insulin —one rabbit being unaffected by sixteen times the dose which brought about convulsions in another— each rabbit seems to have an individual sensitivity which is more or less constant. H. I. COOMBS.

Insulin and blood-fat. A. C. WHITE (Biochem. J., 1925, **19**, 921—926).—Hypoglycæmia caused by the administration of insulin is accompanied in the normal dog by an increase in the blood-fat, the increase affecting the fatty acids more than the cholesterol. The administration of dextrose along with insulin, or later, does not seem to affect the changes in blood-fat brought about by insulin. The effect of insulin on the blood cholesterol is not constant. S. S. ZILVA.

Fate of blood-sugar after insulin injections in normal animals. A. HYND (Biochem. J., 1925, **19**, 1095—1100).—The reducing power of plasma is brought down to that of the corpuscles, which is comparatively low, by the administration of insulin. Whilst the sugar of the plasma is not altered to any extent by hydrolysis before or after insulin, the reducing power of the corpuscles increases in both cases. As the increase in the reducing power is greater after insulin, it cannot be due entirely to the interfering action of peptone produced by the hydrolysis. It is suggested that a non-reducing dextrose

complex may be formed by the action of insulin and that this complex attaches itself to the tissues including the red blood-corpuscles. About a sixth of the sugar disappearing from the plasma after insulin may be accounted for by the erythrocytes acting in this manner. S. S. ZILVA.

Effect of insulin treatment and nutritional conditions on the fat content of rats on vitamin-free diets. K. ONOHARA (Biochem. Z., 1925, **163**, 51—60).—Normal rats treated with 0·8 unit of insulin per kg. body-weight *per diem* for 2—3 weeks show a slightly greater mean fat content than rats not so treated. Rats fed on vitamin-free diets, either mixed, fat-free, or carbohydrate-free, are considerably poorer in fat. On mixed and carbohydrate-free diets insulin has no effect on the fat content, but on fat-free diet the insulin-treated animals are slightly richer in fat than the controls. E. C. SMITH.

Effect of insulin on the blood-fat level in dogs on a vitamin-free diet. K. ONOHARA (Biochem. Z., 1925, **163**, 67—74).—Insulin has no effect on the blood-fat level of fasting dogs on a vitamin-free diet, nor on the blood-fat curve following the ingestion of a fat meal. E. C. SMITH.

Bio-assay of thyroid. R. HUNT.—See B., 1926, 27.

Physiology of the glands. L. ASHER. LXXVIII. Effect of the thyroid gland on the growth-promoting properties of blood. Detection of growth-factors in blood. S. UCHIDA (Biochem. Z., 1925, **163**, 75—94).—A method is described for the determination of the content of growth-promoting substances in rabbit's plasma by addition of the plasma to cultures of chick embryo hearts in Ringer's solution. The plasma of thyroidectomised animals is very deficient in growth-factor, still more so in animals deprived of both thyroid and thymus glands. Animals deprived of thymus show a slight deficiency, but ovariectomy has no effect on the growth-factor content.
E. C. SMITH.

Excretion of calcium, magnesium, and phosphorus (*a*) following thyreoparathyroidectomy, (*b*) following injections of calcium chloride, sodium phosphate, or both, (*c*) following injection of parathyroid extract. I. GREENWALD and J. GROSS (J. Biol. Chem., 1925, **66**, 185—199, 201—215, 217—227).—Following parathyroidectomy in dogs, the excretion of calcium became slightly greater in the fæces and considerably less in the urine, the net result being a decrease in the total calcium excreted; the total phosphorus excreted was increased and that of magnesium little changed. When calcium chloride is injected into normal dogs, most of the calcium is retained, the phosphorus excretion is unchanged and that of magnesium slightly reduced; when sodium phosphate and calcium chloride are given together, the extra calcium and phosphorus excreted is approximately equal to that administered; injection of large amounts of sodium phosphate leads to an increased excretion of calcium, phosphorus, and magnesium. Injection of active parathyroid extract increases the excretion of calcium and phosphorus and does not affect that of magnesium; since the calcium excreted could not have been derived from the food and also, since its increased excretion was accompanied by a parallel increase in that of phosphorus, it is assumed that this experiment indicates a mobilisation of calcium phosphate from the bones under the influence of the parathyroid hormone. C. R. HARINGTON.

Parathyroid hormone. II. J. B. COLLIP and E. P. CLARK (J. Biol. Chem., 1925, **66**, 133—137; cf. A., 1925, i, 754).—After acid extraction of the glands, removal of fat, and preliminary removal of inactive proteins by making alkaline and then adding acid to p_H 5·5 and filtering, the filtrate was saturated with sodium chloride; the active material so precipitated was purified by repeated dissolution in dilute hydrochloric acid and precipitation at the isoelectric point (p_H 4·8), and finally washed with alcohol and ether and dried in a vacuum over sulphuric acid. There was thus obtained an amorphous powder (15·5% N) which gave positive reactions for protein, negative for carbohydrate; it contained sulphur and iron, but no phosphorus; it was easily soluble in acid and alkali and in 80% alcohol; insoluble in absolute alcohol, ether, pyridine, and acetone; it did not dialyse. It was inactivated by boiling for an hour with 10% hydrochloric acid or with 5% sodium hydroxide, and also by the action of pepsin and of trypsin; 0·3 mg. was equivalent to 1 unit of physiologically active substance. C. R. HARINGTON.

Vitamin-*A* in beef, pork, and lamb. R. HOAGLAND and G. G. SNIDER (J. Agric. Res., 1925, **31**, 201—221).—The values of beef, pork, and lamb as sources of vitamin-*A* have been studied by following the growth of young rats receiving rations adequate in other respects, but with varying proportions of dried lean meat as the only source of vitamin-*A*. The energy values of the different rations were practically the same. The samples of beef and pork tested were relatively poor in vitamin-*A*. When 50—95% of the ration consisted of the beef, growth was almost normal, but in no case was normal growth obtained with the pork. The samples of lamb differed considerably; some were rather poor in vitamin-*A*, whereas others were richer than any other samples of meat tested. C. T. GIMINGHAM.

Chemical nature of vitamin-*A*. J. C. DRUMMOND, H. J. CHANNON, and K. H. COWARD (Biochem. J., 1925, **19**, 1047—1067).—Vitamin-*A* can be concentrated without loss in the unsaponifiable fraction of cod-liver oil if precautions against oxidation are taken. The concentrate contains no demonstrable traces of iodine or nitrogen, and 50% of this fraction consists of cholesterol which is inactive. Vitamin-*A* is volatile, passing over on distillation mainly between 180° and 220°/2—3 mm. The active distillate contains a saturated alcohol (m. p. about 60°), spinacene, and one or more than one unsaturated alcohol of b. p. about 200°/2—3 mm. The first two constituents are inactive. Whether the vitamin is an unsaturated alcohol could not be established. Oleyl alcohol, selachyl alcohol, and phytol are inactive. Vitamin-*A* is not identical with lycopin or carotin. The claims

of Takahashi (J. Chem. Soc. Japan, 1922, **43**, 826; A., 1923, i, 968; 1925, i, 1365), to have isolated vitamin-*A* and identified it as an unsaturated alcohol, $C_{27}H_{46}O_2$ (" biosterin "), are criticised.

S. S. ZILVA.

Technique of testing for the presence of vitamin-*A*. J. C. DRUMMOND, K. H. COWARD, and J. HANDY (Biochem. J., 1925, **19**, 1068—1074).—Rats kept on deficient basal diet from which fat is excluded receive small quantities of irradiated cholesterol to supply the antirachitic vitamin. When the weight curve declines owing to the exhaustion of the animal's store of vitamin-*A*, the substance to be tested is administered to the animal. In a positive test, the rats resume growth. If vitamin-*A* is absent from the substance the decline in weight continues.

S. S. ZILVA.

Biochemical colour test. III. Colour reactions associated with vitamin-*A*. W. R. FEARON (Biochem. J., 1925, **19**, 888—895).—Phosphorus pentoxide produces a deep violet colour when added to oils containing vitamin-*A*. The pigment giving this colour can be separated by adsorbing it with phosphorus pentoxide and centrifuging. On hydrolysing the deposit and extracting the pigment, the extract did not give the colour tests, nor did it possess any growth-promoting properties. Active oils depigmented by the above procedure lose their growth-promoting activity. In the presence of a 12% solution of trichloroacetic acid in dry light petroleum, pyrogallol and other polyphenols interact with oils containing vitamin-*A*, giving a stable coloration. Oils inactivated by aëration, inactive vegetable oils, irradiated cholesterol, " oxycholesterol," irradiated hardened fat, and " ostelin " give no colour with pyrogallol. This reaction could not be reproduced by adding the commoner aldehydes and ketones, with and without cholesterol, to medicinal petroleum, aërated liver oil, or vegetable oil.

S. S. ZILVA.

Fat, cholesterol, and sterol metabolism of growing rats in the presence and absence of vitamin-*A*. B. LIANG and L. WACKER (Biochem. Z., 1925, **164**, 371—393).—Rats fed on fat-free diet lacking vitamin-*A* are incapable of laying down fat, but on diets poor in fat and vitamin-*A* they synthesise large amounts of cholesterol. The cholesterol content may be greater than when fed on diets containing sufficient vitamin-*A* and rich in cholesterol. Vitamin-*A* and lipochrome may act as carriers of the endogenous oxygen derived from carbohydrate in process of conversion into fat. Vitamin-*A* is also concerned with the formation of neutral fat from fatty acid and glycerol. Much more sterol is formed in the organism than is contained in the diet, but as most of these substances are excreted in the fæces, very little increase in sterol content is found on normal diets, and none on fat-free diet. E. C. SMITH.

Antirachitic value of irradiated cholesterol and phytosterol. IV. Factors influencing biological activity. A. F. HESS, M. WEINSTOCK, and E. SHERMAN (J. Biol. Chem., 1925, **66**, 145—160).—Whereas irradiated vegetable oil retains its antirachitic activity for at least a year, irradiated cholesterol loses a part of its activity during storage for a month; the loss is greatest if it is stored dry and least if kept in olive oil. The inactivation produced by prolonged irradiation of activated cholesterol (cf. A., 1925, i, 1020) is an irreversible process. Cholesterol can be activated by irradiation in an atmosphere of nitrogen and does not lose its activity in a vacuum or on prolonged contact with acetone, chloroform, or benzene; on recrystallisation from alcohol, it becomes less active; if the crystallisation be repeated, the soluble portion recovered from the mother-liquor is found to be progressively less active; none of the recrystallised products could be completely reactivated by irradiation, and the more soluble portions could not be reactivated at all. Cholesterol isolated from egg-yolk and from bone-marrow was devoid of antirachitic activity (before irradiation); no change in elementary composition could be detected in cholesterol which had been activated by irradiation for 1 hr.

C. R. HARINGTON.

Mammary secretion. VI. Vitamin-*B* and the lactating rat's diet. 1. The quantitative relation of vitamin-*B* to protein. 2. Vitamin-*B* requirements of the lactating and non-lactating rat. G. A. HARTWELL (Biochem. J., 1925, **19**, 1075—1081).—There is a quantitative relation between the protein and vitamin-*B* in the lactating rat's diet. On a synthetic diet containing 20% of caseinogen, 6—8 g. of marmite per 20 g. of caseinogen are needed for the mother to rear her young normally. On a synthetic diet containing 20% of caseinogen, the lactating rat requires at least four times as much vitamin-*B* as does the young, growing animal. The lactating rat can rear some of her young on a synthetic diet free from vitamin-*B*, but conditions are not normal. In a synthetic diet 10% of caseinogen is insufficient for the lactating rat. S. S. ZILVA.

Technique for studying vitamin-*B*. A. H. SMITH, G. R. COWGILL, and H. M. GROLL (J. Biol. Chem., 1925, **66**, 15—21).—The importance is emphasised, when using rats as subjects of vitamin-*B* experiments, of eliminating the possibility of the animals eating their fæces. C. R. HARINGTON.

Glycogen reserves and arterial sugar (free and combined with protein) in experimental scurvy. L. RANDOIN and A. MICHAUX (Compt. rend., 1925, **181**, 1179—1181).—Guinea-pigs fed on a diet deficient in vitamin-*C* have the normal blood-sugar level (both free and combined sugar), and although the liver glycogen reserves are somewhat diminished, some glycogen remains in the liver and muscles of animals dying of scurvy. L. F. HEWITT.

Synthesis of vitamins by yeasts. R. ZAJDEL and C. FUNK (Compt. rend. Soc. Biol., 1925, **92**, 1527—1528; from Chem. Zentr., 1925, II, 1178).—Vitamin-*D* is shown to be indispensable for the growth of yeast in nutrient solutions. On addition of unpurified sugar, growth takes place. The authors suggest that there are several components in vitamin-*D*, one of which occurs in ordinary unpurified sugar. In one case where yeast grew apparently in the absence of

vitamin-*D*, it is supposed that there was a synthesis of the vitamin by wild yeast. G. W. ROBINSON.

Reproduction, growth, and alimentary equilibrium. L. RANDOIN, J. ALQUIER, ASSELIN, and CHARLES (Compt. rend., 1926, **182**, 94—96; cf. A., 1925, i, 210, 1002).—The diets most favourable for the growth of white rats are not the most favourable for reproduction. Butter (or milk) is an essential part of the diet to ensure fertility, caseinogen (or milk) is necessary for the rearing of the young, and a balance between mineral constituents and carbohydrates in the diet is necessary for reproduction and growth. L. F. HEWITT.

Assimilation of carbon dioxide by plants. F. J. NELLENSTEYN.—See B., 1926, 35.

Controlling influence of carbon dioxide. V. Production of ethyl alcohol and acetaldehyde by cells of the higher plants in relation to concentration of oxygen and carbon dioxide. M. THOMAS (Biochem. J., 1925, **19**, 927—947).—In the absence of oxygen, ethyl alcohol and traces of acetaldehyde accumulate in apple cells. This is due to respiration of a zymasic type (anaërobic zymasis). Neither of these compounds accumulates as intermediate or end-product of the respiration of apple cells in air; nor can they be oxidised by the apple tissue. When carbon dioxide is present, zymasic respiration takes place even in the presence of abundance of oxygen (carbon dioxide zymasis). In carbon dioxide zymasis, the ratio of ethyl alcohol to acetaldehyde is 2 : 1, whilst in anaërobic zymasis it is 50 : 1. Mixtures of carbon dioxide and oxygen may therefore be more injurious to apples than anaërobic conditions, owing to the toxicity of the acetaldehyde, which is produced in greater quantities in carbon dioxide zymasis. S. S. ZILVA.

Influence of electrolytes in medium on gaseous exchange of mosses. A. MAYER and L. PLANTEFOL (Compt. rend., 1925, **181**, 1094—1095; cf. A., 1924, i, 809; 1925, i, 1120).—Mosses were soaked in dilute solutions of various salts and acids, withdrawn, dried in the air, and their gaseous exchanges studied. Practically all salts in low concentrations increased the oxidation intensity of the mosses and in higher concentrations retarded it. Different salts of the same anion or cation produced very different effects. Some salts, *e.g.*, calcium chloride, retarded the respiration without increasing it at any concentration. Acids exert their influence in much more dilute solutions, and if the concentration is large enough to inhibit respiration the inhibition period is followed by an accelerated respiration; the other effects described last for several days. The respiratory quotient increases or decreases with the increase or decrease in respiration intensity. L. F. HEWITT.

Equilibrium of cellular constituents and cellular oxidation intensity. Imbibition and oxidation in seeds. R. JACQUOT and A. MAYER (Compt. rend., 1925, **181**, 931—933; cf. A., 1924, i, 809; 1925, i, 1120).—Until the seeds of the broad-bean, maize, and pea-nut have absorbed a certain amount of moisture, no carbon dioxide is liberated; when this limiting value is exceeded, the oxidation increases rapidly to a maximum value as more water is absorbed, and then decreases rapidly from that maximum. The water content necessary for oxidation to commence, the maximum value of carbon dioxide liberation per 100 g. of the moist seeds, and the water content of the seeds at this maximum, are characteristics of each of the seeds examined. The maximum amount of carbon dioxide liberated per 100 g. of water in the seeds is the same for all the seeds (*i.e.*, 17 c.c. of carbon dioxide per 100 g. of water per hour). The hydrobiotic yield has also a maximum value and is approximately the same in each case. L. F. HEWITT.

Coupled fat and carbohydrate metabolism. H. VON EULER (Biochem. Z., 1925, **164**, 18—22).—The development of carbon dioxide by the press juice of sterilised seeds of *Brassica Napus* is increased during the early period of observation by the addition of cozymase solution, but no further increase is observed after 3½ hrs. P. W. CLUTTERBUCK.

Effect of light on tannin formation. MICHEL-DURAND (Compt. rend., 1925, **181**, 1171—1173; cf. A., 1924, i, 477).—Chestnuts and acorns were allowed to germinate and grow in washed sand in darkness and others in sunlight, and in every case from 5% to 23% of tannins was found in the plants. Less acetone-soluble tannins were found in every part, and less water-soluble tannins in every part but the leaves, of chestnut plants grown in darkness than in those grown in sunlight. The same but less marked differences were found in the case of oak plants. L. F. HEWITT.

Effect of light on the alkaloid content of *Lupinus luteus*, L. T. SABALITSCHKA and C. JUNGERMANN (Biochem. Z., 1925, **164**, 279—287; cf. this vol., 99).—The alkaloid content of seedlings grown on a nitrogen-free substrate for 14 days from germination, in the dark, is 74%, that of seedlings grown in daylight is 81%, of the original content of the seeds. When brought into the light for a further 14 days, the alkaloid content increase is 30% more than the corresponding increase in the normal plants. Again placed in the dark for 14 days, the alkaloid content decreases to 60%. Plants grown for 13 weeks in the light when placed in semi-darkness for 1 week show no increase in alkaloid content, whereas normal plants show a 25% increase during that time. E. C. SMITH.

Donnan membrane equilibrium in connexion with living cells. W. S. BUTKEVITSCH and W. W. BUTKEVITSCH (Biochem. Z., 1925, **161**, 468—487).—The phenomena connected with the Donnan membrane equilibrium are important in plant cells—particularly in the root system. In experiments with collodion membranes where silicic acid is present, the diffusion of diffusible anions is promoted. In this way, silicic acid influences the absorption of phosphate, and thus has a beneficial effect on the development of the plant when phosphates are present only in small concentration. The indiffusible sodium ions also affect the absorption of the diffusible potassium ions in the plant. H. I. COOMBS.

Isoelectric points for plant-tissue. W. J. ROBBINS and I. T. SCOTT (J. Agric. Res., 1925, **31**, 385—399).—When potato-tuber tissue was placed in small volumes of dilute buffer solutions and the reaction determined electrometrically, solutions of p_H 6·15 or greater became more acid, those of p_H 6·14 or less, more alkaline. The isoelectric points of potato-tuber tissue and of soya-bean root tips are p_H 6·4 and p_H 6·2—6·44, respectively, of the mycelia of *Gibberella saubinettii*, *Fusarium lycopersi*, and *F. oxysporum*, 6·2, 5·5, and 4·9, respectively.

H. J. CHANNON.

Tolerance of barley for alkali salts in soil. R. E. NEIDIG and H. P. MAGNUSON.—See B., 1926, 24.

Iron solubility tests in culture solutions at different p_H values. R. P. MARSH (New Jersey Agric. Exp. Sta. Ann. Rep., 1923, 252—256; Chem. Abstr., 1925, **19**, 3558).—The solubility of ferric glycerophosphate, soluble ferric phosphate, ferric tartrate, and ferrous sulphate in culture solutions is influenced by the hydrogen-ion concentration of the solutions. When the hydrogen-ion concentration is kept high, ferric glycerophosphate can be used as a source of iron for plants; when it approaches the neutral point, ferric tartrate is preferable.

A. A. ELDRIDGE.

Lignification. I. Nature of lignin: its physiological significance and its determination in timbers. II. Histological studies on the polysaccharides and aromatic constituents of the cell wall. M. M. MEHTA (Biochem. J., 1925, **19**, 958—978, 979—997).—I. Lignin, m. p. 170°, occurs in wood in the free condition, but the major part is in combination with polysaccharides. Free lignin can be extracted from the wood by alcohol. The combined lignin can be obtained by resolving lignocellulose into its constituents completely by heating with 4% sodium hydroxide at 10 atm. for 1 hr. This treatment does not decompose the lignin, which can be precipitated by acidifying the alkaline liquid and isolated in pure condition quantitatively by extraction with alcohol. This method can be utilised as a gravimetric method for the determination of lignin. The combined and free lignin was thus determined in a number of timbers. A microchemical colorimetric method is described. It is based on the fact that lignin gives a blue coloration with phosphotungstic and phosphomolybdic acids in phosphoric acid in presence of sodium carbonate solution. A study of the distribution of lignin in different parts of Scotch fir by the colorimetric method shows its presence in young twigs as well as in leaf and buds. It is assumed that lignin occurs in chemical combination with cellulose and related polysaccharides as an aromatic glucoside. The aromatic constituent just before lignification is not of the nature of " hadromal " described by Czapek (cf. A., 1899, i, 560). Pure, resistant α-cellulose is obtained when lignocellulose is resolved by the above method and can be determined accurately in this way.

II. α-, β-, and γ-Cellulose, α-, β-, and γ-oxycellulose, hydrocellulose, mannan, galactan, pectin, amylohemicellulose, hemicellulose, gums, starch, lichenin, and chitin have been isolated in the purest possible condition and their staining capacities determined. β- and γ-Cellulose show a greater affinity for stains than α-cellulose. Oxycelluloses, unlike α-, β-, and γ-celluloses and hydrocellulose, are stained by ruthenium-red. Two kinds of hydrocellulose can be differentiated by the coloration given by one of them with iodine in potassium iodide solution. Resins react in some respects like lignin and are associated with gums in different parts of the same plant. Lignification sets in very early in the life-history of the plant and occurs in ground-tissue, fibro-vascular bundles, medulla, and cuticularised cells. The relative amounts of different cellulosic constituents vary widely, according to the cultural conditions, general environment, and the nature of the plant. The middle lamella in young stems of pine is composed of neutral pectic substance, whilst in old timber it is composed of lignin, gums, and hemicellulose, pectin being absent.

S. S. ZILVA.

Microchemical identification of potassium [in plants] as picrate. N. PATSCHOVSKY (Ber. deut. Bot. Ges., 1925, **43**, 489—496).—The presence of potassium in botanical sections may be detected by placing on the slide one drop of an alcoholic solution of picric acid, and observing the formation of crystals of potassium picrate. The calcium, sodium, and ammonium salts are much less likely to separate, on account of the greater solubilities, but confirmation may be obtained by placing on the crystals a drop of sodium cobaltinitrite or of perchloric acid solution; potassium picrate is transformed by these into the characteristic cobaltinitrite or perchlorate. Plant organs may be immersed in a solution of picric acid in petroleum, the potassium picrate crystals then developing at the surface. If the test is negative or uncertain, the plant organ may be incinerated, and the ash similarly tested; it is suggested that potassium observed in the ash but not detected by the test in the organ may be present in some organic combination and not as a salt.

S. I. LEVY.

Chemical characteristics of green, yellow, and red leaves. H. COLIN and A. GRANDSIRE (Compt. rend., 1925, **181**, 1168—1170).—In red leaves, the reducing and non-reducing sugars are increased in amount, and the electrical conductivity is increased, but the ash, water, potassium, and calcium contents are decreased, whilst in yellow leaves the reducing sugar content, water and ash, and calcium content are appreciably higher, the electrical conductivity is slightly higher, and the non-reducing sugar and calcium content lower than in green leaves.

L. F. HEWITT.

Influence of manures on yield and morphine content of latex of opium poppy. H. E. ANNETT and H. D. SINGH.—See B., 1926, 74.

Oil content of seeds of opium poppy. H. E. ANNETT and M. N. BOSE.—See B., 1926, 66.

Ash constituents of Indian opium. H. E. ANNETT and M. N. BOSE.—See B., 1926, 74.

Root of *Gentiana lutea*, L. R. BINAGHI and P. FALQUI.—See B., 1926, 106.

Phytochemistry [1. Mannitol in jalap; 2. sucrose in belladonna root; 3. the cyanophoric glucoside in the bark of *Pyrus aucuparia*, Gaertn.; 4. a cyanophoric glucoside in *Achillea millefolium*, L.; 5. hydrocyanic acid in *Chloris petræa*]. L. ROSENTHALER (Arch. Pharm., 1925, **263**, 561—563).—1. (Cf. Buchner's "Repertorium für die Pharmazie," **54**, 221.) When an aqueous extract of the drug is evaporated to dryness, and an alcoholic solution of the residue is allowed to crystallise, mannitol (m. p. 165—166°) is obtained.

2. Crystals of sucrose separate from an alcoholic extract of belladonna root.

3. When the stem bark of *Pyrus aucuparia*, Gaertn., is extracted by the author's method ("Grundzüge der chem. Pflanzenuntersuchung," 2nd edition, p. 32) there is eventually obtained, by crystallisation from chloroform, a glucoside having the enzymolytic index of 560, determined by Bourquelot's method. This, and the fact that on hydrolysis the substance yields *l*-mandelic acid, indicates that a mandelonitrile glucoside is present.

4. The author (Biochem. Z., 1922, **134**, 219) has already shown that *Achillea millefolium*, L., is a cyanophoric plant. Determinations of the enzymolytic index indicate that a benzaldehyde cyanohydrin glucoside, possibly new, is present.

5. The South African grass *Chloris petræa* contains 0·002% of hydrocyanic acid; it also yields on distillation a little acetone. W. A. SILVESTER.

Occurrence of methyl mercaptan in fresh *Raphanus* roots (Daikon, *Raphanus sativus*, L.). N. NAKAMURA (Biochem. Z., 1925, **164**, 31—33).—Methyl mercaptan is isolated as the mercury compound from the distillate from the pulp of the fresh roots. P. W. CLUTTERBUCK.

Constituents of the tegument of the seeds of *Anagyris fœtida*. P. CONDORELLI (Annali Chim. Appl., 1925, **15**, 426—431).—The tegument of these seeds contains, not dextrose (cf. Reale, A., 1888, 188), but galactose, together with a mucilaginous substance, termed *podalirin*, which yields galactose and arabinose on hydrolysis and exhibits the characters of paragalacto-araban (cf. Schulze, A., 1891, 1179). T. H. POPE.

Phytobiochemical studies. II. A. ZLATAROV (Biochem. Z., 1925, **161**, 379—389).—The peas of *Cicer arietinum*, L., contain 1·61% lecithin (by phosphorus analyses). The following *compounds* were isolated from 70 kg. of the meal and analysed: $C_{43}H_{80}O_9NP(C_5H_8O_4)_2$, a lecithin-pentosan, $C_{43}H_{80}O_9NP(C_6H_{12}O_6)$, a lecithin-glucose, and $C_{43}H_{80}O_9NP$, a lecithin. They were easily oxidised and were kept in an atmosphere of carbon dioxide. When hydrolysed with 2% sulphuric acid they yielded no purine compounds, but gave a good yield of betaine. (Cf. A., 1916, i, 620.) H. I. COOMBS.

Nitrogen constituents of celery plants in health and disease. G. H. COONS and L. J. KLOTZ (J. Agric. Res., 1925, **31**, 287—300).—Two necrotic diseases of the leaves of celery, caused by the fungi *Cercospora apii*, Fres., and *Septoria apii*, Chester, have been investigated from a chemical point of view. In both cases, there is distinctly less total nitrogen in diseased than in healthy leaves; diseased tissue contains less nitric, amino-acid, and acid amide nitrogen, and more ammonia, "humin," and protein nitrogen. Nitrites are present in diseased but not in healthy leaves. The results are interpreted on the basis of the metabolism of fungi in cultures. It is considered that when the purely carbonaceous food supply is exhausted, the parasite must decompose nitrogenous constituents to obtain the requisite carbon and that a stage is reached when there is more nitrogen available than is required for protein synthesis etc., the excess appearing as ammonia and being lost in this form. C. T. GIMINGHAM.

Glucosides of indigenous orchids. P. DELAUNEY (Bull. Soc. Chim. biol., 1925, **7**, 1144—1147).—See A., 1925, i, 487.

Presence of loroglossoside (loroglossin) in *Listera ovata*, R. Br., and *Epipactis palustris*, Crantz. C. CHARAUX and P. DELAUNEY (Bull. Soc. Chim. biol., 1925, **7**, 1148—1150).—See A., 1925, i, 874.

Bromine-containing gland cells (bromuques) in *Antithamnion*, Naeg. C. SAUVAGEAU (Compt. rend., 1925, **181**, 1041—1043).—The colourless, highly refractive "gland cells" of *Antithamnionella sarniensis*, Lyle, *A. plumula*, Thur., *A. refractum*, Thur., *A. boreale*, Kjellm., *A. Pylaisæi*, Kjellm., and *A. Butleriæ*, Coll., contain bromine in such a form that on treatment with fluorescein, eosin, identified spectrometrically, is produced. This property does not disappear when the plant is dead and dried. It is suggested that the bromine is dissolved in a carbohydrate in the plant. L. F. HEWITT.

Formation of resin in conifers. I. Formation of resin in the needles of *Pinus cembra*. G. V. PIGULEVSKI and V. V. VLADIMIROVA (J. Russ. Phys. Chem. Soc., 1925, **56**, 325—334; cf. *ibid.*, 1924, **55**, 1).—The needles of *Pinus cembra* contain up to 10% of resin, the accumulation of which starts immediately the buds burst, follows a course parallel to that of the development of the needles, and has its greatest intensity when the increase of the dry matter of the needles is most rapid. The formation of ethereal oil in the needles occurs later than that of resin, and is at its maximum only after the accumulation of dry matter has begun to fail. Some increase in the resin content occurs during the second and third years of the life of the needles, and evidently occurs at the expense of the ethereal oil, of which the high-boiling constituents gradually disappear. The resin contains considerable proportions of acid and esters; the content of acid is less in the early than in the later stages of development of the needles, but diminishes in needles aged one or two years. T. H. POPE.

Formation of resin in conifers. II. Formation of resin in *Pinus cembra*. G. V. PIGULEVSKI (J. Russ. Phys. Chem. Soc., 1925, **56**, 335—348; cf. preceding abstract).—Confirmation is obtained of the view that the bulk of the secretion of the needles of *Pinus cembra*, composed of the resin and of part of the ethereal oil, is formed during the period of growth

of the needles, and is a function of the accumulation of dry matter. After severe frost, a marked increase in the secretion is observed on cutting the points of the needles; this phenomenon depends, not on increased secretion, but on increase in the pressure on the walls of the resin ducts, this producing compression of the tissues. After frost, the secretion contained 33% of ethereal oil. T. H. Pope.

Formation of resin in conifers. III. Formation of resin in *Abies sibirica*. G. V. Pigulevski and V. F. Grigorieva (J. Russ. Phys. Chem. Soc., 1925, **56**, 349—358; cf. preceding abstracts).—The needles of *Abies sibirica* contain up to 14% of resin, the formation of which proceeds parallel to that of dry matter and precedes that of ethereal oil. The resin contains esters and acid, the latter tending to diminish in amount during the period of vegetation. The ratio of ethereal oil to resin in the secretion is 1 : 2·7, so that the secretion contains 27·6% of the former. T. H. Pope.

Formation of ethereal oil in conifers. VII. Formation and transformation of ethereal oil in *Pinus strobus*. G. V. Pigulevski and V. V. Vladimirova (J. Russ. Phys. Chem. Soc., 1925, **56**, 359—366).—The dry needles of *Pinus strobus* contain up to 1% of ethereal oil, which accumulates as the needles grow and reaches its maximum development after the formation of dry matter has begun to fail. The higher-boiling components of the oil gradually diminish in quantity, possibly owing to transformation of the sesquiterpenes into non-volatile products. With this tree, the secretion consists of 15·9% of ethereal oil and 84·1% of resin. T. H. Pope.

Apparatus for the rapid evaporation of unstable solutions [sera etc.]. W. Gäde and W. Straub (Biochem. Z., 1925, **165**, 247—249).—The apparatus, which can be evacuated, consists of a vessel containing the solution, heated in a water-bath, connected with a second vessel containing sulphuric acid, cooled in a cooling bath. P. W. Clutterbuck.

Micrometer syringe. J. W. Trevan (Biochem. J., 1925, **19**, 1111—1114).—The principle of the instrument is based on the displacement of a volume of fluid by the well-fitting piston of a glass syringe. The displacement is measured by a Starret micrometer. The degree of accuracy of the instrument is demonstrated by a series of titration experiments; 0·01 c.c. of fluid is measurable with an error of less than ±1%.
S. S. Zilva.

General principle for the determination of different substances in body-fluids. L. Lorber (Biochem. Z., 1925, **162**, 354—358).—In order to avoid precipitation methods, the amount of any substance in a body-fluid is determined directly in the whole fluid before and after addition of a known amount of that substance, when, by use of an equation, the actual amount of substance in the fluid is calculable. The way in which this principle might be applied to titrimetric, colorimetric, nephelometric, fermentative, and eudiometric determinations is indicated.
P. W. Clutterbuck.

Modification of the method of isothermic distillation for the determination of the molecular concentration of blood serum. C. Hrynakovski and A. Rychter (Bull. Soc. Chim. biol., 1925, **7**, 1131—1138).—Barger's method for the determination of mol. wt., as modified by Rast, has been further modified to allow of the attainment of equilibrium and the measurement to be carried out at a constant temperature of 36·5° (±0·3°). Comparison under these conditions with a standard solution of urea shows human blood-serum to have a concentration of 0·292—0·302*M*.
C. P. Stewart.

Preservation of blood samples for analysis. A. T. Cameron and J. E. Williamson (Can. Med. Assoc. J., 1925, **15**, 393—394).—Sander's method (J. Biol. Chem., 1923, **58**, 1) is satisfactory for 4 days' preservation for analysis of dextrose, urea, creatinine, non-protein nitrogen, and cholesterol, but not of uric acid. Chemical Abstracts.

Micro-determination of dextrose by Bang's method. E. Cohn and A. Wagner (Biochem. Z., 1925, **160**, 43—51).—A large number of determinations of blood-sugar by Bang's second reduction method indicate that this method fulfils all its author's claims in regard to accuracy. P. W. Clutterbuck.

Determination of proteins in human blood-serum. I, II, III. W. Starlinger and K. Hartl (Biochem. Z., 1925, **160**, 113—128, 129—146, 147—154).—A very full, critical study of the gravimetric, Kjeldahl, quantitative precipitation, refractometric, polarimetric, nephelometric, diaphanometric, colorimetric, and viscosi-refractometric methods for the determination of proteins in human serum.
P. W. Clutterbuck.

Comparison of methods of protein precipitation. H. Wunschendorff (Bull. Soc. Chim. biol., 1925, **7**, 1158—1167; cf. A., 1925, i, 1346).—Metaphosphoric acid fails to precipitate proteins completely. The precipitate obtained by the use of trichloroacetic acid contains the whole of the protein, but appears to adsorb some non-protein material, depending on the concentrations of the acid and protein. Tungstic acid gives complete precipitation with less adsorption, but filtration is so slow that there may be appreciable hydrolysis of the protein. The use of colloidal ferric hydroxide, as previously described by the author, is recommended.
C. P. Stewart.

Micro-determination of chloride in blood and other media containing proteins. M. Claudius (Acta med. Scand., 1924, **61**, 4—7; from Chem. Zentr., 1925, II, 1198).—Twenty c.c. of blood or serum are treated with 0·2 c.c. of 0·04*N*-silver nitrate and 4—5 drops of strong nitric acid. The liquid is heated until the coagulum dissolves and finally concentrated by boiling to 0·25 c.c. One drop of 4% potassium permanganate is added and the precipitated manganese dioxide dissolved by addition of a drop of nitric acid. After cooling, one drop of 4% ferric nitrate and 5 c.c. of ethyl alcohol are added, and the solution is titrated with 0·01*N*-potassium thiocyanate in ethyl-alcoholic solution. G. W. Robinson.

Colorimetric micro-method for the determination of lactic acid in blood. B. MENDEL and I. GOLDSCHEIDER (Biochem. Z., 1925, **164**, 163—174).—After removal of protein with metaphosphoric acid and of carbohydrate with copper sulphate and lime, the blood filtrate is treated with concentrated sulphuric acid and the acetaldehyde produced gives with veratrol a red colour. The determination takes 1½ hrs., and requires 1 c.c. of blood. The limiting concentration of lactic acid is about 5 mg.%. Acetone, β-hydroxybutyric acid, acetoacetic acid, urea, uric acid, creatine, creatinine, glycine, alanine, and propionic acid do not give the red colour. Acetaldehyde, formaldehyde, and pyruvic acid give the colour before heating (distinction from lactic acid), but are present in blood only in negligible amount.
P. W. CLUTTERBUCK.

Application of phosphotungstic and phosphomolybdic acids to the determination of uric acid in milk and blood. G. REIF (Biochem. Z., 1925, **161**, 128—138).—A phosphotungstic–phosphomolybdic acid reagent is used for the production of a violet coloration with uric acid solutions which has the advantage of being permanent. Substances other than uric acid occurring in blood and interfering with this reaction may be removed from the solution by extraction with chloroform. C. RIMINGTON.

Micro-determination of urea in 0·1 c.c. of blood. B. POHORECKA-LELESZ (Bull. Soc. Chim. biol., 1925, **7**, 1085—1088).—The urea contained in 0·1—0·2 c.c. of a fluid containing that substance in a concentration similar to that in which it occurs in blood is hydrolysed by urease at 38—40° in a special apparatus. The mixture is rendered slightly alkaline by means of borate, and the ammonia is removed by a current of air and collected in dilute sulphuric acid. It is then determined by neutralising the sulphuric acid and adding an excess of sodium hypobromite. The excess of hypobromite is determined by adding potassium iodide and hydrochloric acid and the iodine liberated is titrated with sodium thiosulphate.
W. O. KERMACK.

Micro-Kjeldahl method without distillation. B. POHORECKA-LELESZ (Bull. Soc. Chim. biol., 1925, **7**, 1038—1043).—To 1 c.c. of urine diluted twenty times are added 1 c.c. of sulphuric acid and 1 c.c. of a 30% solution of potassium oxalate, the use of this salt being preferable to that of copper sulphate. After the combustion is complete, 2 c.c. of approximately 0·1*N*-sodium hypobromite are added to the mixture, which has been previously made neutral to methyl-red.

To determine the excess of hypobromite, excess of potassium iodide solution and 2 c.c. of *N*-hydrochloric acid are added. The iodine liberated is titrated with 0·02*N*-sodium thiosulphate. Allowance is made for the ammonium sulphate in the sulphuric acid used, as determined by a blank test. W. O. KERMACK.

Simple micro-determination of diastase in body-fluids. L. LORBER (Biochem. Z., 1925, **163**, 480—487).—The application is described of the author's sugar micro-determination (cf. A., 1925, i, 852) to the determination of the diastatic activity of body-fluids. The method claims to permit the comparison of the activities of different fluids by making experimental allowance for the differences, *e.g.*, p_H, between the various fluids. R. K. CANNAN.

Determination of free acid in gastric juice. H. E. BÜTTNER (Klin. Woch., 1925, **4**, 877—879; from Chem. Zentr., 1925, II, 1078).—In the titration of the hydrochloric acid in gastric juice, using alkali, combined hydrochloric acid is set free and the original free hydrogen ions are thus not determined. This may be avoided by colorimetric determination, using 0·1% methyl-violet. The values thus obtained are 50% lower than those obtained by direct titration.
G. W. ROBINSON.

Nephelometric determination of various substances. Determination of sulphate in urine. L. LORBER (Biochem. Z., 1925, **163**, 476—479; see A., 1925, i, 852).—The turbidity produced by the direct addition of barium chloride and acid to urine containing a known addition of sulphate is reduced by dilution to the same intensity as that produced in the urine without addition. From the dilution the urinary sulphate concentration can be calculated. An accuracy of 5% is claimed. R. K. CANNAN.

Determination of total sulphates in tissues. W. DENIS and S. LECHE (J. Biol. Chem., 1925, **65**, 561—563).—The tissue is autoclaved for 1 hr. at 200° with 5 parts of *N*-hydrochloric acid and the sulphuric acid determined in the filtered solution by precipitation as barium sulphate. The error of the method is ±5%. C. R. HARINGTON.

Volumetric determination of phosphoric acid in yeast. STAIGER (Brennereiztg., 1924, **41**, 209—210; from Chem. Zentr., 1925, II, 1105).—The solution of the ash from 5 g. of yeast (which should not contain more than 0·07 g. P_2O_5), after removal of silica, is titrated by the Pfyl method.
G. W. ROBINSON.

Measurement of fluids in perfusion experiments. M. KOCHMANN (Arch. exp. Path. Pharm., 1925, **109**, 358—361).—Apparatus for the automatic measurement of volume and rate of flow in perfusions is described. S. I. LEVY.

Pharmacological evaluation of atropine and scopolamine solutions, and of their stability. G. KÜHL (Arch. exp. Path. Pharm., 1925, **109**, 295—299).—The effect of injected solutions on the blood pressures of cats treated with acetylcholine hydrochloride has been found to be a suitable pharmacological method for determination of atropine and scopolamine solutions. No diminution in effect was observed after heating the solutions to 100° for 30 min. in presence of either acids or alkalis.
S. I. LEVY.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MARCH, 1926.

BIBLIOTEKA POLITECHNIKI ŚLĄSKIEJ

General, Physical, and Inorganic Chemistry.

Secondary spectrum of hydrogen at higher pressures. II. I. SANDEMAN (Proc. Roy. Soc., 1926, **A**, **110**, 326—341; cf. A., 1925, ii, 909).—The arc spectrum of hydrogen at higher pressures has been used to detect further regularities in the secondary spectrum. With its aid, a P and an R series have been selected, fitting with Richardson and Tanaka's 83 Q (A., 1925, ii, 11) into a P, Q, and R combination, and closely conforming with the combination principle. This band is one of a system of four to which P, Q, and R series have been allocated, and of which the null lines are given by the Rydberg formula $18567{\cdot}47-109678{\cdot}3/(n+0{\cdot}159883)^2$, where n takes the values 6, 7, 8, and 9. Indications have also been obtained of a band corresponding with the integer 10. A. B. MANNING.

Continuous hydrogen spectrum. II. H. SCHÜLER and K. L. WOLF (Z. Physik, 1926, **35**, 477—489; cf. A., 1925, ii, 829).—This spectrum is regarded as produced by the recombination of two unexcited atoms in an electric field; it begins between the lines H_β and H_γ and extends towards the ultra-violet. Photographs were taken of the electrical discharge through vapours of lithium, sodium, potassium, magnesium, calcium, zinc, and cadmium to which a little hydrogen was added. In the first three cases, where the resonance lines of the metals correspond with voltages below 2·9, no continuous spectrum was produced; in the other cases, the continuous spectrum observed is ascribed to collisions of the second type between the atoms of the excited metal and the hydrogen molecule causing dissociation followed by recombination. As 10 volts are necessary for the production of the excited hydrogen atom, and about 3 volts for the dissociation of the molecule, giving the 13 volts corresponding with the absorption line 1000 Å. observed by Lyman, these figures are in accord with the long wave-length limit of the continuous spectrum and the beginning of the emission spectrum in the ultra-violet.

The continuous spectrum cannot be regarded as an electron affinity spectrum, as the long wave limit would, in that case, be found in the infra-red.

E. B. LUDLAM.

Continuous absorption and emission spectra of the halogens. K. L. WOLF (Z. Physik, 1926, **35**, 490—494).—The views regarding hydrogen (preceding abstract) are extended to the halogens. The long wave-length limits of the emission and absorption bands of chlorine and bromine permit of their interpretation as spectra produced by the recombination of normal atoms in the presence of an electric field. In the case of iodine, apparently, the spectrum is only produced by the combination of a normal atom with an excited atom in a metastable, p_1 state. The value calculated for the difference of the spectral terms is in rough agreement with the difference observed between the long wave limit of the absorption and emission spectrum. E. B. LUDLAM.

Structure of the D_3-line of helium. W. A. MACNAIR and W. H. MCCURDY (Nature, 1926, **117**, 159).—An attempt to resolve the strong component of the doublet into two components was unsuccessful; thus the structure of the $1\pi-m\delta$ series of helium does not correspond with that of the equivalent series of the alkaline-earth metals.

A. A. ELDRIDGE.

Interpretation of spectra emitted by solid nitrogen and inert gases. L. VEGARD (Compt. rend., 1926, **182**, 211—213).—Spectra obtained by the bombardment of solid nitrogen and solidified mixtures of argon and traces of nitrogen by canal rays and swift cathode rays (A., 1925, ii, 474) are interpreted mathematically in the light of Deslandres' equation and Bohr's theory. It is supposed that the lines of each series appear as the results of the passage of electrons between a fixed energy level and successive levels of oscillation. Lines characteristic of the crystalline form of nitrogen have been found, and the series obtained using argon containing traces of nitrogen closely resemble those obtained with pure nitrogen. J. GRANT.

Line absorption spectra of the alkali metals. A. L. M. SOWERBY and S. BARRATT (Proc. Roy. Soc., 1926, **A**, **110**, 190—197).—The absorption lines of all the alkali metals show the combination lines $1s-md$ in the absence of an electric field. This is contrary to the selection principle, which limits the absorption spectra to the principal series $1s-mp$ (cf. Foote, Mohler, and Meggers, Phil. Mag., 1922, [vi], **43**, 659). The wave-lengths of the $1s-3d$ lines are as follows: lithium 3196·6, sodium 3427, rubidium 5165, cæsium 6894·7, 6848·5, and those of the $1s-4d$ lines of cæsium are 4425·8, 4417·7 Å. The absorption lines observed for cæsium do not agree with the calculated values and indicate that the present accepted term values are inaccurate. The influence of the presence of argon on the $1s-2d$ line for potassium was examined to determine whether the development of this series was due to the influence of neigh-

bouring atoms. No effect was observed even when the argon was at 2 atm. pressure. It is estimated from the relative absorption intensities of the lines $1s$—$2p$ and $1s$—$3d$ of potassium and rubidium that 12,000 atoms absorb the first member of the principal series for one which can absorb the latter. This ratio is the same for both metals. F. G. SOPER.

Absorption spectra of the vapours of aluminium, gallium, indium, and thallium in the ultra-violet. J. G. FRAYNE and A. W. SMITH (Physical Rev., 1926, [ii], **27**, 23—30).—With aluminium at about 1200°, the first seven pairs of the first subordinate series were absorbed; no lines of the second subordinate series were absorbed. The appearance of the aluminium lines was not anticipated from the point of view of the Bohr theory. Gallium at 1500° yielded 17 prominent lines, 13 being new. Lines from the $2p_1$ level were just as readily absorbed as lines from the $2p_2$ level. Indium at 1200° gave 18 lines, including all Grotrian's lines and $2p_2$—ms (2278 Å.). With thallium at 400°, lines from the $2p_2$ level appear, widening into bands with rise of temperature; at 800°, lines from the $2p_1$ level appear, remaining as fine absorption lines. The line $2p_2$—$6d$ (2168 Å.) is new. In the arc, the aluminium lines $2p_2$—md and $2p_1$—md (m=5—11) were completely absorbed, as also with indium were $2p_1$—$2s$ and $2p_1$—$3d$, in addition to the resonance lines $2p_2$—$2s$ and $2p_2$—$3d$. The $2p_1$ lines of gallium and indium may also be resonance lines. A. A. ELDRIDGE.

L_{II} L_{III} levels of the atoms silicon, phosphorus, sulphur, and chlorine. S. K. ALLISON (J. Washington Acad. Sci., 1926, **16**, 7—10).—X-Ray measurements by a number of investigators make it clear that the values of the energy levels L_{II} L_{III} of certain light atoms depend on the particular chemical combination considered. Such values have been calculated for silicon, phosphorus, sulphur, and chlorine, or for some of their compounds, and compared with photo-electric determinations of the energy of these levels in the hydrides of the same elements made by Holweck (A., 1925, ii, 336). For the hydrides of silicon, phosphorus, and sulphur, the levels have very nearly the same energy as for the elements alone, but between the elements and the higher oxides there is an appreciable difference in this respect. M. S. BURR.

Spark spectrum of potassium. W. DAHMEN (Z. Physik, 1926, **35**, 528—539).—The data for the spark spectrum are set forth and their analysis is attempted. E. B. LUDLAM.

Soft X-ray absorption limits of certain elements. (MISS) U. ANDREWES, (MISS) A. C. DAVIES, and F. HORTON (Proc. Roy. Soc., 1926, **A**, **110**, 64—90).—The electron energies associated with some of the longer wave-length absorption stages of chromium, manganese, iron, cobalt, nickel, copper, and zinc have been measured. The metals were examined in a specially designed X-ray tube in which one metal target could be substituted for another as required, and the X-rays emitted were detected by their photo-electric effects on a platinum disc guarded by platinum grids. The energies of the bombarding electrons in volts were plotted against the photo-electric current per unit bombarding current, and the critical potentials, in volts, given by the breaks in these curves, are as follows: chromium, 60, 70, 143, 160, 173; manganese, 68, 83, 100, 152, 174, 184; iron, 47, 73, 90, 106, 166, 181; cobalt, 94, 113, 171, 191; nickel, 104, 178, 196; copper, 112, 193, 206; zinc, 119, 200, 214. Extrapolation of the Moseley curves for the various absorption limits down to low atomic numbers shows that these values must be associated with absorption of energy by electrons in the M sub-group. The critical potentials obtained are attributed to selective absorption resulting in the transference of electrons from the sub-groups M_I and $M_{II, III}$, to various virtual orbits outside the normally occupied region of the atom, and not to actual ionisation. Evidence for this view is adduced from comparisons of measurements of absorption limits and of emission lines. F. G. SOPER.

Metastable P term in the manganese arc spectrum. R. A. SAWYER (Nature, 1926, **117**, 155).—Six lines observed (reversed) by Zumstein in a heavy manganese arc, and arising from low-lying energy levels in the atom, form a normal pp' group. A. A. ELDRIDGE.

Arc spectrum of palladium. K. BECHERT and M. A. CATALÁN (Z. Physik, 1926, **35**, 449—463; Anal. Fís. Quím., 1925, **23**, 457—476).—The spectrum shows uneven multiplicity, singlets and triplets being established. The ground term is a singlet S term with j=0. A list of the lines is given with their intensities and designation; their number is considerably smaller than for the analogous nickel and platinum. The Bohr magneton curve for the iron group (argon to zinc) is compared with that of the palladium group (krypton to cadmium). E. B. LUDLAM.

L X-ray absorption spectrum of antimony. A. JÖNSSON (Z. Physik, 1926, **35**, 387—389).—The L_{III} absorption edge of antimony has been measured for the pure element and for its compounds. The value 2993 X for the metal is reduced by about 5 for tervalent compounds and a little more for the quinquevalent compounds. Antimony pentasulphide exhibits very low displacement. Evidence of fine structure is shown in the compounds Sb_2O_3,nH_2O and SbOCl. R. A. MORTON.

Vacuum spark spectra of some of the heavier elements, and series classification in the spectra of ionised atoms homologous with copper, silver, and gold. J. A. CARROLL (Phil. Trans., 1926, **A**, **225**, 357—420).—For the spectra in the extreme ultra-violet Millikan's vacuum spark apparatus was used and the photographs were taken on Schumann plates. Reference lines were obtainable from impurities, or from standard lines of the iron spectrum of the second or third order spectrum. Detailed description and analysis are given of the spectra of Hg II, Ga III, In III, Tl III, Ge IV, Sn IV, and Pb IV. A new rule of the variation of diffused doublet separations with ionisation is proposed. Plates of the photographs are reproduced. E. B. LUDLAM.

New light-source and its possible uses. H. SCHÜLER (Z. Physik, 1926, **35**, 323—337).—In a discharge tube with a hollow cylindrical cathode an intense light is exhibited inside the cathode. This effect is not due to charges on the surrounding glass walls. The phenomenon has been used as the basis of a new experimental arrangement for running a discharge in gases or metallic vapours under widely differing conditions of excitation. A special form of slit has been devised whereby a single photograph can record simultaneously the spectra corresponding with a cross-section of the end-on discharge tube. The only factor capable of causing differences in the photograph is the excitation differences in the discharge. These differences provide a valuable method for spectrum analysis, *e.g.*, spark and arc lines, singlets, and triplets are readily distinguished. Emission caused by molecular collisions of the second kind may also be studied in this way. The technique has been adapted to work on the duration of excited state for resonance lines (*e.g.*, of mercury). Photographs showing the Stark effect for zinc vapour under fields from 10,000 to 25,000 volts/cm. have been obtained which seem specially suitable for revealing higher series terms. R. A. MORTON.

Specific lines of the arc spectrum. A. T. WILLIAMS (Anales soc. cient. Argentina, 1925, **99**, 13—84).—Characteristic arc lines not yet classified may be attributed to series corresponding with unstable states of elements. The intensity of arc lines is in harmony with Bohr's theory. The ratio of the number of arc lines to the number of spark lines varies periodically with the atomic number, the minima occurring at the end of each period, being zero for the halogens. The ionisation potential should show a reverse relation.

CHEMICAL ABSTRACTS.

Spinning electrons and the structure of spectra. G. E. UHLENBECK and S. GOUDSMIT (Nature, 1926, **117**, 264—265).—A development of the hypothesis of the spinning electron. Corresponding with each stationary state of an imaginary atom in which the electron has no spin, there must in general exist a set of states which differ in the orientation of the spin axis relative to the orbital plane; the energy difference of these states is proportional to the fourth power of the nuclear charge, and depends also on the quantum numbers which define the state of motion of the non-spinning electron. The theory leads to a modification of the explanation of the fine structure of the hydrogen-like spectra, and is also applicable to the structure of *X*-ray spectra. In the latter case, the screening doublets are regarded as "spin" doublets, since the sole reason for their appearance is the difference in orientation of the spin axis relative to the orbital plane. The analogy between the multiplet structure of optical spectra and the structure of *X*-ray spectra is immediately explained by the theory. The difficulties presented by anomalous Zeeman effects also disappear, and it may be possible to develop a quantitative theory of the Zeeman effect.

A. A. ELDRIDGE.

Rules of spectral structure. O. LAPORTE and W. F. MEGGERS (J. Opt. Soc. Amer., 1925, **11**, 459—463).—Three empirical rules concerning the spectral terms of the elements are suggested. The first deals with a periodic regularity in the terms of the elements between argon and copper. The second is the suggestion that the "raies ultimes" are combinations of the lowest term with the first higher non-metastable term of the same series system, definite preference being shown for an azimuthal quantum change of −1, even if the energy difference is somewhat larger than for other strong combinations. Finally, it is suggested that the "resonance lines" are combinations of the lowest term with a term of the highest multiplicity. Hence, if the normal state of the atom is one of the highest multiplicity, resonance lines and the "raies ultimes" will coincide, but not otherwise. S. BARRATT.

Theory of the continuous *X*-ray spectrum. M. S. VALLARTA (J. Math. Phys. Mass. Inst. Tech., 1925, [v], **1**, 1—7; cf. Bronstein, A., 1925, ii, 727).—The main point of the theory is that the continuous spectrum with its short wave-length limit is due to the stoppage (deceleration) of the stream of high-velocity electrons on reaching the anti-cathode, in contrast to the "characteristic" spectrum, which is radiation excited in the atom of the anti-cathode by electron impact. One consequence of the theory is that the short wave-length limit should be slightly different for different angles of observation. The shift would be too small to be detected for elements heavier than aluminium and for voltages above 1 kilovolt. E. B. LUDLAM.

***X*-Ray spectrometer with which wave-lengths are read directly on an ordinary micrometer screw.** W. W. NICHOLAS (J. Opt. Soc. Amer., 1926, **12**, 45—46).—The crystal table is rotated by means of an arm, terminating in a ball which bears against a movable plane surface, parallel with the axis of the table. The displacement of this surface, which is controlled by a micrometer screw, may be made numerically proportional to the wave-length corresponding with the given angular rotation of the table. Means are described by which measurements of wave-length with this instrument may be made independent of temperature and of inaccuracies in the micrometer screw. F. G. TRYHORN.

Continuous absorption along an optical series and structure of high-frequency absorption bands. R. BRUNETTI (Atti R. Accad. Lincei, 1925, [vi], **2**, 252—256; cf. Fricke, A., 1921, ii, 6).—At the edge, on the higher-frequency side of the absorption bands of the elements in the region of moderately high frequency, are two or three minima. They are situated on a background of decreasing intensity which occurs just before the rise of intensity marking the edge of the band. These, regarded by Kossel as inverted lines corresponding with the early terms of a semi-optical series, are now thought to be later terms of the high-frequency series to which the band is referred. The minimum immediately preceding the rise of intensity marking the edge of the absorption band—generally the second—is regarded as the

true limit of the series. The occasional presence of three minima is due to the overlapping of two such series having a common limit. The distance between the two minima of which, in the majority of cases, the fine structure consists, *i.e.*, the distance in Å. between the inversion band of the first line of the semi-optical series and its limit expressed in energy units, will, because of the small dispersion, differ little from the work necessary to carry an electron without altering its velocity from the first optical level to infinity. Expressed in volts, this distance closely approximates to the ionisation potential of the excited atom, *i.e.*, to the difference between the ionisation potential and the resonance potential of the normal atom. This result is verified by applying it to the β-radiation of the K spectrum of sodium and to the K-series of sulphur of chlorine. Moreover, the $2p_1$ orbits of sodium and of magnesium penetrate the interior of the atomic residue; this is assumed to account for the inverted semi-optical series obtained with solid elements and gases at atmospheric pressure. W. E. Ellis.

Magnitude of the K-absorption discontinuity. F. K. Richtmyer (Physical Rev., 1926, [ii], **27**, 1—17).—Work previously abstracted (Warburton and Richtmyer, A., 1925, ii, 1103) is presented in greater detail with minor corrections. Values of $R_L^K(=k_K/k_L)$ and τ_a (the corrected atomic absorption coefficient at the K limit $\times 10^{21}$) are, respectively, as follows: molybdenum, 7·5, 13·3; silver, 7·8, 11·0; tin, 6·6, 8·90; tungsten, 5·65, 3·19; gold, 5·65, 2·57; lead, 5·40, 2·37. The results do not support any existing theory. A. A. Eldridge.

Resonance absorption in the region of X-rays. V. Posejpal (Compt. rend., 1926, **182**, 272—274).—The absorption of the K-series of tungsten has been examined by placing thin tungsten leaves of different thicknesses between the slit of a Seeman spectrograph and the photographic plate, so that the spectrum was covered by a central absorption band, on which the densities of the α_2, α_1, and β_1 rays were measured. The mass absorption coefficient μ/ρ was thus obtained and compared with the values μ_0/ρ calculated by the formula of Bragg and Peirce. For the ray β_1 the absorption is normal, but for the rays α_1 and α_2 the absorption is much higher than the calculated value, indicating strong selective absorption for these rays, in agreement with the author's previous suggestion (Posejpal, Soc. Roy. Sci. Bohême, 1925) that a resonance absorption occurs when the atom is excited at the L_2 or L_3 level. Similar differences are found for the mass coefficients of absorption of fluorescence $\tau'/\rho=\mu/\rho-0{\cdot}2$. If the experimental and calculated values differ by $\tau'/\rho=\tau/\rho-\tau_a/\rho$, the ratio of the values of τ'/ρ for the α_1 and α_2 rays should equal the ratio of the numbers of electrons in the L_3 and L_2 levels which equals 2. The mean of the experimental values gives the ratio as 1·6.

W. Hume-Rothery.

Zeeman effect and multiplet structure. A. Bramley (J. Franklin Inst., 1926, **201**, 3—16).—It is assumed that the stationary orbits of electrons are not (as in Bohr's original theory) dynamical orbits for which the radiation may be neglected, but are geodesics in a four-dimensional Weyl space. Thence the following formula is deduced for the terms in the spectrum of any one element,

$$H=W\left[1-\frac{j(j+1)}{r^2-(2k-1)^2}\cdot\frac{KW^4}{r^K}\right]+mw\left[\frac{1}{2}+\frac{r^2-(2k-1)^2}{8j(j+1)}\right],\ r^2\neq(2k-1)^2,$$

where k, j are the azimuthal and inner quantum numbers, r is the multiplicity of the term, w the Larmor precession, W the series term of the lowest frequency component of the unperturbed multiplet, K a function of the atomic number. This formula should represent both the undisturbed and the Zeeman separations of the multiplet. The formula is compared with experiment for the barium, strontium, and calcium doublets and triplets.

C. J. Smithells.

Mechanical models for the Zeeman effect. C. G. Darwin (Phil. Mag., 1926, [vii], **1**, 161—195).—The possibility is discussed of constructing mechanical models of the atom for representing spectral phenomena. The mathematical theory of vibrating systems is developed, and a simplification of Voigt's model of the D-lines (Ann. Physik, 1913, [iv], **41**, 403; 1914, [iv], **42**, 210), which invests it with greater physical significance, is given. No success has been attained in constructing a satisfactory form of model for the triplet. In spite of the rather striking success with the doublet, it seems probable that, although models can always be devised for any type of line, they will not in general possess the simplicity which would make them useful.

A. B. Manning.

Electro-optical researches on sodium vapour. H. Kopfermann and R. Ladenburg (Ann. Physik, 1925, [iv], **78**, 659—679).—It has been shown that sodium vapour exhibits a positive electrical double refraction in the immediate vicinity of the D_2-line. A similar effect for the D_1-line was not detected and cannot be as much as one-tenth so great as that for the D_2-line. It is suggested that this effect is not due to the asymmetrical orientation of the atoms in the electric field, but rather to the inverse Stark effect in which, whilst the π and σ components of the D_2-line are shifted differently towards the red, those of the D_1-line are shifted to the same extent. From measurements of magnetic rotation of the plane of polarisation it is shown that under a field of 30,000 volts/cm. the π component of the D_2-line is moved about 0·001 Å. nearer the red than the σ component. By allotting Kramers' proposed magnetic quantum numbers, the results are employed to discuss the positions of the electrical levels associated with the p and s terms of the spectrum of sodium.

A. E. Mitchell.

Sphere of action of excited atoms. W. Schütz (Z. Physik, 1925, **35**, 269—275).—Light from a quartz mercury vapour lamp is thrown on a quartz vessel containing mercury vapour; the resonance radiation produced is focussed on a second vessel containing mercury vapour which can be subjected to a magnetic field up to 20,000 gauss. The radiation excited in this second vessel is focussed on a photographic plate. Between the two vessels can be

placed an absorption tube containing mercury vapour and a calcite prism; a second absorption tube containing mercury can be placed in front of the photographic plate. Thus it was possible to study the absorption of the primary and secondary resonance radiation with and without the polariser and without a magnetic field or with the magnetic field parallel or perpendicular to the plane of polarisation. The light excited by vibrations parallel to the magnetic field was expected to excite only the middle (π) Zeeman line, but the outer (σ) lines also appeared, their intensity depending on the vapour pressure of the mercury, but not appreciably on the strength of the magnetic field. To account for this result, the hypothesis is advanced that the number of collisions must be 50—100 times greater than that given by the kinetic theory of gases. This is called the "sensitivity" factor, and the conception is applied to several cases of resonance phenomena.

E. B. LUDLAM.

Quadratic Stark effect of the alkalis. W. THOMAS (Z. Physik, 1926, **35**, 556; cf. this vol., 3). —Explanatory note to the previous paper.

E. B. LUDLAM.

Spectrographic studies of the Compton effect. M. DE BROGLIE and A. DAUVILLIER (J. Phys. Radium, 1925, [vi], **6**, 369—375).—A *résumé* of work previously published (see A., 1924, ii, 581).

"Modified scattered" *X*-radiation. C. G. BARKLA and S. R. KHASTGIR (Nature, 1926, **117**, 228—229).—It is definitely known that even after the *J*-transformation has taken place in a scattered *X*-radiation, and this has become a "modified scattered" radiation when its absorbability is measured in certain substances, it subsequently has the same absorbability as the primary radiation when measured in certain other substances. Thus, either (*a*) the second spectral line in Compton's experiments does not represent another wave-length in the secondary radiation, or (*b*) wave-length may change without a corresponding change in the activity of an *X*-radiation.

A. A. ELDRIDGE.

Critical potentials of hydrogen in the presence of catalytic nickel and copper. J. H. WOLFENDEN (Proc. Roy. Soc., 1926, **A**, **110**, 464—476).—Gauger's measurements of the critical potentials of hydrogen in the presence of catalytic nickel (A., 1924, ii, 200) are criticised, and a modified method is described. Targets of catalytic nickel, plain nickel, and catalytic copper were bombarded with electrons from a platinum filament coated with barium and strontium oxides, in the presence of hydrogen at very low pressures. The accelerating voltage was raised in steps of 0·25 volt, and the ionisation produced was determined for each value of the accelerating voltage. A repetition of Gauger's work, in which measurements were made of the photo-electric effect due to the excited radiation, gave no definite results. The ionisation curves at pressures of 10^{-2} mm. exhibit a marked discontinuity corresponding with the ionisation potential of the hydrogen molecule. The curves are exactly similar with catalytic and with plain nickel. The curves at pressures of 10^{-4} mm. exhibit breaks at 13·4 and 11·4 volts, the former representing the ionisation potential of the hydrogen atom. All three surfaces examined give similar curves. The effects observed at the lower pressures are associated with hydrogen at the catalyst surface, and prove the existence of atomic hydrogen in systems comprised of the gas in contact with catalytic nickel, plain nickel, and catalytic copper. The experiments, however, do not exclusively correlate the presence of atomic hydrogen with catalytic activity.

A. B. MANNING.

Influence of temperature on the photo-electric effect of alkali metals. H. E. IVES and A. L. JOHNSRUD (J. Opt. Soc. Amer., 1925, **11**, 565—579).—The variation of photo-electric current with temperature, between +20° and −180°, for sodium, potassium, and rubidium is continuous, without abrupt changes. The effect is relatively small for sodium. The behaviour of rubidium is similar to that of potassium (cf. A., 1924, ii, 444).

Smooth, crystalline surfaces of potassium, obtained by cooling slowly the liquid metal, show a much greater effect than the rough ones previously studied. The variation for yellow light is 10—15 times for the above temperature range. It is concluded that the effect is intimately connected with surface strains.

S. BARRATT.

Photo-electric conductivity in selenium. B. GUDDEN and R. POHL (Z. Physik, 1925, **35**, 243—259).—Crystals of the red modification of selenium were obtained about 2 mm. long, but containing so many small holes as to be useless for obtaining an absorption spectrum. When exposed to visible light, an immediate "primary" photo-electric current was produced, the strength of which was proportional to the intensity of the light. The maximum effect was produced by wave-length 700 μμ. The effect of photo-electric excitation is to extend the absorption band towards longer wave-lengths, and illumination with light in this extended region hastens the return of the displaced electrons. The behaviour closely resembles that of sodium chloride crystals which have been coloured by exposure to *X*-rays. The photo-sensitivity of metallic selenium and technical selenium cells is discussed and regarded as due to "secondary" conduction analogous to the "coherer." It is pointed out that the magnitude of the current is of an entirely different order from anything obtainable as a saturation current of photo-electrons from the surface of a metal. The results depend on experimental conditions, mode of preparation, intensity of light, period of illumination, and applied *E.M.F.* to such an extent as to make theorising premature.

E. B. LUDLAM.

Photo-electric radiation pyrometer. F. A. LINDEMANN and T. C. KEELEY. See B., 1926, 70.

Photo-ionisation and relative absorption probabilities of cæsium vapour. F. L. MOHLER, P. D. FOOTE, and R. L. CHENAULT (Physical Rev., 1926, [ii], **27**, 37—50).—In the range examined, 3184—2600 Å., experimental values of the Einstein probability coefficient B_λ are given by an empirical relation, $B_\lambda = B_{\lambda_1} e^{-a(\lambda_1 - \lambda)}$, where $\lambda_1 = 3184$ and B_{λ_1}

is the corresponding value of B_ν. Ionisation, due to the production of excited atoms which are ionised by atomic collision, is produced only at wave-lengths corresponding with the principal series lines.

A. A. ELDRIDGE.

Positive rays produced in thermionic vacuum tubes containing alkali metal vapours. H. E. IVES (J. Franklin Inst., 1926, **201**, 47—69).—Investigation of the current–voltage curve in thermionic emission from a tungsten filament in an evacuated bulb, the walls of which were covered with alkali metal, showed not only a shift in the position of the curve compared with that for a normal high-vacuum cell, but also a change in shape. This change in the saturation curve is similar to that produced by mercury vapour owing to ionisation, but occurs below the ionising potential of the alkali metal vapour. Further, the positive ions may be obtained when there are no electrons present at all. The experiments establish the fact that it is possible to produce positive ions of the alkali metals by allowing their vapours to come in contact with a heated tungsten filament, in a temperature range limited by the coating of the filament with a layer of alkali metal (lower limit) and the emission of electrons from the filament (upper limit). It appears that the carriers are aggregates of metal atoms positively charged. The facts are explained on the assumption that the metal particles are dissociated on striking the filament, which also exerts an attractive force on the electrons.

C. J. SMITHELLS.

Döppler effect in canal rays of hydrogen, oxygen, and nitrogen. H. E. KREFFT (J. Sci. Assoc. Vizianagaram, 1925, **2**, 21—40; cf. A., 1925, ii, 3).—The Döppler effect of H_β, the spark lines of oxygen 4592 and 4254 Å., and the spark line of nitrogen 4530·3 Å. have been studied. In the region 5000—4400 Å., the following lines show the Döppler effect: 5005·7, 5002·7, 4643·4, 4630·9, 4601·3, 4530·3, and 4432·0 Å. The Döppler effects of the spark lines of oxygen and nitrogen are similar. The intensity minimum separating the Döppler effect from the undisplaced lines is much broader for these gases than for the Balmer arc lines of hydrogen. Also the velocities of the extinction maxima for the former are approximately as $1 : \sqrt{2}$, but for the Balmer lines the ratio is considerably larger. The carrier of the Balmer arc lines is the neutral atom, and of the spark lines the positively charged atom, and the differences observed are probably the expression of a general law, so that the Döppler effect of a spectral line might be used to determine whether it is an arc or a spark line. The dependence of the mean free path of light emission on velocity does not appear to be so great for Balmer lines as hitherto supposed. When the canal rays of hydrogen are passed through oxygen or nitrogen, the intensity of light emitted by the moving particle is increased. If hydrogen in the discharge tube is mixed with other gases, modifications of the processes taking place in the cathode fall are obtained. Velocity distribution in the canal rays cannot be completely explained by assuming that both atoms and molecules are accelerated in the cathode fall, the molecules being split up later into atoms, but observations on a Döppler effect in the Balmer lines before the cathode show that, already in the cathode fall, charges are produced which greatly influence the velocity distribution in the canal rays. Thus the latter afford a means of studying events in the cathode fall.

M. S. BURR.

Free path of slow protons in helium. G. P. THOMSON (Nature, 1926, **117**, 235).—The scattering of protons in helium is maximal for rays of energy about 10,000 volts (cf. Dempster, this vol., 4). The scattering of protons in hydrogen increases with decreasing energy of the rays, but less rapidly than if the scattering were due to forces of the inverse square type.

A. A. ELDRIDGE.

New source of positive ions. C. H. KUNSMAN (Science, 1925, **62**, 269—270).—A previously fused mixture of iron oxide with 1% of an oxide of an alkali or alkaline-earth metal, with or without 1% of aluminium oxide, when used as a hot anode or employed as a coating for a platinum anode, gave after partial reduction steady positive ion currents up to 10^{-4} amp./cm.^{2} in a vacuum (10^{-6} mm.).

A. A. ELDRIDGE.

Production of ultra-violet light by impact of low-speed electrons on a metal surface. P. BRICOUT (Compt. rend., 1926, **182**, 213—215).—A radiation having a wave-length between 2300 and 2100 Å. has been detected spectrographically in the bombardment of a platinum anode by a stream of electrons drawn from a glowing filament in a high electrostatic field. The filament was held axially in a silica bulb with the anode placed close to it. Both were surrounded by a molybdenum cylinder, this and the anode being maintained at potentials positive to the filament of several thousand volts and about 6 volts, respectively. The silica tube being exhausted as highly as possible, the discharge can be considered as purely electronic, the radiation being due to the excitation of the metal atoms by the electronic shocks.

J. GRANT.

Deduction of the essential properties of nucleus and electron from the metric-electromagnetic field. H. REISSNER (Physikal. Z., 1925, **26**, 925—932; cf. A., 1925, ii, 349).—Theoretical. The earlier treatment is extended and use is made of both the Maxwell equations and the Einstein field equations.

R. A. MORTON.

Cooling effect on oxide cathodes. G. MICHEL and H. J. SPANNER (Z. Physik, 1926, **35**, 395—400).—Platinum wires coated with oxides of the alkaline earths were used as filaments inside a cylindrical anode in a tube from which all remaining traces of gas were removed by vaporising nickel from the anode. The difference in the current needed to maintain the filament at the same temperature, with and without applied potential on the anode, was measured by a Wheatstone bridge method. The work of escape of the electrons, expressed in volts, was: tungsten 4·57, calcium oxide 2·45, strontium oxide 2·27, barium oxide 1·69.

E. B. LUDLAM.

Laws governing the pulling of electrons out of metals by intense electrical fields. R. A. MILLIKAN and C. F. EYRING (Physical Rev., 1926, [ii], **27**, 51—67).—In explanation of results of determinations of the current from thoriated tungsten filaments in a vacuum, due to radial fields up to 2×10^6 volts/cm., it is suggested that the field currents are due to conduction electrons pulled from minute peaks on the surface; fatigue effects may be due to the rounding off of these peaks. The conduction electrons, unlike the thermions, do not share in the thermal energy of agitation of the atoms.

A. A. ELDRIDGE.

Discharge of electricity through gases. J. S. FOSTER (Nature, 1926, **117**, 197).—A brief discussion of the field distributions obtained with Lo Surdo tubes.

A. A. ELDRIDGE.

Langevin's theory of ionic mobility. H. R. HASSÉ (Phil. Mag., 1926, [vii], **1**, 139—160).—The importance of Langevin's theory of ionic mobility (Ann. Chim., 1905, [viii], **5**, 245) is emphasised, and its scope and method are briefly outlined. The values of A in Langevin's expression for the mobility, $k=A(1+m/M)^{\frac{1}{2}}/\sqrt{\rho(K-1)}$, have been recalculated as a function of λ, where $\lambda^2=8\pi p\sigma^4/(K-1)e^2$, M is the mass of the ion, m that of a molecule of the gas, ρ is the density, p the pressure, and K the dielectric constant of the gas, e is the charge on an electron, and σ the distance between the centres of the molecule and the ion at the instant of collision. Given the magnitude of the attractive forces, the mobility passes through a maximum for a particular value of σ. To calculate the mobility, some assumption must be made as to the values to be adopted for the radii of the molecule and the ion. The assumption that the molecule behaves as an elastic sphere of radius s, which is determined from measurements of the viscosity, leads to values for the mobility of a univalent ion far larger than those obtained experimentally. The molecules must therefore form a cluster round the ion, and various assumptions are made as to the size and arrangement of the cluster, with, however, only partial agreement between the calculated and observed mobilities. In particular, the theory as at present developed fails to account for the fact that the mobility of a positive ion depends only on the nature of the gas through which it is diffusing.

A. B. MANNING.

Mobility of ions in air. I. Negative ions in moist air. A. M. TYNDALL and G. C. GRINDLEY (Proc. Roy. Soc., 1926, **A**, **110**, 341—358).—The mobility of negative ions in air at atmospheric pressure has been determined by an improved absolute method, involving the application of an alternating field of the "square wave" type between two parallel plates, and the production of ions by α-ray flashes synchronised with the field. When the current arriving at the electrometer is plotted with the frequency of the alternating field, a curve with a sharp peak is obtained, the position of which gives an accurate measure of the mobility. In ordinarily dry air, the mobility of the negative ion is 2·15 cm./sec. per volt/cm. With the addition of water vapour, the mobility falls rapidly at first and then more slowly to the value 1·60 in saturated air.

A. B. MANNING.

Mobility of ions in air. II. Positive ions of short age. A. M. TYNDALL and G. C. GRINDLEY (Proc. Roy. Soc., 1926, **A**, **110**, 358—364; cf. preceding abstract).—The method of the previous paper has been applied to the measurement of the mobility of positive ions of short age. Evidence was found of the existence of two types of positive ions, an initial ion and a final ion. The initial positive ion has a mobility which is indistinguishable from that of a negative ion, and is affected by water vapour in the same way. The presence of water vapour, however, has a retarding influence on the rate of transformation into final ions.

A. B. MANNING.

Mobility of gaseous ions in gaseous hydrogen chloride and hydrogen chloride–air mixtures. L. B. LOEB (Proc. Nat. Acad. Sci., 1926, **12**, 35—41; cf. A., 1925, ii, 7).—Determinations with highly purified gaseous hydrogen chloride show that at 20° and 760 mm. the mobilities of the positive and negative ions are 0·65 and 0·56 cm./sec. per volt/cm., respectively. These figures constitute the first exception to the generalisation that the mobility of a negative ion is never less than that of a positive ion. Mobility measurements at 60 and 16·3 mm. demonstrate the validity of the inverse pressure law. The constant of attachment of electrons to molecules of hydrogen chloride to form negative ions is nearly as low as that for gaseous chlorine. The experimentally determined mobilities in hydrogen chloride–air mixtures over the range 20—100% hydrogen chloride are represented in a fairly satisfactory manner by the author's mixture relationship (*loc. cit.*). At low hydrogen chloride concentrations, the mobilities are extremely sensitive to slight changes in the hydrogen chloride content. During the process of purification of hydrogen chloride a peculiar pink solid modification was observed.

J. S. CARTER.

Mobility of gas ions in hydrogen chloride mixtures and the nature of the ion. L. B. LOEB (Proc. Nat. Acad. Sci., 1926, **12**, 42—48; cf. Phil. Mag., 1924, [vi], **48**, 446, and preceding abstract).—The initial lowering of mobilities with traces of hydrogen chloride indicates that an ion gathers round it a higher concentration of hydrogen chloride than is present in the rest of the mixture. Assuming that molecules of hydrogen chloride and air are attracted to the ion with forces varying inversely as the fifth power of the distance, calculations show that the molecules of higher dielectric constant are present in far greater numbers in the immediate vicinity of an ion than in the rest of the gas. The cluster of molecules closely bound to the ion may be fairly stable, whilst the rest of these molecules constitute a very labile cluster.

J. S. CARTER.

Density of boric oxide glass and the suspected variation in the atomic weight of boron. H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON (J.C.S., 1926, 70—79).—Beads of pure boric oxide glass have been prepared from six boron minerals from different parts of the world, and their density

accurately determined by a flotation method. This consisted in sealing the beads, which were about 3 mm. in diameter, in glass tubes containing the same mixture of dry, inert organic liquids of suitable density (pentachloroethane and trimethylene dibromide containing 61·07% by volume of the former); then observations were made of the temperature of flotation of the beads in each sample. Separate determinations were made of the density and thermal expansion of the liquid mixture. The mean density of fused boric acid in the neighbourhood of 18° is 1·7952, whilst that of the different samples varies from 1·79711 to 1·79404, corresponding with variations in the atomic weight of boron from 10·847 to 10·788. The atomic weights thus obtained from three of the samples agree well with those previously determined from the BCl_3 : 3Ag ratio for the same samples, 10·847, 10·823, and 10·818, as against 10·841, 10·825, and 10·818 (A., 1925, ii, 346). A. B. MANNING.

Separation of chlorine into isotopes. The light fraction. W. D. HARKINS and F. A. JENKINS (J. Amer. Chem. Soc., 1926, **48**, 58—69; cf. A., 1924, ii, 142).—See A., 1925, ii, 1108.

Uranium-*X*: extraction and determination. R. DE (J. Sci. Assoc. Vizianagaram, 1925, **2**, 43—52).—The various methods in use for the extraction of the group of radioactive products known as uranium-*X* have been compared and discussed. A measure of the uranium-*X* content of the uranyl nitrate employed has been obtained by converting the salt into the oxide U_3O_8, preparing films of varying thickness but of the same area, measuring their β-ray activity, and determining by extrapolation the limiting activity per mg. of U_3O_8. The general method of separation is by the use of an adsorbing agent in the uranyl nitrate solution. Ferric hydroxide sol and cerium fluoride proved to be the best adsorbents, whilst the yield with lamp-black was very poor. The ferric hydroxide method is most convenient, since repeated extractions can be carried out without further purification of the uranium salt. The separation is best carried out by dissolving uranium nitrate in a definite volume of saturated sodium fluoride, allowing to remain for several hours, and adding a small amount of ferric hydroxide sol. The sol coagulates and settles in a few hours, carrying down uranium-*X*, and is freed from uranyl salts by filtration. On replacing sodium fluoride by equivalent quantities of sodium chloride, nitrate, or sulphate, only very poor yields are obtained. The acetate gives a better yield, but not so good as the fluoride. This behaviour may be due to the fact that the uranyl ion has an inhibiting effect on precipitation, but is largely removed by fluoride or acetate to form a complex ion; or it may be due to the insolubility of the fluoride and acetate of uranium-X_1, since this is an isotope of thorium. Experiments have also been made to determine whether, when uranium-X_1 is first formed from the uranyl radical, it is present as an unstable peroxy-salt, $U\text{-}X_1O_2(NO_3)_2$, but no definite indications of the existence of this compound have been obtained. In connexion with these experiments, cerium oxalate and zirconium iodate were shown to carry down a fairly high percentage of uranium-*X*.
M. S. BURR.

Long-range α-particles emitted by radioactive substances. (MLLE.) I. CURIE and N. YAMADA (J. Phys. Radium, 1925, [vi], **6**, 376—380).—An experimental verification of the inverse proportionality between the range of α-particles and the pressure, up to several atm. pressure. The method of counting scintillations on a zinc sulphide screen is used, the medium (dry air, oxygen, or carbon dioxide) and the active deposit being contained in a strong brass vessel. Methods of measuring the ratio of the number of long-range α-particles to those of ordinary range are also described. C. H. D. CLARK.

Determination of the content of radon in the atmosphere. F. BÉHOUNEK (J. Phys. Radium, 1925, [vi], **6**, 397—400).—An apparatus is described for determining radon in air, the method depending on the solubility of the gas in carbon disulphide, which increases considerably as the temperature is lowered. At −80°, the coefficient of absorption is 328. About 150 litres of air are first enclosed in the apparatus, and then caused to circulate for an hour through two Dewar flasks, each containing 230 c.c. of carbon disulphide cooled at −80°. The quantity of radon extracted is compared with that from a standard radium solution, and is found to be 0·861 of the whole. The method has the advantage of avoiding the use of liquid air and of speed in sampling and carrying out a determination. An accuracy of ±3% is claimed.
C. H. D. CLARK.

Detection of magnetic moment of the nucleus by α-particle deflexions. W. WESSEL (Ann. Physik, 1925, [iv], **78**, 757—785).—Mathematical. The magnetic moment is not to be detected by means of single α-particle deflexions. More complex deflexions give a change varying as the primary α-particle velocity to the sixth power, and the nuclear charge to the minus fourth power. For the light elements magnesium and aluminium, magnetic moments of the order of a Bohr unit are easily detectable.
R. A. MORTON.

Long-range particles emitted by polonium and the active deposits of radium and thorium. N. YAMADA (J. Phys. Radium, 1925, [vi], **6**, 380—389).—See A., 1925, ii, 255, 621, 834.

δ-Rays produced by α-particles in different gases. J. CHADWICK and K. G. EMELÉUS (Phil. Mag., 1926, [vii], **1**, 1—12).—The production of δ-rays in air, argon, helium, and hydrogen has been investigated by photographing the tracks of α-particles in a Wilson cloud chamber. The active deposit of thorium was used as the source of the α-particles. The δ-rays are observed as short tracks of varying length radiating from the main α-particle track. The maximum lengths of the δ-ray tracks were 2 mm. in hydrogen, 2·6 mm. in helium, and about 0·45 mm. in air and argon, all at atmospheric pressure, which accords with the view of a definite initial maximum velocity independent of the gas. Assuming the range to be proportional to the cube of the velocity, the maximum velocity of the δ-particle is almost twice that of the α-particle. The number of δ-rays distinctly projecting from the initial portion of the α-particle tracks was about 10 per cm., and was

roughly the same in all cases (at atmospheric pressure). The number per cm. remained about the same along the α-particle track until about 3 cm. from the end, when it fell off very rapidly. These results are in accord with the view that the δ-ray arises from the collision of the α-particle with an electron in the atoms through which it passes, assuming, for the distances involved in these collisions, the α-particle and the electron to behave as point charges, and the law of force between them to be that of the inverse square. A. B. MANNING.

Regularity in the action of electromagnetic waves. Disruptive action on [atomic] nuclei. E. BRUMMER (Z. Elektrochem., 1926, **32**, 7—13).—A regularity in the action of electromagnetic waves is demonstrated, viz., that the smaller the wave-length the nearer is the effect to the atomic nucleus. From this it is concluded that sufficiently short waves would have a disruptive action on the nucleus. These "active" wave-lengths are calculated from the energy possessed by α-particles in the Rutherford and other disintegration experiments and also from the deficiency in mass (packing effect) of the nitrogen and helium nuclei. From the first method, the value λ=about 10^{-11} cm. is obtained, whilst from the second approximately the same value is found for nitrogen, but about 10^{-12} cm. for helium. The longest of these active wave-lengths is about one thirty-fifth of that of the shortest γ-ray known. N. H. HARTSHORNE.

Absorption of high-frequency radiation in water. L. MYSSOVSKI and L. TUWIM (Z. Physik, 1925, **35**, 299—303).—The absorption of penetrating radiation in the water of Lake Onega was determined last summer by observing the rate of discharge of an electroscope at five positions from 10 to 19 metres below the surface. The absorption coefficient is less than one-tenth that of the γ-rays from radium-*C*. The possibility exists, however, that the effect may be due to some secondary radiation.
E. B. LUDLAM.

Transmutation of elements. (MISS) A. C. DAVIES and F. HORTON (Nature, 1926, **117**, 152).—The recent experiments of Miethe and Stammreich, Nagaoka, and Smits are discussed. The authors consider that information regarding the nature of such transmutations should be sought in attempts to detect the lighter as well as the heavier products of possible transmutations. A. A. ELDRIDGE.

Structure of lead. H. COLLINS (Chem. News, 1926, **132**, 85—89).—Speculative.

Didactic classification table of the elements. A. PIUTTI (Gazzetta, 1925, **55**, 754—756).—The elements are arranged on a spiral with hydrogen at the centre, so that the members of any one group or sub-group fall along a radius-vector. W. E. ELLIS.

Radiation arising from the mutual annihilation of protons and electrons. A. L. HUGHES and G. E. M. JAUNCEY (Nature, 1926, **117**, 193—194).—A consideration of the various ways in which a quantum can be produced by the mutual annihilation of an electron and a proton on collision in which the energy of the quantum is supplied by the mass energy annihilated. A solution satisfying five postulated conditions is found on consideration of a three-body collision, between two electrons and one proton, resulting in a quantum and one electron, or between two protons and one electron. A. A. ELDRIDGE.

Three fundamental frequencies. M. HOME (Nature, 1926, **117**, 194).—The wave-length due to the complete disappearance of the mass of a slow electron when, if ever, it reappears as radiation is calculated as 0·024 Å.; if m in $h\nu=mc^2$ (whence $\lambda = 2{\cdot}18\times10^{-37}/m$) is given the value of the mass of the hydrogen atom, λ=0·000013 Å.; if m=0·032, derived from the congestion of four hydrogen atoms into a helium atom, λ=0·0004 Å.
A. A. ELDRIDGE.

Polarisation of radiation excited by electron impact. A. ELLETT, P. D. FOOTE, and F. L. MOHLER (Physical Rev., 1926, [ii], **27**, 31—36).—With the mercury line 2537Å., but not with the sodium *D*-lines, polarisation (30%) of the radiation perpendicular to the electron beam was observed. A uniform magnetic field of 3 gauss, parallel to the electron beam, was without effect, but when the field was perpendicular to the beam the radiation along the field was unpolarised, and the polarisation of that perpendicular to the field was reduced to 13%.
A. A. ELDRIDGE.

Quantum theory of radiation. A. LANDÉ (Z. Physik, 1926, **35**, 317—322).—Theoretical.
R. A. MORTON.

Models of electron structure, quantum action, and the gravitational field. W. M. THORNTON (Phil. Mag., 1926, [vii], **1**, 13—31).—Models for illustrating the electrical structure of matter are described, based on the assumption of a vortex filament æther. By increasing or decreasing the basic twist in a filament of æther, loops are produced in the shape of the simple elastic curve, which represent, respectively, protons and electrons. The models can be used to illustrate the relative masses of the proton and electron, the magnetic field produced by a moving charge, the attraction of opposite charges, the structure of the Rutherford–Bohr hydrogen atom, quantum action, and gravitation. A. B. MANNING.

Influence of the "inner electronic structure" of atoms on the ionic radius. M. VON STACKELBERG (Z. physikal. Chem., 1925, **118**, 342—346).—The increase in the dimensions of the space lattice of the elements in any group of the periodic classification is due to the formation of a new electron shell and is opposed by the increase in the nuclear charge. From considerations of the effect of changes in the nuclear charge, an attempt is made to explain the Grimm effect (cf. A., 1922, ii, 127) and the lanthanide contraction. H. TERREY.

Nitrogen in the sun. M. SAHA (Nature, 1926, **117**, 268—269).—Although the presence of nitrogen in the sun is indicated by the cyanogen bands, no lines of the element have been observed; in the stellar sequence, the only unambiguous line is 3995 Å., probably due to N^+. Eucken's values (A., 1925, ii, 207) for the energy of dissociation of nitrogen ($4{\cdot}4\times10^5$

cal.) and oxygen ($4{\cdot}25\times10^5$ cal.) molecules are not supported by spectroscopic data. A. A. ELDRIDGE.

Fine structure of the near infra-red absorption bands of water vapour. W. W. SLEATOR and E. R. PHELPS (Astrophys. J., 1925, **62**, 28—48).—Using improved gratings, the "bands" at 6·26, 3·11, 1·87, and 1·38 μ of water vapour have been examined with the aid of a thermopile; data are tabulated for 126, 56, 52, and 28 lines, respectively. A. A. ELDRIDGE.

Origin of the satellites in the ultra-violet OH bands. W. W. WATSON (Nature, 1926, **117**, 157).—A table is given of "satellite" Q_1 and Q_2 series which, if combined with the P and R lines, satisfy the combination relation $Q(m)-P(m+1)=R(m)-Q(m+1)$, and it is considered probable that most of the remaining satellites can also be represented by combinations between the terms in the main branches. In view of their general similarities to the OH bands, the MgH bands are assumed also to owe their combination defect to the existence of displaced Q levels. A. A. ELDRIDGE.

Analysis of certain molecular spectra. D. M. DENNISON (Phil. Mag., 1926, [vii], **1**, 195—218; cf. Astrophys. J., 1925, **62**, 84).—An analysis has been made of the infra-red absorption spectra of the hydrogen halides, carbon dioxide, and ammonia. It is assumed that the behaviour of the nuclei in the neighbourhood of their equilibrium positions may be described by means of central forces acting between them, and an attempt is made to compare the relative intensities of the fundamental and harmonic vibrations by use of the constants of the potential energy function (cf. Kratzer, A., 1921, ii, 142). For the diatomic molecules, the agreement between calculated and observed intensities is satisfactory. In the carbon dioxide molecule, the oxygen atoms are assumed to be equidistant from the carbon atom, the three atoms, however, not being in the same straight line. By correlating the observed band spectrum with the theoretical frequencies, the constants entering into the energy function and the angle at the apex of the isosceles triangle formed by the three atoms are determined. The calculated relative intensities of the three bands are 1·8, 0·01, 1·8 (observed, 2·0, 0·5, 1·8). The fine structure of the bands corresponds satisfactorily with that predicted from the model considered. A similar analysis has been made in the case of axially symmetrical molecules with four atoms, and applied to the infra-red spectrum of ammonia. The theoretical model predicts only four frequencies, so that of the six bands observed by Schierkolk (A., 1925, ii, 180) the four strongest are taken as fundamental, the two others being regarded as due to impurities, or to associated or ionised molecules. The agreement between observed and calculated relative intensities is not satisfactory throughout the four bands, but, if they are considered independently in pairs, there is fairly good agreement for the bands corresponding with the same direction of vibration of the electric moment. The relation of the absolute values of the absorption of the fundamental bands to the "effective charges" on the nuclei is discussed. A. B. MANNING.

Band spectrum of tin monochloride exhibiting isotope effects. W. JEVONS (Proc. Roy. Soc., 1926, **A, 110**, 365—390).—The spectrum of the uncondensed discharge through stannic chloride vapour shows two sets of bands, hitherto unrecorded, occupying the regions 3910—3486 and 3405—2830 Å. They are attributed to a chloride of tin, the latter set definitely to the monochloride SnCl. The band heads have been measured in the first order of a grating spectrograph, but none of the bands has been resolved into lines. The heads of the bands in the more refrangible set have been arranged into two systems, and vibrational quantum numbers have been assigned to the bands in each system. Several heads which were incapable of inclusion in the two systems are attributable to the chloride containing the Cl^{37} isotope. A. B. MANNING.

Absorption spectrum and photochemical decomposition of acetone. C. W. PORTER and C. IDDINGS (J. Amer. Chem. Soc., 1926, **48**, 40—44).—The absorption curve of gaseous acetone has been determined between 3500 and 2000 Å. All the light absorbed is effective in bringing about photochemical decomposition. R. CUTHILL.

Tesla-luminescence spectra. VI. Amino-derivatives. W. H. MCVICKER, J. K. MARSH, and A. W. STEWART (J.C.S., 1926, **128**, 17—20).—The Tesla-luminescence spectra of a number of aromatic amino-derivatives are described and compared. Attachment of the amino-group directly to the benzene ring moves the region of emission towards the red end. Replacement of the hydrogen atoms of the amino-group by alkyl radicals has no profound influence on the character of the emission. The introduction of one phenyl group weakens the intensity of the spectrum as a whole, whilst a second phenyl radical increases the intensity slightly, although not enough to bring it back to the intensity of aniline. Introduction of an amino-group to form phenylhydrazine has a marked influence on the spectrum, weakening the intensity and decreasing the extent of the emission. Substituting imino-groups for methylene groups weakens the intensity and truncates the spectrum at the violet end. A. B. MANNING.

Absorption of ultra-violet light by natural amino-acids and by ceratose. L. MARCHLEWSKI and (MLLE.) A. NOWOTNÓWNA (Bull. Inter. Acad. Polonaise, 1925, **5—6, A**, 153—163).—Extinction coefficients have been determined with light of 2200—3000 Å. for the following amino-acids in aqueous solution: glycine, *d*-alanine, leucine, *iso*leucine, aspartic and glutamic acids, asparagine, cystine, histidine hydrochloride, phenylalanine, tyrosine, and tryptophan, and also for the albumose, ceratose, from wool, the data being tabulated and also shown graphically with molecular absorptions plotted against wave-lengths. Bands attributed to tyrosine and tryptophan are found in the absorption curve of ceratose. G. M. BENNETT.

Infra-red absorption spectra of organic derivatives of ammonia. II. α-Naphthylamine and some mono- and di-alkyl-α-naphthylamines. F. K. BELL (J. Amer. Chem. Soc., 1925, **47**, 3039—3045).—The infra-red absorption spectrum of

α-naphthylamine recorded by Stang (Physical Rev., 1917, [ii], 9, 542) is essentially confirmed and extended to 12·0 μ. α-Naphthylamine is generally more opaque to infra-red radiation than is naphthalene, this relationship resembling that observed between benzene and aniline. The spectra for the alkyl-α-naphthylamines show a general similarity to that of the parent base for wave-lengths beyond 4·0 μ. In the shorter wave-lengths, the spectra are analogous to those of aniline and the alkylanilines. In passing from the primary to the tertiary amines, the absorption band at 2·8 μ due to ammonia is gradually weakened, being practically absent in the case of the tertiary amines. The infra-red absorption spectrum of β-naphthylamine is very similar to that of the α-isomeride.

F. G. Willson.

Absorption spectra and activated states of naphthalene and its methyl derivatives. H. G. de Laszlo (Z. physikal. Chem., 1925, **118**, 369—414).—An extension of a previous paper (A., 1924, ii, 513). The absorption spectra of naphthalene and of its methyl derivatives have been studied by experiments on the vapours, and on solutions of the substances. The results indicate that there are five different electronic states of the naphthalene molecule, each of the four "excited" states being represented by a region of absorption. Changes from one of these "excited," or activated states to another account for the fluorescence and cathodoluminescence spectra. From the moment of inertia corresponding with the infra-red absorption spectrum, it is inferred that the carbon atoms in the molecules of naphthalene vapour are closer than 1 Å. The value derived from crystal structure is 1·54 Å., and it is suggested that in the vapour the outer electrons encircle more than one atomic nucleus, and so allow closer approach of the atoms than is possible in the solid. The absorption spectrum of β-methylnaphthalene resembles that of naphthalene more closely than does that of the α-derivative. In both compounds, the bands are moved towards the red by the introduction of the methyl group, the shift being of the same order as with benzene, but rather smaller. The methyl group tends to destroy the fine structure of the bands, an effect which is still more marked with the dimethyl derivatives.

S. Barratt.

Absorption spectra of morphine solutions in the ultra-violet. L. A. Bontempi (Anal. soc. cient. Argentina, 1925, **99**, 209—228).—On addition of sodium hydroxide to a morphine hydrochloride solution, the absorption is displaced towards the red, the maximum effect being observed with 1 equivalent or more of sodium hydroxide. It is considered that whereas hydrogen chloride has no effect on the spectrum, the displacement is due to some rearrangement taking place at the moment of liberation of the base. The displacement is ascribed to the tertiary phenol group. The interpretation of the phenomenon is discussed. Chemical Abstracts.

Effect of solvents on the absorption spectrum of a simple azo dye [benzeneazophenol]. W. R. Brode (J. Physical Chem., 1926, **30**, 56—69).—The absorption spectrum of benzeneazophenol in thirty organic solvents, including various aliphatic alcohols and esters, aromatic solvents, carbon tetrachloride and disulphide, chloroform, acetone, methyl ethyl ketone, and acetic and formic acids, has been investigated. The cell thickness was 1 cm., the concentration 0·144 g./litre, and the temperature 21—23°. Kundt's law, that the absorption band of a dye is shifted towards the red end of the spectrum with an increase in the refractive index of the solvent, appears not to hold in the case of benzeneazophenol. Further, there appears to be no definite relation between the refractive indices or the dielectric constants of these solvents and the frequency of the absorption band of the dye dissolved therein. The effect of mixed solvents was determined with solutions of benzene and alcohol, carbon tetrachloride and alcohol, and light petroleum and alcohol or benzene. The dye, in these cases, appears to give the absorption frequency for the most polar solvent, even if this is present in small amount, and there is then a slight dilution effect. The height of the band appears to be greater for polar than for non-polar solvents. A graph showing the absorption limits of the solvents used is given and their region of total absorption has been observed throughout the ultra-violet to a frequency (vibrations/seconds $\times 10^{12}$) of 1360 for a thickness of 1 cm.

L. S. Theobald.

Intensities of band lines. E. C. Kemble (Z. Physik, 1925, **35**, 286—292).—The author extends his theory of the oscillation–rotation spectra and obtains a formula for the electron displacement bands. The theories of Fowler and Dieke are viewed with distrust as being opposed to the principle of correspondence.

E. B. Ludlam.

Intensity measurements in band spectra. R. Sewig (Z. Physik, 1926, **35**, 511—523).—The bands measured were those of cyanogen (carbon arc in air under different conditions, also with addition of argon and of neon) and nitrogen. The photographs taken with a concave-grating spectrograph were measured by means of a Koch and Goos microphotometer. It is concluded that the various attempts to formulate a theory for the course of the intensities in a branch, or the relative intensities of the corresponding lines in different branches, are inadequate.

E. B. Ludlam.

Spectrophotometry by great dispersion. R. Frerichs (Z. Physik, 1926, **35**, 524—527).—The light from the source on its way to the slit of a concave-grating spectrograph passes through gauzes of different mesh mounted on a rotating cylinder, and before reaching the photographic plate passes through slits on a frame which is rotated synchronously with the gauzes by means of a flexible drive. This method was used by Sewig (preceding abstract).

E. B. Ludlam.

Determinations of the mean life in the activated state of fluorescent molecules. F. Perrin (Compt. rend., 1926, **182**, 219—221; cf. A., 1925, ii, 353).—On the assumption of the existence of circular oscillation, a corrected relationship is given connecting the mean life in the activated state of a fluorescent molecule (τ) with the degree of polarisation (p) of the

fluorescent light, and the volume occupied by 1 g.-mol. of the substance. By expressing p as a function of viscosity, values of τ are obtained of $0{\cdot}16\times10^{-8}$ and $0{\cdot}14\times10^{-8}$ sec. for erythrosin and rose-bengal, respectively, in alcoholic solutions; τ is also proportional to τ_0 (the value of τ if the emission of light was the only cause of the return of the activated molecule to the normal state), and τ_0 may be found from Einstein's probability formula for the passage from one stationary state to another. Thence, for fluorescence in aqueous alkali solutions, $\tau=0{\cdot}4\times10^{-8}$ sec.

J. GRANT.

Luminescence. (MISS) D. G. ENGLE and B. S. HOPKINS (J. Opt. Soc. Amer., 1925, **11**, 599—615).—A photo-electric cell has been applied to the study of fluorescent light from zinc sulphide and similar substances. Various materials are classed as sensitising or desensitising agents for the fluorescent substances. S. BARRATT.

Depolarising influence of alternating magnetic fields on resonance radiation. G. BREIT (J. Opt. Soc. Amer., 1925, **11**, 465—471).

Electrical influencing of polarisation of resonance fluorescence of mercury. W. HANLE (Z. Physik, 1926, **35**, 346—364).—The Stark effect for the resonance lines of all atoms except hydrogen is very small. For mercury under 14,000 volts/cm. it is certainly less than 5×10^{-5} Å. Observations on the polarisation of resonance fluorescence provide a very sensitive means of measuring Stark effects. According to the methods employed, the effect with mercury can be increased or diminished. An ellipticity of the fluorescence radiation has been observed which is not due to the Kerr effect (electrical birefringence), but to a Stark effect occurring in the act of fluorescence itself. A quantum interpretation is advanced for the experiments in which it is assumed that for small fields little or no electrical directional quantisation occurs. A series of experiments in combined magnetic and electric fields shows that only the stronger field is effective in polarising the radiation. The field which brings about a larger frequency displacement is regarded as the stronger, and one or the other undergoes rigorous directional quantisation. The Faraday effect for the line 2536·7 Å. has been observed with fields down to a few gauss. R. A. MORTON.

Damping of mercury resonance lines by collision. W. ORTHMANN (Ann. Physik, 1925, [iv], **78**, 601—640).—Expressions have been deduced by means of which the total absorption of the rays in any thickness of mercury vapour may be calculated, and it is shown that at constant density a decrease in absorption is indicated by an increase in the width of the absorption lines. Measurements of the absorption with various mercury vapour densities have been made, and the results are in accord with the theory. The amount of absorption decreases with increasing temperature at constant density. When hydrogen is mixed with mercury vapour, the total absorption decreases with increasing hydrogen pressure, and when the pressure is kept constant, the absorption decreases with increasing temperature. The same decrease of absorption is obtained by increasing the temperature from T_1 to T_2 or by multiplying the original pressure by $\sqrt{T_2/T_1}$. It is concluded that the decrease in absorption accompanied by the broadening of the absorption lines is caused by the collision of the mercury atoms with hydrogen molecules. A. E. MITCHELL.

Energy required to split hydrogen chloride [molecule] into atomic ions. E. C. KEMBLE (J. Opt. Soc. Amer., 1926, **12**, 1—13; cf. Physical Rev., 1922, [ii], **19**, 394).—Theoretical. A recalculation of the ionisation–dissociation potential of the hydrogen chloride molecule has been made on the assumption that it may be broken up adiabatically and reversibly into ions, without any electronic transference such as would accompany its dissociation into neutral atoms. Energy formulæ for various quantised states of the molecule are evaluated from an analysis of the infra-red band spectrum, a correction being made for a small displacement of the lines as a result of the isotope effect. The value 10·93 volts is obtained by a graphical method for the ionisation–dissociation potential. This value is about 2·8 volts lower than that calculated by Born, and if his value should be proved correct, this discrepancy must be taken as proof of the incorrectness of the above assumption. F. G. TRYHORN.

Energy levels of the carbon monoxide molecule. R. T. BIRGE (Nature, 1926, **117**, 229—230).—Of the four band systems observed by Duncan (Astrophys. J., 1925, **62**, 145) and considered to be nitrogen band systems, the second negative group is the first negative group of carbon, the seventh positive group is the fourth positive group of carbon, and the fifth positive group is probably the third positive group of carbon. The ionisation potential of carbon monoxide is calculated as 14·2 volts, the best experimental values being 14·3 and 14·1 volts. Previous data (A., 1925, ii, 829, 836) concerning the fourth positive group of carbon are revised; direct evidence is adduced ascribing the group to carbon monoxide. The electronic energy levels for carbon monoxide are evaluated as follows in volts, taking X as the zero level: A 8·0, B 10·7, X' 14·2, A' 16·7, B' 19·8. A. A. ELDRIDGE.

Spectral distribution of the sensitivity of a photo-electric element. K. LEONTIEV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 8—9; from Chem. Zentr., 1925, II, 384).—Oxidised copper electrodes were submitted to light of varying wave-lengths from a Nernst lamp. The photo-electric current was studied in relation to wave-length and energy absorption. Maximum absorption of energy occurred for 520 $\mu\mu$. Addition of colouring matters to the electrolyte increased the sensitivity of the electrode, the maximum sensitising effect being always at wave-lengths greater than that for which maximum absorption occurred. G. W. ROBINSON.

Photo-electric conductivity in single crystals and in crystal aggregates. A. JOFFÉ and E. ZECHNOWITZER (Z. Physik, 1926, **35**, 446—448).—A single crystal of rock-salt was heated at temperatures between 500° and 600° and subjected to increasing strain. The electrical conductivity did not

increase so long as no new surfaces or cracks were formed. E. B. LUDLAM.

Photo-electric and optical measurements on blue and yellow rock-salt crystals. Z. GYULAI (Z. Physik, 1926, **35**, 411—420).—The photo-electric effect on natural blue and violet crystals of rock-salt shows decided selectivity and is probably due to a surface action on colloidal particles of sodium. E. B. LUDLAM.

Chemical effect of *X*-rays. N. PESKOV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 68; from Chem. Zentr., 1925, II, 383).—Diastase and *o*-nitrobenzyl alcohol which are otherwise insensitive are sensitised to *X*-rays by barium or bismuth salts, probably on account of secondary electrons emitted by these elements. G. W. ROBINSON.

Non-metallic elements. Connexions between their dielectric and other physical properties. II. G. L. ADDENBROOKE (Phil. Mag., 1926, [vii], **1**, 225—243; cf. A., 1924, ii, 440).—The available data of the dielectric constants and refractive indices of the non-metallic elements in the gaseous and liquid states are collected and the relationships between them discussed from the point of view of the author's theory of the storage of energy in a dielectric under the influence of an electric field. A. B. MANNING.

Dielectric constant of weak electrolytes. T. NAYDER (Bull. Inter. Acad. Polonaise, 1925, **7, A**, 247—258).—Jezewski's method (*ibid.*, 1920, 88) has been used to measure the dielectric constants, at temperatures between 16° and 44°, of solutions of benzoic acid, picric acid, and salicylic acid in nitrobenzene and benzene. The dielectric constant of benzene was found to be 2·293 at 13·8°, and of nitrobenzene 36·05, 34·50, 32·69, and 30·74 at the respective temperatures 17°, 24·25°, 33·95°, and 44·5°. The effect of the solutes is to increase the dielectric constant in the case of benzene solutions, and to depress it in the case of nitrobenzene. The diminution of the constant of nitrobenzene by a given amount of solute is independent of temperature. F. G. TRYHORN.

Quantum theory of the dielectric constant of hydrogen chloride and similar gases. L. PAULING (Proc. Nat. Acad. Sci., 1926, **12**, 32—35; cf. W. Pauli, jun., Z. Physik, 1921, **6**, 319).—A mathematical treatment of the dielectric constant of diatomic dipoles based on the quantum theory. The experimental data of Zahn for hydrogen chloride (A., 1924, ii, 809) are in fair agreement with the curve corresponding with a value of $0{\cdot}3316\times10^{-18}$ c.g.s. unit for the permanent electric moment μ of the molecule and 0·00077 for $4\pi N_0\alpha$, N_0 being the number of mols./c.c. under standard conditions and α the coefficient of induced polarisation of a molecule. The values differ from those from the same data with the classical theory (*loc. cit.*). The quantum theory value for $4\pi N_0\alpha$ is in accordance with the Maxwell relation $4\pi N_0\alpha=n_0^2-1$, where n_0 is the refractive index of the gas under standard conditions for light of frequency far removed from any frequency characteristic of the molecule. For hydrogen bromide, the values of μ and $4\pi N_0\alpha$ are $0{\cdot}252\times10^{-18}$ and 0·00102, respectively. The electric moment for hydrogen chloride corresponds with that of a dipole composed of a proton and an electron 0·0694 Å. apart; for hydrogen bromide, this distance is 0·0528 Å. J. S. CARTER.

Influence of molecular structure on the dipolar character of ethylenic isomerides. Calculation of molecular moment. J. ERRERA (J. Phys. Radium, 1925, [vi], **6**, 390—396).—A study of the molecular polarisation of the isomerides of certain halogen-substituted ethylenes. The molar polarisation P is the sum of three terms P_E, P_A, and P_P, which signify polarisation due to electronic movements (molecular refraction as given by the Lorentz–Lorenz formula), to movements of atoms and radicals, and to the orientation of molecules (permanent dipoles) respectively. The presence of the latter is shown by a difference between the square of the refractive index and the dielectric constant of the substance. A method of calculating the values of the three quantities named is given, and it is thus shown that the *cis*-form of compounds such as *s*-dichloroethylene have permanent dipoles which are absent in the *trans*-form, whilst the asymmetric compounds have an intermediate character. Since the dipoles disappear on solidification, it is found, according to expectation, that the solid *cis*-forms have the same specific inductive capacity as the ordinary *trans*-forms.

The effect of temperature on molar polarisation is also studied, and, in order to allow for molecular association in the liquid state, the influence of dilution with benzene (which has no permanent dipoles) on refractive index and dielectric constant is examined. By using the value of the molar polarisation found in dilute solution (where association is small) in conjunction with Debye's formula, the following molecular moments are found: *cis*-dichloroethylene, $1{\cdot}89\times10^{-18}$; *cis*-dibromoethylene, $1{\cdot}35\times10^{-18}$; *cis*-diiodoethylene, $0{\cdot}71\times10^{-18}$; *cis*-chlorobromoethylene, $1{\cdot}55\times10^{-18}$. The moments of the corresponding halogen acid vapours, previously determined, are in the same order; thus, HCl>HBr>HI. It is found that the molecular moments of the symmetrically substituted ethylenes, when halved, are about 5% less than the values found for their corresponding acids. It is therefore supposed that the distance separating halogen and hydrogen in the molecules of the *cis*-substituted ethylenes is smaller than in the corresponding acids in the same proportion. C. H. D. CLARK.

Born's dipole theory of anisotropic liquids. L. S. ORNSTEIN (Z. Physik, 1926, **35**, 394).—According to Born's theory an anisotropic liquid when placed in a magnetic field should acquire an electric charge on the surface inclined towards the field direction. Szivessy (A., 1925, ii, 1123) tested this view for several liquids, using a very sensitive method, and did not observe Born's phenomenon. The author has shown (Ann. Physik, 1924, [iv], **74**, 445) that the influence of a magnetic field on the dielectric constant can be explained if the crystalline liquid is regarded as an aggregate of elementary crystals. Szivessy's negative results are due to the fact that the magnetic

field causes a change in the dielectric constant, but no potential change. R. A. MORTON.

Transition compounds between salts and metallic alloys. M. PADOA (Gazzetta, 1925, **55**, 975—983).—The electrical conductivity has been measured between −81° and 400° of thin rods of the three arsenides Sn_2As_3, SnAs, and Sn_3As_2. In each case, the conductivity passes through a maximum at 25°, 0°, and −25°, respectively. By heating the rods for several hours at 100°, the conductivities were slightly raised, but the positions of the maxima were not altered. It is pointed out that if the salt form of these compounds is produced from the non-ionised form with the evolution of heat, lowering of temperature should produce an increase of conductivity, due to an alteration in the equilibrium between the two forms. Below a certain temperature, however, the conductivity will diminish as a result of the decreased thermal agitation of the atoms. The combination of these two effects will cause the conductivity to pass through a maximum, a behaviour confirmed by the above experiments. F. G. TRYHORN.

Additivity of the molecular volumes of volatile inorganic compounds. E. RABINOWITSCH (Ber., 1925, **58**, [*B*], 2790—2798).—The atomic volumes of all elements in one and the same period are equal to a first approximation in volatile inorganic compounds and amount to 5·5 c.c. in the first, 11 c.c. in the second, 23 c.c. in the third, 28 c.c. in the fourth, and 37·5 c.c. in the fifth period. The course which these characteristic constants show in their relationship to the periodic number is analogous to that observed for a series of other physical constants of the rare gases and volatile compounds (cf. A., 1925, ii, 760); the difference between the atomic volume of the corresponding rare gas and that of the element is 5·5 c.c. The differences between the observed and calculated values on this basis are generally comparatively small, and lie generally in such direction that the calculated values are low; the uncertainty concerning the densities of the compounds at the b. p. renders premature any attempt to secure better harmony by the introduction of individual corrections, depending, for example, on different stages of valency. With certain compounds, the data are very discordant. In the cases of water, sulphur trioxide, and, to a less extent, of ammonia, this may be ascribed to association; the observed are much lower than the calculated values. With hydrogen fluoride, the observed values are greater than those calculated, and a similar divergence is evident for the other halogen acids. In the cases of hydrogen, nitrogen, oxygen, and fluorine, the experimental values for the diatomic molecules are much greater than the theoretical values; for chlorine and bromine, the agreement is good, whereas for iodine the divergence is in the opposite direction. Carbon monoxide has a "too high" molecular volume, whereas other volatile oxides, such as carbon dioxide and the oxides of nitrogen have values agreeing closely with the theoretical. The reason may possibly be sought in the unsaturated character of carbon monoxide, but it is then difficult to explain why the unsaturated oxides of nitrogen exhibit so little difference from the calculated values. It is probably not accidental that the most volatile substances exhibit strong divergence from additivity in their molecular volumes. H. WREN.

Generalisations of the Rayleigh formula for molecular scattering. J. Q. STEWART (J. Opt. Soc. Amer., 1925, **11**, 581—597).—A theoretical paper dealing with a generalised form of the Rayleigh scattering formula, and of the scattering formulæ developed by Smoluchowski and others for dense media and anisotropic liquids. The classical point of view is maintained throughout. S. BARRATT.

Specific rotatory dispersion of serum proteins. E. A. HAFNER (Biochem. Z., 1926, **166**, 424—430).—The specific rotations and rotatory dispersions of serum-albumin and globulin, salted out by means of ammonium sulphate from ox-serum and purified, differ considerably, the two proteins possessing therefore very distinct chemical structures. P. W. CLUTTERBUCK.

Polarimetry of mixtures of optically active organic acids and aldehydes or ketones. M. PASSERINI (Gazzetta, 1925, **55**, 726—729).—Abnormally low values of the molecular rotatory power of tartaric, quinic, camphorcarboxylic, and mandelic acids in acetone, methyl ethyl ketone, acetaldehyde, propaldehyde, and ethyl acetoacetate indicate that solvent and solute combine to form compounds probably of the structure $CRR'(OH)\cdot CO_2R''$ (cf. A., 1921, i, 743, 895; 1923, i, 1013), a conclusion supported by purely chemical investigations (A., 1924, i, 1319). The mutarotation of quinic acid in acetaldehyde indicates a balanced action between the components, the equilibrium point of which is attained after 2 days. Acetic acid does not affect the rotatory power of menthone or camphor, results which are in accord with the chemical properties of these substances (cf. A., 1921, i, 895). W. E. ELLIS.

Structure of molecules in relation to their optical anisotropy. K. R. RAMANATHAN (Proc. Roy. Soc., 1926, **A**, **110**, 123—133; cf. A., 1923, ii, 598).—The optical anisotropy of benzene has been calculated for two different structures on the theory that the optical anisotropy of gaseous molecules, which is responsible for the partial depolarisation of the light scattered in a direction perpendicular to the incident beam, is mainly due to the mutual influence of the electrical doublets induced in the different atoms of the molecule by the electrical field of the incident radiation. If the six carbon atoms lie in a plane, the calculated anisotropy is too high even when the hydrogen atoms are ignored. If, however, the carbon atoms are arranged in a puckered ring as in diamond and the hydrogens are joined to the carbons at the tetrahedral angle, the calculated value of the optical anisotropy and also that of the molecular refractivity agree well with the observed results. The calculation is extended to *cyclo*hexane and a fair agreement is observed. F. G. SOPER.

Valency. VII. Surface polarity and the reaction of ethylene and chlorine. Effect of the adsorbed water layer. R. G. W. NORRISH and G. G. JONES (J.C.S., 1926, 55—62).—The rate of

reaction between ethylene and chlorine has been determined in cylindrical glass tubes, with the inner surface uncovered or covered with a layer of paraffin wax or stearic acid. The initial partial pressure of each gas was 200 mm., air being added to bring the total initial pressure to about 700 mm. The bimolecular reaction coefficient was used as a measure of the reactivity of a given surface. By taking special precautions, a paraffin wax surface was prepared with a reactivity some 1200 times smaller than that of glass, and about one-seventieth that previously found for a paraffin wax surface in experiments on the union of ethylene and bromine. It has been shown that water vapour present at a partial pressure of 6 mm. increases the reactivity of the glass surface by 30%, whilst it has no effect on the paraffin wax surface. These results are discussed from the point of view of surface polarity, and in the light of our knowledge of the adsorbed water film existing at the surface of many solid substances.

A. B. MANNING.

Nomenclature in Werner's theory of inorganic complexes. T. STEOHE (Z. angew. Chem., 1926, **39**, 36—38).—It is suggested that a new suffix be introduced to apply to the co-ordination number of an atom as distinct from its principal valency, the German suffix suggested being "-ortig" for the former in distinction to "-wertig" for the latter, so that the nitrogen atom in ammonium chloride would be called "3-wertig" and "4-ortig." Salts of nitrogenous organic bases should be termed "-ium" salts.

W. T. K. BRAUNHOLTZ.

Magnetic properties of the carbonyl radical. P. PASCAL (Compt. rend., 1926, **182**, 215—217; cf. A., 1925, ii, 371, 634).—The value of the atomic susceptibility hitherto assigned to oxygen does not apply to the carbonyl radical, oxygen being paramagnetic in aldehydes and ketones, and irregularly diamagnetic when linked with groups containing elements having residual affinity (*e.g.*, nitrogen). The increase in diamagnetism in the latter case is greater if the nitrogen itself is substituted by a negative radical, and *vice versa*. Corrections for various radicals and linkings are given which bring the carbonyl radical into line with the additive laws of diamagnetism.

J. GRANT.

Confirmation of presence of a non-tetrahedral carbon atom in crystals of pentaerythritol. M. L. HUGGINS and S. B. HENDRICKS (J. Amer. Chem. Soc., 1926, **48**, 164—167).—The results of Mark and Weissenberg (A., 1923, i, 1055) have been verified and supported by Laue photographic data. R. CUTHILL.

Foreshadowing elements of atomic numbers 75, 85, 87, and 93 by means of *X*-rays. F. H. LORING (Nature, 1926, **117**, 153).—Polemical and explanatory.

A. A. ELDRIDGE.

Occurrence of dvi-manganese in manganous salts. V. DOLEJŠEK, G. DRUCE, and J. HEYROVSKÝ (Nature, 1926, **117**, 159).—The association of dvi-manganese with manganese is affirmed.

A. A. ELDRIDGE.

Instrument for the rapid production of Laue photographs. J. T. NORTON (J. Opt. Soc. Amer., 1926, **12**, 27—29).—A description of a pinhole camera by means of which Laue photographs may be obtained on a high-speed dental film by an exposure of from 5 to 10 min. The crystalline specimen is attached by collodion to a pinhole 0·028 in. in diameter, bored in a brass plate $\frac{1}{8}$ in. in thickness. This ratio of diameter to length of the aperture was found satisfactory in producing a parallel beam of *X*-rays.

F. G. TRYHORN.

Beryllium oxide as a mineral, and its crystal structure. G. AMINOFF (Z. Kryst., 1925, **62**, 113—122).—A mineral from Längban, containing 98% BeO, is named "bromellite"; it is dihexagonal pyramidal, $c=1·6288$; hardness 9; uniaxial +; $\epsilon=1·733$; $\omega=1·719$. McKeehan's results for the structure of artificial beryllium oxide (A., 1922, ii, 766) are verified; $c=4·36$, $a=2·68$ Å.

CHEMICAL ABSTRACTS.

Crystalline structure of chrysoberyl. W. L. BRAGG and G. B. BROWN (Proc. Roy. Soc., 1926, **A**, **110**, 34—63).—The unit cell of chrysoberyl, $BeAl_2O_4$, contains 4 molecules and its axes have the values $a=4·420$, $b=9·390$, $c=5·470\pm0·1\%$ Å. The dimensions are in accord with hexagonal close packing of the oxygen atoms, which agrees with the observed relative intensities of the spectra. The aluminium atoms lie in spaces between six oxygen atoms and cause slight distortion. Four of the aluminium atoms lie at symmetry centres and four on reflexion planes. The position of the beryllium atoms cannot be deduced from the results, as these atoms play so little part in *X*-ray diffraction, but each beryllium atom is assigned to a position between four oxygen ions. About eighty reflexions occur in the photographs and a similar number have been measured with the ionisation spectrometer, all of which are explained by the structure which is proposed.

F. G. SOPER.

Structure of ethane and diborane, B_2H_6. H. MARK and E. POHLAND (Z. Kryst., 1925, **62**, 103—112).—Both compounds are hexagonal, with 4 molecules in the unit cell. For ethane and diborane, respectively, $a=4·46$, $4·54$; $c=8·19$, $8·69$ Å., volume=70·6, 78·0 Å^3. The distance of nearest approach of the carbon atoms is 1·5—1·6 Å., and of the boron atoms, 1·8—1·9 Å.

CHEMICAL ABSTRACTS.

Structure of ammonia. H. MARK and E. POHLAND (Z. Kryst., 1925, **61**, 532—537).—Between −77° and −160°, the unit cube of ammonia contains 4 molecules and has $a=5·19$ Å., the nitrogen atoms being arranged according to T^4, with $u=0·220$.

CHEMICAL ABSTRACTS.

Application of *X*-ray analysis of crystalline powders to chemical problems. G. R. LEVI (Atti Congr. Naz. Chim. Ind., 1924, 257—265; from Chem. Zentr., 1925, II, 448).—Crystallographic data, with photomicrographs relating to the *X*-ray analysis of magnesium oxide, magnesium hydroxide, and magnesium carbonate, respectively.

G. W. ROBINSON.

Structure of α-quartz. R. E. GIBBS (Proc. Roy. Soc., 1926, **A**, **110**, 443—455; cf. this vol., 13).—The structure of α-quartz cannot be completely determined from its symmetry and *X*-ray data; intensity measurements and a study of its general physical

properties have therefore been used to determine the unknown variables. The intensities of reflexion from a number of planes have been measured by oscillation, rotation, Laue photographs, and by use of the ionisation spectrometer. They show that the oxygen atoms do not lie either in the same basal planes as the silicons or half-way between, but probably occupy positions $c/9$ above and below them. The variation in physical properties accompanying the transition from β- to α-quartz indicates only a small structural change, although the tetrahedral character of the former structure is lost. A structure for α-quartz is proposed in which the crystal is non-molecular, the oxygen atoms occupy the basal planes as described above, and the silicon atoms are moved about 0·3 Å. from their β-positions. The structure satisfies symmetry conditions, and also gives satisfactory agreement between calculated and observed intensities of reflexion. The causes of pyro- and piezo-electricity are discussed; the proposed structure leads to a calculated value for the coefficient of piezo-electricity of the same order of magnitude as the accepted value.

A. B. MANNING.

Crystal structure of β-quartz. R. W. G. WYCKOFF (Amer. J. Sci., 1926, [v], **11**, 101—112).—Examination of α-quartz (stable at the ordinary temperature) by the Laue method indicates a hexagonal cell of dimensions $a=4·903$ and $c=5·393$ Å. From powder, spectrum, and Laue photographs of β-quartz (above 575°) it is found that this modification has a similar cell of $a=5·01$ and $c=5·47$ Å., with 3 molecules to the cell. In all photographs, first, second, third, and higher orders reflexions from (0001) are absent; hence the space-groups are D_6^4 and D_6^5. For the placing of oxygen atoms in relation to silicon atoms, $0·197\pm0·004$ is arrived at, from a study of spectral intensities, as the most probable parameter. Each silicon is surrounded by a tetrahedron of oxygen atoms, and there is no evidence of any grouping into molecules.

W. A. CASPARI.

Structure investigations by the Debye-Scherrer method. S. VON OLSHAUSEN (Z. Kryst., 1925, **61**, 463—514).—Data are given for potassium iodide, rubidium chloride, aluminium, niobium, manganese, red phosphorus, lead selenide (clausthalite), mercuric sulphide (cubic and hexagonal), arsenic, tellurium, selenium, nickel, iron, arsenic sulphide (gersdorffite), and calcium carbonate (calcite, aragonite, and vaterite). Vaterite is hexagonal. A mathematical method for interpreting the diffraction patterns is described.

CHEMICAL ABSTRACTS.

Crystal structure of some metallic sulphides. L. S. RAMSDELL (Amer. Mineral., 1925, **10**, 281—304).—Crystal structure should be the criterion of isomorphism. Argentite, hessite, eucairite, and naumannite are ruled out of the galena group because of dissimilar structures, whilst clausthalite and altaite are isomorphous with galena. The pyrite group is verified by X-ray examination, except for chloanthite and smaltite. Cinnabar has a simple rhombohedral structure and is not isomorphous with covellite. Argentite and acanthite give identical X-ray pictures. Values obtained for the atomic radii of selenium and tellurium from lead selenide and telluride, considering that of sulphur to be 1·04 Å., are 1·15 Å. and 1·27 Å.

CHEMICAL ABSTRACTS.

Orientation of crystals produced by heating strained iron. C. F. ELAM (J. Iron and Steel Inst., 1925, **112**, 111—112).—See A., 1925, ii, 946.

Electrolytic deposition of metals. II. X-Ray investigation of electrolytic nickel. G. L. CLARK and P. K. FRÖLICH.—See B., 1926, 131.

Crystal structure of cadmium and nickel hydroxides. G. NATTA (Atti R. Accad. Lincei, 1925, [vi], **2**, 495—499).—An X-ray examination has been made, by the Debye–Scherrer method, of nickel hydroxide, using nickel and copper anticathodes, and of cadmium hydroxide using iron and copper anticathodes. Both hydroxides have a rhombohedral structure, analogous to that of the hydroxides of manganese and magnesium. The following values were found for the dimensions of the elementary cells, which in each case contain 1 molecule of the hydroxide, and for the calculated specific gravities: $Ni(OH)_2$, $a=3·07$, $c=4·605$ Å., $V=37·6$ Å.^{3}, d 3·602; $Cd(OH)_2$, $a=3·47$, $c=4·64$ Å., $V=49·0$ Å.^{3}, d 4·92.

F. G. TRYHORN.

Isomorphism of the molybdates of the rare-earth metals with those of calcium, strontium, barium, and lead. V. Deductions from the X-ray analysis of the molybdates of cerium, lanthanum, praseodymium, neodymium, and samarium. Mixed crystals of the molybdates of cerium and calcium. F. ZAMBONINI and R. G. LEVI (Atti R. Accad. Lincei, 1925, [vi], **2**, 462—464; cf. A., 1925, ii, 1133).—From data previously reported for the X-ray photograms of the above molybdates, the identity of their crystal structure is deduced. For the molybdates of the above-mentioned rare earths the values of a and c, and of the volume of the elementary cell, decrease with increase of the atomic weight of the rare-earth metal. It is shown that in this isomorphous series the elementary cells contain equivalent volumes of the respective compounds. Mixed crystals of the molybdates of calcium and cerium have been prepared containing, respectively, 6·5% and 29·0% of cerium molybdate. The values of the lattice constants for these mixed crystals lie between those of the two components.

F. G. TRYHORN.

Geochemical distribution of the elements. IV. Crystalline structure of the oxides of the rare-earth elements. V. M. GOLDSCHMIDT, F. ULRICH, and T. BARTH (Norske Videnskaps-Akad. Oslo, I, 1925, No. 5; from Chem. Zentr., 1925, II, 448—450).—The sesquioxides of the rare-earth elements occur in at least three crystalline forms, A, B, and C, respectively. A is hexagonal, has a good cleavage parallel to the basal face, and is softer than the other crystalline forms. This type occurs in the case of lanthanum sesquioxide at 550°, 1100°, 1300°, and at its m. p. It may be obtained for cerium sesquioxide by ignition of cerium dioxide in a current of hydrogen, for palladium sesquioxide by melting palladium dioxide in an acetylene blast, for neodymium

sesquioxide by heating at 1755° or at its m. p., and for samarium sesquioxide by rapid cooling from the molten state. In the interval occupied by the form *B*, there are probably two types, B_1 and B_2, respectively, of which the former occurs at higher temperatures than the latter. B_1 is probably pseudotrigonal. This type of samarium sesquioxide may be obtained by slow cooling, that of palladium sesquioxide at 900° and 1300°, that of neodymium sesquioxide at 1300°, that of europium sesquioxide at 1100°, and that of gadolinium sesquioxide at 1300°. The last oxide heated at 900° forms the type B_2. The occurrence of this type in the case of the other sesquioxides has not been clearly proved. The crystalline form *C* is regular. From Debye–Scherrer diagrams, it appears to belong to the group O_{10}^{h} and contains 16 molecules in each constituent unit. The lattice spacing d_{100} is 10 Å. The type is characteristic for scandium sesquioxide and yttrium sesquioxide. In the former case, it is obtained by heating at 1350° or by crystallisation from the molten material. Yttrium sesquioxide occurs only in this crystalline form. The conditions under which it is obtained for the other sesquioxides are as follows: samarium at 620°, 640°, and 730°; europium at 735° and 750°; gadolinium at 600° and 750°; terbium at 900°; dysprosium, holmium, erbium, thulium, ytterbium, and lutecium at 1100°. The crystalline forms can be partly transformed into each other by heating, It is confirmed that cerium dioxide and thorium dioxide belong to the fluorspar type (cf. Goldschmidt and Thomassen, A., 1923, ii, 644). Black praseodymium oxide and brown terbium oxide have the same structure and length of side, although they do not correspond exactly with the formula RO_2. In addition to this type, there occurs another type in the case of cerium dioxide and terbium dioxide, the length of side of which is approximately twice as great and corresponds with the *C* type. It is uncertain to what extent mixed crystals or double oxides of the type RO_2,R_2O_3 are present. The actual composition corresponds with the formulæ Tb_2O_7 and Pr_6O_{11}, and the lengths of side of the principal lattice are 5·278 and 5·488 Å., and of the subsidiary lattice, 10·55 and 10·98 Å., respectively. The following are the lattice dimensions of the cubical form *C* of the sesquioxides of the different elements in Å.: scandium 9·79, yttrium 10·60, samarium 10·85, europium 10·84, gadolinium 10·79, terbium 10·70, dysprosium 10·63, holmium 10·58, erbium 10·54, thulium 10·52, ytterbium 10·39, lutecium 10·37, The lattice dimension of thalenite, a mineral mixed crystal, is 10·56 Å. It is seen that within a vertical series of the periodic table the lattice dimension increases with atomic number, whilst in a horizontal series it decreases. Chemical properties and lattice dimensions of the *C* type run parallel. In the case of the *A* type, the lattice dimensions decrease in the order lanthanum, cerium, praseodymium, neodymium, and in the case of the B_1 type, in the order neodymium, samarium, europium, gadolinium. In the *A* type, whilst the atomic number increases from 57 to 60, the lattice dimension decreases by 0·9%; in the *B* type, an increase in atomic number from 60 to 69 corresponds with a decrease in lattice dimension of 1·1%; whilst in the *C* type an increase in atomic number from 62 to 71 corresponds with a decrease in lattice dimension of 0·5%. The decrease is smallest in the lanthanum series. Cerium sesquioxide has a greater lattice volume than cerium dioxide. The cerium and the yttrium earths cannot be sharply distinguished crystallographically. The temperatures of the *A*—*B* transformation of the sesquioxides are approximately as follows for the different elements: lanthanum 400°, cerium 600°, praseodymium 850°, neodymium 1000°, element 61 1400°, samarium 1900°. The corresponding temperatures for the *B*—*C* transformation are: samarium 750°, europium 800°, gadolinium 850°, terbium 1100°, dysprosium 1600°. The sesquioxides of holmium, erbium, thulium, ytterbium, and lutecium occur only in the *C* type. G. W. Robinson.

X-Ray investigation of some finely divided minerals, artificial products, and dense rocks. F. Rinne (Z. Kryst., 1924, **60**, 55—69).—*X*-Ray diffraction patterns of the following are described: bauxite, hydrargillite, diasporite, alumina, ferric oxide, silica, opal, vanadium pentoxide, kaolin, allophane, talc, serpentine, meerschaum, calcite, aragonite, vaterite, magnesite, hydrozincite, turquoise, boracite, stassfurtite, asphalt, ozokerite, dopplerite, limestone, flint, obsidian, etc.

Chemical Abstracts.

Electrical conductivity of silver–zinc alloys. G. J. Petrenko (Z. anorg. Chem., 1925, **149**, 395—400; cf. A., 1906, ii, 284; 1913, ii, 135).—The electrical conductivity of silver–zinc alloys was measured at 25° and 100°. The existence of a compound AgZn is indicated by maxima in the conductivity and in its temperature coefficient. The compound forms solid solutions with both zinc and silver. The conductivity shows a minimum at a composition corresponding with Ag_2Zn_3, and breaks at approximately Ag_2Zn_5 and $AgZn_6$. A. Geake.

Detection [of wireless waves] at the faces of crystals of galena and pyrites. P. Gaubert (Compt. rend., 1926, **182**, 143—146).—The fact that certain faces of certain crystals are superior for the detection of wireless waves has hitherto been explained by theories based on the orientation of the atoms. The various faces presented by crystals of galena and pyrites have been examined in this connexion, and an alternative theory is propounded. The distribution of sensitive points in all directions parallel to the cleavage planes of the crystals was examined. Cubo-octahedral forms of galena showed sensitive points only on the octahedral faces, whilst with crystals of pyrites, the best points were found on cubic faces alone or in combination with (001) and (210). This is explained on the author's hypothesis by the fact that the purest forms of galena and pyrites are the cubic and octahedral forms, respectively. These forms are changed in the first case to octahedral and in the second to cubic by the introduction of minute quantities of impurities to the crystallising mass or solution, the impurity being deposited only on the faces of the new form induced. This is in accordance with the observations of Collet (Ann. Physique, 1921, [ix], **13**, 265) and Pélabon (Compt. rend., 1925, **181**, 776), who

formed detectors by the deposition of a very thin film of dielectric on the surface of a metal.

L. L. BIRCUMSHAW.

Electrical symmetry of nickel. A. PERRIER and C. E. BOREL (Arch. Sci. phys. nat., 1925, [v], **7**, 375—388; cf. this vol., 115).—Details are given of a method of measuring the dilatation of nickel strips at high temperatures when subjected to electric or magnetic fields. To prevent hysteresis effects, the metal was chilled from above the Curie point before application of the fields. The elongation of the strips was found to be a linear function of the longitudinal magnetic field, when correction was made for the effect of the terrestrial field. The longitudinal susceptibility is lowered by the simultaneous existence of transverse magnetic fields. An analysis of the measurements leads to a value $+0{\cdot}15\times10^{-14}$ e.s.u. for the magnetic moment of nickel, corresponding with three magnetons. This value is about one hundredth of that found for iron, although the nature of the metals points to comparable magnetic moments. The disparity of these values is not inexplicable on a theoretical basis, but as the present experimental value is open to doubt as a result of the difficulty of eliminating thermal expansion and contraction in the nickel test-pieces, a repetition of the measurements is promised under improved experimental conditions.

F. G. TRYHORN.

Paramagnetism independent of temperature. P. WEISS (Compt. rend., 1926, **182**, 105—106; cf. A., 1924, ii, 586).—A number of hypotheses to explain the phenomenon of constant paramagnetism shown by potassium dichromate and luteocobaltic chloride in solution are considered and rejected, and the opinion is expressed that the phenomenon must be intra-atomic in nature. L. L. BIRCUMSHAW.

Magnetic properties of single crystals of iron. W. GERLACH (Physikal. Z., 1925, **26**, 914—915).—Single crystals of electrolytic iron exhibit a very small hysteresis loss and a scarcely detectable residual magnetism. R. A. MORTON.

Tensile properties of single iron crystals and influence of crystal size on the tensile properties of iron. C. A. EDWARDS and L. B. PFEIL (J. Iron and Steel Inst., 1925, **112**, 79—110).—See A., 1925, ii, 946.

Plasticity of amorphous and crystalline solids. R. BECKER (Physikal. Z., 1925, **26**, 919—925).—Plastic deformation of solids depends on three factors: freedom of movement, fluctuations in tension, and tenacity. For amorphous substances, the plasticity is determined by the ease with which molecules can move; the flow of an amorphous solid is similar to viscosity in the gaseous state. For crystalline substances, this phenomenon is significant in recrystallisation. The plasticity of crystals is determined by spontaneous variations in tension; under a given force a single unit may lengthen in cross-section by λ, and Z units per second may undergo this change. If W is the probability that any given unit may be so affected, the rate of flow is $\mu=\lambda ZW$. By the movement along sliding planes, a large number of atoms may be jerked simultaneously. It is shown theoretically that the plasticity should depend on temperature, and this is confirmed by experiments on single crystals of tungsten. This confirmation was rendered difficult by the fact that the tenacity of crystals varies with temperature. All three factors enter into the viscous flow of metals above their recrystallisation temperature. R. A. MORTON.

Experiments with liquid helium. X. Electric resistance of pure metals etc. XIV. Influence of elastic deformation on the superconductivity of tin and indium. G. J. SIZOO and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 656—666).—The resistance of a tin wire at the temperature below which the resistance begins to disappear (temperature of liquid helium) is less in a stretched than in an unstretched state, the stretched condition conducing to the appearance of the super-conductive state. Hydrostatic pressure applied to both tin and indium wires lowers the temperature at which resistance disappears. J. W. BAKER.

Photographic measurement of electrostriction in carbon tetrachloride. M. PAUTHENIER (Compt. rend., 1926, **182**, 121—123; cf. Bruhat and Pauthenier, J. Phys. Radium, 1925, [vi], **6**, 1).—An optical method is described, the very small birefringence of carbon tetrachloride being neglected. A beam of light from a carbon arc is passed through a tube of carbon tetrachloride placed in a strong alternating electric field, the other beam passing outside the system, and the displacement of the fringes is measured with a micrometer microscope. From the displacement δ, the function A is calculated from the formula $\delta=l\Delta n/\lambda=AlE^2/\lambda$, where Δn is the alteration of refractive index for light of wave-length λ, and l is the length of the electric field E traversed by the beam. E varied from 0 to 78·7 kilovolts/cm. A was found to be $0{\cdot}25\times10^{-11}$. Thermodynamic calculation gives $A_{\text{isoth.}}=0{\cdot}33\times10^{-11}$ and $A_{\text{adiab.}}=0{\cdot}24\times10^{-11}$, from which it is concluded that the electrostriction is of the latter type.

L. L. BIRCUMSHAW.

Anomalies observed in the magnetic properties of gases. A. GLASER (Ann. Physik, 1925, [iv], **78**, 641—658).

Dispersion of the optical constants of mercury. B. O'BRIEN (Physical Rev., 1926, [ii], **27**, 93—98).—Values of the refractive index, absorption coefficient, and percentage reflectivity at normal incidence for the range 4358—3022 Å. are: 4358 Å., 0·88, 3·47, 77; 4047 Å., 0·79, 3·40, 78; 3650 Å., 0·64, 2·97, 78; 3130 Å., 0·44, 2·53, 79; 3022 Å., 0·55, 2·25, 70.

A. A. ELDRIDGE.

Light-scattering coefficient of some saturated vapours. S. EWING (J. Opt. Soc. Amer., 1926, **12**, 15—26).—The scattering coefficients have been determined, by a photographic method, for ethyl ether, benzene, chloroform, and ethyl and methyl alcohols, at a temperature of 60° for ethyl ether, and at 99·8° for the other substances. The results of other workers have indicated that, in respect of scattering, white light behaves as if all the incident energy is

concentrated in a certain effective wave-length. A method is described by which this effective wave-length for the source employed (a locomotive headlight) was determined as 4446 ± 7 Å. The values obtained for the scattering coefficients, multiplied by 10^5, were: ethyl ether 4·585, benzene 1·553, chloroform 1·803, ethyl alcohol 0·432, methyl alcohol 0·295. These values agree satisfactorily with those calculated from the Einstein–Smoluchowski formula, except in the case of methyl alcohol, the calculated value for which is 0·855. The mean value for the number of molecules per c.c. computed from these measurements is $(2{\cdot}69 \pm 0{\cdot}03) \times 10^{19}$.

F. G. TRYHORN.

Temperature–conductance curves of solid salts. I. Halides of sodium. T. E. PHIPPS, W. D. LANSING, and T. G. COOKE (J. Amer. Chem. Soc., 1926, **48**, 112—125).—The salts are used in the form of highly compressed discs of the powdered salt, which are found to behave nearly the same as single crystals. For sodium chloride, if the logarithms of the specific conductance, κ, are taken as ordinates and the reciprocals of the absolute temperature T as abscissæ, the resulting graph is rectilinear up to about 500°, at which point the slope becomes suddenly approximately doubled and continues afterwards constant at this value (cf. von Seelen, A., 1925, ii, 185). The curve for sodium bromide is closely similar. For sodium iodide, the second portion of the curve is succeeded by a nearly perpendicular section, which finally becomes horizontal. With the fluoride, the curve consists of a single straight line up to about 800°, beyond which it slowly becomes nearly vertical, until it falls off again in slope a little below the m. p. It is suggested that the first rectilinear portion of all the curves represents conduction by the sodium ion alone (cf. von Seelen, *loc. cit.*), the slope giving the heat of liberation of the sodium ion in the respective lattices. The sudden increase in slope is probably due to the halogen ion commencing to conduct, the anomalous behaviour of the fluoride being attributable to the known rigidity of its lattice. The vertical portion of the curve, where present, may be caused by change in crystalline form or by one set of ions moving out of lattice alinement, or both. If it be assumed that the conductivity of a solid at temperatures remote from its m. p. is proportional only to the number of ions which have more than a certain threshold energy, ε, it is shown that $\varepsilon = 3{\cdot}16 \times 10^{-16} d \log \kappa / d(1/T)$ ergs/ion. Using the values of ε calculated in this way from the slopes of the curves, and assuming the applicability of the Debye equation for the specific heat of a monatomic solid to the salts in question, the value of $\varepsilon/h\nu_0$, where ν_0 is the natural frequency of the atom in the lattice and h is the Planck constant, has the constant values of approximately 40 and 80 for the first two portions of the above curves. This is taken to mean that a sodium ion in any sodium halide lattice must acquire about 40 quanta in order to be free to conduct. An examination of the data of Tubandt and Lorenz (A., 1914, ii, 516) for the conductivity of halides of silver and thallium leads to similar conclusions.

R. CUTHILL.

Experimental determination of the thermal conductivities of gases. H. GREGORY and C. T. ARCHER (Proc. Roy. Soc., 1926, **A**, **110**, 91—122).—An accurate hot-wire method for the determination of the thermal conductivities of gases is described. The loss of heat by conduction along the leading wires is eliminated by the use of two tubes differing only in length as two arms of a Callendar–Griffiths bridge, the losses being the same for both tubes. The pressure at which convection losses disappear is determined by comparison of the conductivity in wide and in narrow tubes, and the loss by radiation by similar measurements in high vacua. The wire temperature was varied from 24° to 14° for air and from 8·4° to 4·7° for hydrogen, the outside of the glass tube being maintained at 0°. The temperature gradient was determined after correction for the thermal conductivity of the glass wall. From the formula, $K_\theta = K_0(1+\gamma\theta)$, connecting thermal conductivity with temperature, the following results are obtained: hydrogen $\gamma = 0{\cdot}00265$, $K_0 = 0{\cdot}0004043$; air $\gamma = 0{\cdot}000297$, $K_0 = 0{\cdot}0000583 \pm 0{\cdot}33\%$.

F. G. SOPER.

Thermal expansion of tungsten. P. HIDNERT and W. T. SWEENEY (U.S. Bur. Standards, Sci. Paper 515, 1925, **20**, 483—487).—A summary of existing data is given. The expansion was found to be expressed by the equation $L_t = L_0[1+(4{\cdot}28t + 0{\cdot}00058t^2)10^{-6}]$ between −105° and +502°. The increase of the coefficient with temperature is regular; from 0° to 500°, the average coefficient is $4{\cdot}6 \times 10^{-6}$ per degree. The tungsten was 99·98% pure.

E. B. LUDLAM.

Measurement of very low temperatures. XXXII. Thermal expansion of Jena glass 16^{III}. F. P. G. A. J. VAN AGT and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 667—673).—The linear expansion of Jena glass 16^{III} has been determined at intervals between the temperatures 100° and −252·8° by measuring the movement of the inner wall of a vacuum tube, cooled to the b. p. of ethylene, oxygen, and hydrogen, respectively, relative to the outer wall, which was kept at the ordinary temperature. The coefficients of linear expansion between the temperature limits 97·8° to 13·1°, 13·1° to −102·8°, −102·8° to −182·5°, and −182·5° to −252·8° are 7·93, 6·64, 5·10, and 1·65, $\times 10^{-6}$, respectively. A formula representing the results is deduced, the observations agreeing better with the law of Debye (expansion coefficient proportional to T^3) than that of Born (expansion coefficient proportional to T). The form of the curve of the expansion coefficient is probably the same for most solid substances.

J. W. BAKER.

Specific heats of hydrocyanic acid. (MRS.) E. H. INGOLD (J.C.S., 1926, 26—29).—Partington and Carroll's criticism (A., 1925, ii, 373) regarding the purity of the material used in the author's determination of the ratio of the specific heats of hydrocyanic acid (J.C.S., 1922, **121**, 1604) is unfounded. Their further criticism that the results obtained by the author are due not, as was suggested, to the thermal effect accompanying isomeric change, but to the

thermal effect accompanying polymerisation, is invalid. The variation of the vapour density from the theoretical at the lowest temperature investigated is due to the ordinary deviation from the gas laws, and not to polymerisation. A. B. MANNING.

Heat capacity and entropy of lead bromide and bromine. W. M. LATIMER and H. D. HOENSHEL (J. Amer. Chem. Soc., 1926, **48**, 19—28; cf. Suhrmann and Lüde, A., 1925, ii, 96).—The heat capacities of bromine and lead bromide have been measured at temperatures from 14° Abs. to the ordinary temperature by means of a vacuum calorimeter and a lead resistance thermometer. At sufficiently low temperatures, $C_p=aT^b$, where a and b are constants characteristic of the substance. From these data, the entropy of bromine $S_{298}=18{\cdot}4\pm0{\cdot}2$ cal./degree, and for lead bromide $S_{298}=13{\cdot}25\pm0{\cdot}15$ cal./degree per average g.-atom. From this latter value and data for the heat of formation of lead bromide from its elements an independent value $S_{298}=18{\cdot}6\pm1{\cdot}0$ cal./degree for bromine is derived. R. CUTHILL.

Heat capacities of some metallic oxides. G. S. PARKS and K. K. KELLEY (J. Physical Chem., 1926, **30**, 47—55).—The heat capacities of the oxides of magnesium, calcium, aluminium, and tervalent iron, and of magnetite were determined at low temperatures. The entropies and free energies have been calculated. The magnesium oxide showed none of the common impurities; the calcium oxide (Kahlbaum) contained 98·8% CaO, 0·4% H_2O, and no silica; the alumina was in the form of small, almost colourless sapphires with 99·3% Al_2O_3. Of the two samples of ferric oxide used, one consisted of large crystals of specular hæmatite (99·2% Fe_2O_3, 0·5% H_2O, 0·5% SiO_2); the other was a Kahlbaum product prepared from the oxalate (99·5% Fe_2O_3, 0·5% moisture, presumably). *X*-Ray analysis indicated a large proportion of amorphous material therein. The magnetite was similar to that used by Sosman and Hostetter (A., 1916, ii, 331), showing, on analysis, 99·00% Fe_3O_4, 0·63% Fe_2O_3, and 0·37% impurities, chiefly quartz. All samples were studied either in powder form or as small crystals not larger than 3—4 mm. The data found for the heat capacities from 87° to 295° Abs. are tabulated. With magnetite, a region of heat absorption occurs over the interval 113—117° Abs., and this may be due, not to a transformation in crystal structure, but to a change in the magnetic properties of the substance. The heat capacity for the aluminium oxide (corundum) is relatively low, confirming the view that a low heat capacity is a concomitant of exceptional hardness. Further, over the whole temperature range studied, the Kahlbaum sample of ferric oxide had a higher specific heat than the hæmatite crystals, indicating that a finely divided and somewhat amorphous powder possesses a larger heat capacity than bigger crystals of the same chemical composition.

Following Lewis and Gibson (A., 1920, ii, 585), the entropies at 298° Abs. are for magnesium oxide (formula weight) 6·6, calcium oxide 9·6, alumina 12·8, ferric oxide (hæmatite) 21·5, and magnetite (including 1·4 units at heat absorption point) 35·1 cal./degree. The free energies of formation at the same temperature are −137,000, −145,300, −356,300, −178,400, and −246,800 cal., respectively.

L. S. THEOBALD.

Relation of molecular heats of non-associated liquids to those of their vapours. W. A. HOLZSCHMIDT (Z. Physik, 1925, **35**, 313—315).—It is shown that the empirical relationships already known can be deduced from a consideration of van der Waals' corresponding states. Thus, $c_p-c_v=k$, $k=10$ when the temperature is 0·6 times the critical temperature, and $c_p-C_v=14$ (c denoting liquid, C vapour). E. B. LUDLAM.

Melting point of graphite. E. RYSCHKEWITSCH and F. MERCK (Z. Elektrochem., 1926, **32**, 42—45; cf. A., 1925, ii, 276).—Further determinations of the m. p. of graphite have been made with an improved apparatus in which the argon atmosphere could be raised to a higher pressure and in which the radiation from the graphite rod was emitted more nearly under "black" conditions. No systematic change of m. p. with pressure was observed over the range studied, viz., 2—9 atm. The results were more concordant than formerly and the m. p. is now given as 3845 ± 45° Abs. N. H. HARTSHORNE.

Alkali metals under high pressure. [Effect on the melting constants, electrical resistance, and volume.] P. W. BRIDGMAN (Physical Rev., 1926, [ii], **27**, 68—86).—Tabulated data for rubidium and cæsium are given of the m. p., change in volume on melting, and latent heat at pressures from 1 to 4000 kg./cm.², of the electrical resistance from 1 to 12,000 kg./cm.², and of the relative volumes from 1 to 15,000 kg./cm.²; these results are considered together with those for lithium, sodium, and potassium. The melting curve shows neither a maximum nor a critical point; at high pressures, however, a complete reversal of the order of normal m. p. is to be anticipated. The effect of pressure on the electrical resistance of cæsium is unique, there being a minimum at 4000 kg./cm.² Cæsium is the most compressible solid element yet measured directly. The electron, rather than the atom, seems to be the significant unit of structure for volume. An abnormally open electronic structure is indicated for potassium. Numerically, the compressibility of all the alkali metals is of the order of magnitude of that of a perfect gas under a high internal pressure, taking the electron as the gas unit.

A. A. ELDRIDGE.

Critical constants of furfuraldehyde. W. V. EVANS and M. B. AYLESWORTH (Ind. Eng. Chem., 1926, **18**, 24—27).—A large sample of furfuraldehyde was purified by distilling three times with sodium carbonate, and a litre of the constant-boiling product fractionated in a vacuum, and the fraction of least colour coming over at constant temperature re-distilled. Furfuraldehyde thus prepared had b. p. 161·7°/760 mm. and n_D 1·52608. The critical solution temperature curve was plotted, and the highest point of the mean temperature against concentration curve was 120·9° for critical solution concentration of 50·7%. The vapour pressure was determined from 40° to 170·6° or from a pressure of 8 to 966 mm.,

and the change in temperature for a change in pressure of 1 mm. was 0·05° in the b. p. region.
D. G. HEWER.

Heat of reaction in the formation of calcium cyanamide from calcium carbide. H. H. FRANCK and F. HOCHWALD.—See B., 1926, 88.

Application of spectro-photography to measurement of high temperatures. I. O. GRIFFITH.—See B., 1926, 79.

Relation between chemical constants and critical magnitudes of normal liquids. W. A. HOLZSCHMIDT (Z. Physik, 1925, **35**, 304—312).—In the equation $C=x-b/R \cdot \log T_k+\log p_k$, C is the chemical constant, x is a universal constant, about 6·2, b is the difference of the molecular heats of the liquid and saturated vapour at 0° Abs.; b/R is approx. 1·75. The values so obtained are in good agreement with those obtained from Nernst's formula.
E. B. LUDLAM.

Density and atomic weight of helium. II. G. P. BAXTER and H. W. STARKWEATHER (Proc. Nat. Acad. Sci., 1926, **12**, 20—22; cf. A., 1925, ii, 1045).—A repetition of previous work using larger globes and employing the most recent value for the force of gravity, 980·398. The average values for the densities at 0° and 380 and 760 mm. at sea-level, lat. 45°, are 0·08923 and 0·17846, respectively. Taking the density of oxygen at 0° and 760 mm. at sea-level, lat. 45°, to be 1·42898, previously recorded erroneously as 1·42901 (A., 1925, ii, 188), the atomic weight of helium is 4·000, uncertainty affecting the fourth decimal only. J. S. CARTER.

Vapour pressure of carbon. H. ALTERTHUM and F. KOREF (Z. Elektrochem., 1925, **31**, 658—662).—The vapour pressure–temperature curves calculated from maximum arc temperatures diverge considerably from those obtained by measuring the rate of vaporisation, the former method giving considerably higher vapour pressure values, which are regarded as the true vapour pressure of carbon. Assuming the presence of an adsorption layer on the vaporising surface, and, further, that the concentration of this layer is proportional to the drop in vapour pressure which it causes, the concentration is found to be 8×10^{-2} atm. at 3500° Abs. where the vapour pressure is 7×10^{-2} atm., and $2{\cdot}89 \times 10^{-4}$ atm. at 2000° Abs. where the vapour pressure is $6{\cdot}8 \times 10^{-8}$ atm. From the concentration–temperature curve an approximation to the heat of adsorption between 2000° and 3500°, namely, 51,900 cal./mol., is calculated. W. A. CASPARI.

Determination of the vapour tensions of mercury, cadmium, and zinc by a modified manometric method. C. H. M. JENKINS (Proc. Roy. Soc., 1926, **A**, **110**, 456—463).—An apparatus has been designed for measuring the vapour tensions of metals or alloys by a static method, and has been used to determine the vapour tensions of mercury, cadmium, and zinc over wide ranges of temperature. The metal is used as the liquid in a V-shaped manometer, the vapour pressure in the closed limb being balanced by an externally applied pressure of nitrogen in the other limb. The apparatus is made from a glass or silica tube 18 in. in length and $\frac{5}{8}$ in. internal diameter, bent into a 60° V at one end. In the closed end of the V-tube a sealed thermocouple sheath is inserted, projecting about $\frac{3}{4}$ in. into the tube. The temperature is measured by a platinum platinum–rhodium couple. The straight part of the manometer tube serves as a reflux condenser. It is connected to a mercury manometer with a range of 0—1600 mm. The V-tube is enclosed in an electric furnace, which can be rotated about a horizontal axis, so that any gas collecting in the closed end of the tube may be allowed to escape. Before making determinations, the liquid is boiled at a vapour tension of at least 100 mm. Readings are taken by adjusting the pressure at steadily maintained temperatures until the two liquid surfaces in the V-tube are level. The pressure is then read. Values are tabulated for mercury from 200° (14 mm.) to 397·5° (1490 mm.), for cadmium from 500° (14 mm.) to 836° (1535 mm.), and for zinc from 625° (16 mm.) to 982° (1517 mm.). A. B. MANNING.

Ideal gas laws in systems of one and two components. O. MAASS and J. H. MENNIE (Proc. Roy. Soc., 1926, **A**, **110**, 198—232).—The equation of van der Waals has been deduced from a new point of view which leads to the equation $(p+a/v^2)\{v-\beta(1+c/T)\}=RT$, the b of van der Waals' equation being a function of the temperature and of the mean free path; $\beta=8\sqrt{2}\,\pi r^3N/(1+c/273)$, and c is a constant. The equation is shown to reproduce satisfactorily experimental results obtained for carbon dioxide, the density of which has been measured with an accuracy of 0·05% over the range −77° to 200° and at pressures up to 1 atm. The density of water vapour has been measured over the range 98—200° with an accuracy of 0·1%, but the results diverge from those calculated on the basis of the equation of state, and it is assumed that association of single molecules of water vapour into dihydrol occurs to the extent of 0·9% at 100° and atm. pressure. Measurements have been made of the deviations from Dalton's law for mixtures of water vapour and ammonia, and water vapour and carbon dioxide over the range 98—200°. The mutual attraction of the components in these systems is relatively small and is attributed to the relatively non-polar character of monohydrol as contrasted with the polar character of dihydrol. The attraction diminishes with increasing temperature in accordance with the decrease in the proportion of dihydrol molecules. F. G. SOPER.

Isothermals of diatomic substances and their binary mixtures. XXXII. **Behaviour of hydrogen according to the law of corresponding states.** F. P. G. A. J. VAN AGT (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 687—692).—The values of B_A and T previously obtained for hydrogen (cf. this vol., 234) are converted into their reduced magnitudes B' and t, and the curve obtained by plotting the values of $p_k/RT_k \times B$ against t is compared with that obtained from the mean reduced equation of state. The corresponding curves for

neon, nitrogen, and argon form a regular series and show a close correspondence with the increase of the critical temperature, in agreement with the rule given by Onnes and Keesom (Comm. Leiden Suppl. 23). The curve for oxygen is, however, an exception in that it approximates to that of nitrogen. All the curves probably intersect at about $t=1$.

J. W. Baker.

Deduction of equation of state from specific heat. L. Schames (Physikal. Z., 1925, **26**, 731—732).—Mathematical. The difficulty in deducing an equation of state from the Clausius equation lies in the limits of the double integration. This has been overcome and the theoretical solution arrived at may be employed practically by the use of graphical methods. R. A. Morton.

Absolute value of entropy. M. Saha and R. Sur (Phil. Mag., 1926, [vii], **1**, 279—288).—Attention is directed to a difficulty in evaluating the phase integral $H=\ldots\int\int\ldots dq_1dp_1dq_2dp_2\ldots$ when using Planck's method for calculating the entropy of a system. The modified method due to Ehrenfest and Trkal (A., 1920, ii, 738) is outlined, and a relation is deduced between the probability of the state of the system (W) and Ehrenfest's total phase space $\{\gamma\}$, $W=\{\gamma\}/h^fN!$, where h is Planck's constant, and N is the number of particles in the system, each possessing f degrees of freedom. The entropy of a system of diatomic molecules, calculated on the basis of this relationship, is given by $S=Nk\log\{e^{1/2}4\pi Vm^{3/2}a^{1/2}b^{1/2}(2\pi kT)^{5/2}/Nh^5\}$, where k is Boltzmann's gas constant, m is the mass, and a and b are the moments of inertia of the molecule.

A. B. Manning.

Isothermals of monatomic substances and their binary mixtures. XXV. The same for diatomic substances. XXXI. Compressibility of hydrogen and helium between 90° and 14° Abs. F. P. G. A. J. van Agt and H. K. Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 674—686).—The isothermals of hydrogen and helium are redetermined at 20·5° (cf. Martinez and Onnes, A., 1923, ii, 734) and the measurements extended to lower temperatures, 18·0°, 16·5°, 15·5°, and 14·5°. Two determinations at higher temperatures, 90·2° and 69·9°, are also recorded. The values of δ_A and pv_A are tabulated and the values of the coefficients A_A and B_A in the empirical equation of state calculated in the usual manner. The new measurements support the conclusion previously reached (Martinez and Onnes, *loc. cit.*), that the quanta exert no influence on the form of the isothermal. J. W. Baker.

Effect of temperature on the viscosity of air. F. A. Williams (Proc. Roy. Soc., 1926, **A**, **110**, 141—167).—The coefficient of viscosity of dry air free from carbon dioxide has been measured over the temperature range 15—1002° by comparison of the times required for equal quantities of air to transpire through a silica capillary tube at the various temperatures. Millikan's value for the viscosity of air at 23°, $1{\cdot}824\times10^{-4}\pm0{\cdot}1\%$, was used for the calibration of the apparatus. The results between 250° and 1000°, after correction for slip, can be accurately expressed by Sutherland's formula, $\eta\propto T^{1/2}/(1+C/T)$, where C has the value 172·6, T is the absolute temperature, and the viscosity coefficient at 300° is $2{\cdot}886\times10^{-4}$ c.g.s.u. Below 250°, the value of the constant C falls off as the temperature decreases. F. G. Soper.

Kinetic theory of the viscosity of liquids. M. Satô (Sci. Rep. Tôhoku Imp. Univ., 1925, **14**, 403—444).—The viscosity of liquids is discussed mathematically on the assumption of Debye (Physikal. Z., 1912, **13**, 1) and Born (A., 1920, ii, 527) that molecules are dipoles of constant moment. Expressions are thus obtained for the viscosity and the temperature coefficient of viscosity of a liquid. Values so calculated for ethyl and methyl alcohol are in good agreement with experimental results. The theory indicates a variation of viscosity of liquids in an electric field and is confirmed qualitatively by some results of Sellerio (Nuovo Cim., 1916, [vi], **11**, 395). It indicates also a variation of dielectric constant, due to the velocity gradient, in a flowing liquid and a fibrous structure of the molecules in a viscous fluid in motion.

A. E. Mitchell.

Refractometry of binary liquid systems. W. Anosov (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 10—11; from Chem. Zentr., 1925, II, 384).—The refractive indices of mixtures of benzene and *m*-xylene, benzene and stannic chloride, benzene and carbon disulphide, benzene and nitrobenzene, methyl ether and chloroform, and alcohol and chloroform have been determined. The dependence on composition resembles that for internal friction.

G. W. Robinson.

Magnetic susceptibility of binary liquid systems. N. Trifonov (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 10—11; from Chem. Zentr., 1925, II, 386).—The magnetic susceptibility is not generally an additive property. A linear relationship holds only for the system benzene–*m*-xylene. The curves are concave to the abscissa for benzene–nitrobenzene and for benzene–stannic chloride, but convex for benzene–carbon disulphide. The curve for chloroform–methyl ether shows a maximum for 51·5 mol.% of chloroform and that for stannic chloride–ethyl acetate a maximum corresponding with a compound $SnCl_4,2C_4H_8O_2$.

G. W. Robinson.

Constant paramagnetism of solutions. P. Collet (Compt. rend., 1925, **181**, 1057—1058).—Previous experiments (A., 1924, ii, 586) have shown that the paramagnetism of potassium dichromate solutions is independent of temperature from 14° to 50°, a constant value of $63{\cdot}3\times10^{-6}$ having been obtained for the coefficient of atomic permeability of chromium. The same value has now been obtained for the solid salt from 12° to 90°, using the attraction method. A solution of luteocobaltic chloride studied by the ascension method from 14° to 50° gave an atomic permeability for the cobalt atom of $14{\cdot}4\times10^{-6}$. All these values fall on the curve mentioned in the earlier paper. J. Grant.

Relation between viscosity and vapour pressure of binary mixtures. N. A. YAJNIK, M. D. BHALLA, R. C. TALWAR, and M. A. SOOFI (Z. physikal. Chem., 1925, **118**, 305—317).—Porter's rule (A., 1912, ii, 434) relating equalities in viscosity for two different pure liquids to the respective absolute temperatures has been successfully applied to pairs of binary mixtures. The corresponding relation for vapour pressures holds also. If the vapour pressure–composition curve of a mixture is a straight line, the viscosity–composition curve is also a straight line. If the vapour pressure curve has a maximum, the viscosity curve has a minimum, and *vice versa*. Vapour pressure and viscosity data for fifteen binary mixtures are given. L. F. GILBERT.

Partial pressures of water vapour and of sulphuric acid vapour over concentrated solutions of sulphuric acid at high temperatures. J. S. THOMAS and W. F. BARKER (J.C.S., 1925, **127**, 2820—2831).—The partial pressures of the water vapour and sulphuric acid vapour in contact with sulphuric acid–water mixtures containing from 89% to 99·3% of sulphuric acid have been determined at temperatures between 180° and 300° by a dynamic method already described (*ibid.*, 1923, **123**, 3256) and the previously determined sulphuric acid partial pressures have been corrected. Both the partial pressures and the total pressures can be represented by Rankine's equation, and the three constants for this equation have been calculated in every case. The pressures calculated from the experimental data depend on whether dissociation of the sulphuric acid is assumed to take place or not, the values of the total pressure calculated on the assumption that dissociation is complete being consistent with the known b. p. data. The assumption that no dissociation takes place leads to calculated b. p. which are too high. The total pressure isothermals exhibit a well-marked minimum at 98·2% sulphuric acid. The form of the partial pressure isothermals is in qualitative agreement with the Duhem–Margules equation. Lack of quantitative agreement is probably due to dissociation of the acid vapour. E. E. WALKER.

Partial pressures of aqueous ethyl alcohol. H. J. E. DOBSON (J.C.S., 1925, **127**, 2866—2873).—The partial vapour pressures of mixtures of ethyl alcohol and water have been determined at 25° by the dynamic method. The composition of the vapour was determined by passing a stream of nitrogen through a series of three bubblers in a thermostat so arranged that the composition of the last of these remained virtually unchanged. The distillate passed through an electrically heated tube to a U-tube immersed in liquid air (or solid carbon dioxide and ether), where it was condensed. The composition of the condensate was determined pyknometrically. The mass of the vapour was generally determined separately by means of apparatus already described (A., 1924, ii, 306), the mixed alcohol and water vapour being absorbed in concentrated sulphuric acid. The results show that the discontinuities in the partial pressure curves observed by Foote and Scholes (A, 1911, ii, 859) at 25° and by Vrevsky (A, 1912, ii, 1139) at 30·7° are due to analytical errors. E. E. WALKER.

Partial formaldehyde vapour pressures of aqueous solutions of formaldehyde. II. W. LEDBURY and E. W. BLAIR (J.C.S., 1925, **127**, 2832—2839; cf. A., 1925, ii, 400).—The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde have been determined by the dynamic method at 35° and 45°. Small additions of methyl alcohol enhance the vapour pressure. The partial pressure of formaldehyde vapour is much higher in methyl-alcoholic solution than in aqueous solution. Methyl alcohol is supposed to shift the equilibrium between the polymerised and simple formaldehyde molecules in the direction of the latter, thus increasing the partial pressure of the formaldehyde vapour. This equilibrium, which also varies with temperature, is reached slowly at 0° and 20°, but much more rapidly at 35° and 40°. The vapour pressure of aqueous solutions of formaldehyde is given by the expression $\log_{10} p = \alpha - B/T$, where α has the values 9·47, 9·70, 9·81, and 9·87 for solutions of 10%, 20%, 30%, and 40% strength, respectively, and B has the value 2905 for all solutions. E. E. WALKER.

Distillation of hydrochloric acid and nitric acid. E. ÖMAN (Svensk Kem. Tidskr., 1924, **36**, 322—340; from Chem. Zentr., 1925, II, 1342—1343).—The author has studied the distillation curve for aqueous hydrochloric acid. In calculating the distillation factor, the total amount of hydrochloric acid in the liquid phase is taken, although the non-ionised portion only can appear in the vapour phase. The points on the distillation curve were obtained by determining the amount of hydrochloric acid in four to eight successive partial distillates from an original solution of known concentration, the mean composition of two successive distillates being taken to represent the composition of the vapour in equilibrium with the liquid after the collection of the first distillate. The following values were found for the distillation factor: for 10% hydrochloric acid 0·05, for 18·0% 0·55, for 20·24% 1·0. The curve is linear from 14·5% to 17·5%; above the latter concentration, there is a change of direction, which suggests a transformation point of hydrates.

The author has further determined the distillation factors for solutions of arsenic trichloride in aqueous hydrochloric acid. The distillation factors are given for the beginning and end of each partial distillation. In every case, the distillation factor is greater than unity. Arsenic trichloride, therefore, accumulates in the distillate, although its b. p. (130·2°) is higher than the maximum b. p. of aqueous hydrochloric acid (110°). Hydrochloric acid may be freed from arsenic trichloride by the passage of a current of hydrogen chloride. The application of these results to the Schneider distillation is discussed. In the absence of any device to facilitate the liberation of vapour, vaporisation occurs only at the surface of the liquid, which becomes relatively poorer in hydrochloric acid, and a greater quantity of distillate is required for the removal of the arsenic trichloride.

The distillation factor for a 13·15% solution saturated with sodium chloride is unity. The increase

in the distillation factor is due to the repressive effect of sodium chloride on the ionisation of hydrochloric acid. A similar result is obtained when sulphuric acid is added. The increase in the percentage of sulphuric acid in the liquid during distillation introduces a complication in the distillation curves. Even when the distillation factor reaches unity, constancy is not maintained. With 10% of sulphuric acid present, hydrochloric acid can be removed until the liquid remaining contains 17% of hydrochloric acid; with higher proportions of sulphuric acid, more hydrochloric acid can be removed.

The constant b. p. mixture of nitric acid and water contains 68% of nitric acid. From a study of the distillation of concentrated solutions of nitric acid, it is concluded that there is no dissociation when the concentration of nitric acid exceeds 92%.

G. W. ROBINSON.

Distillation of hydrochloric acid and nitric acid. L. RAMBERG (Svensk Kem. Tidskr., 1925, **37**, 31—36; from Chem. Zentr., 1925, II, 1343—1344; cf. preceding abstract).—Polemical. A criticism of Öman's explanation of the Schneider arsenic distillation, together with a reply by Öman.

G. W. ROBINSON.

Kinetic theory of the specific heat of solutions. N. DE KOLOSSOWSKY (Gazzetta, 1925, **55**, 844—858; cf. A., 1925, ii, 765, 791, 859, 870, 1163).—A *résumé* is given of the author's theory, and additional experimental data for the viscosity, temperature coefficient of viscosity, and the molecular heats of a number of solvents and solutions are recorded. The molecular heats of the solutions are in satisfactory agreement with those calculated.

F. G. TRYHORN.

Solid solutions between compounds of elements of different valency. Lithium chloride and anhydrous magnesium chloride. G. BRUNI and A. FERRARI (Atti R. Accad. Lincei, 1925, [vi], **2**, 457—462).—An *X*-ray analysis has been made of lithium chloride, of anhydrous magnesium chloride, and of mixed crystals of these substances in the proportions $LiCl:MgCl_2$ and $4LiCl:MgCl_2$. Both compounds have a cubic lattice. The unit cell of lithium chloride has an edge of 5·10 Å., and d (calc.) 2·12. The corresponding values for magnesium chloride are 5·09 Å. and 2·47, respectively. The photograms of the mixed crystals, as well as those of mechanical mixtures, differ from those of the pure components only in the intensity of the lines. The unit cells contain one molecule in the case of magnesium chloride, and four molecules in that of lithium chloride.

F. G. TRYHORN.

Separation of mixed liquids by the action of salts. C. SANDONNINI and G. GEROSA (Gazzetta, 1925, **55**, 916—938; cf. A., 1925, ii, 765).—Measurements have been made of the heats of solution and of dilution of potassium and sodium chloride in water, acetone–water mixtures, and ethyl alcohol–water mixtures, and of the heats of mixing of acetone and alcohol with aqueous solutions of the above salts. The curves for the heat of mixing of acetone and water, and of alcohol and water, in the presence of the salts are similar in form to those for the pure liquids, but the amount of heat evolved is smaller. The heat evolution has a maximum value for mixtures containing about 35% of acetone and about 30% of alcohol, respectively. The diminution of the heat of mixing in the presence of the salts and the difference between the observed heats of solution of the salts in the mixed liquids and the values calculated by the mixture law are attributed to the "inactivation" of part of the water by the salt. The bearing of this concept on the formation of conjugate solutions by the addition of a salt to a mixed liquid is discussed, and it is shown that the constitution of the mixture itself must be taken into account as well as the solubility relations of the salt and the liquids. In general, the separation of the mixed liquid into two phases will occur more readily with those liquids which have a positive heat of mixing, the separation being promoted in this case by rise of temperature.

F. G. TRYHORN.

Salting out effect. Influence of electrolytes on solubility of iodine in water. J. S. CARTER (J.C.S., 1925, **127**, 2861—2866).—The solubility of iodine in water in the presence of various electrolytes at 10°, 25°, and 35° has been determined. The solubility of iodine in the presence of salts can be expressed by the equation $\log S = \log S_0 - kc$, where S and S_0 are the solubilities of iodine in the presence and absence of electrolyte, respectively, and c is the concentration of salt. Concentrations in each case are expressed with reference to 1000 mols. of water. Agreement is good in the case of sodium nitrate and sulphate, and also in the case of sodium chloride when due allowance is made for the influence of the polyiodide present, over the whole range of salt concentration. Agreement falls off in the higher concentrations of sodium dihydrogen phosphate. The solubility of iodine is increased by nitric and decreased by sulphuric acid, following no simple law in either case.

E. E. WALKER.

Solubility of barium propionate. H. J. WING and T. J. THOMPSON (J. Amer. Chem. Soc., 1926, **48**, 104—106).—The solubility has been determined from 0° to 100°, over which range the solid in equilibrium with the solution is the monohydrate. The solubility, expressed in parts of anhydrous salt per 100 parts of water, decreases from 57·5 at 0·3° to 56·3 at 15° and then increases to 82·7 at 100·7°. Contrary to the results obtained by Krasnicki (A., 1888, i, 359), the solubility curve is thus convex to the temperature axis.

R. CUTHILL.

Solubility of sodium iodide in ethyl alcohol. F. E. KING and J. R. PARTINGTON (J.C.S., 1926, 20—22).—Ten determinations of the solubility of sodium iodide in ethyl alcohol at 25°, precautions being taken to exclude moisture, yielded values between 42·13 and 42·89 g./100 g. of alcohol, the mean value being 42·57 g./100 g. of alcohol. The solution had d_4^{25} 1·037.

J. S. CARTER.

Solubilities of sodium, potassium, and calcium ferrocyanides. (MISS) M. FARROW (J.C.S., 1926, 49—55).—The formula, $Ca_2Fe(CN)_6,11H_2O$, for crystalline calcium ferrocyanide (cf. Cumming, A., 1924, ii, 353) is confirmed. Titration of ferrocyanide

solutions with permanganate according to the method of de Haeu (Treadwell, " Quantitative Analysis," p. 632) gives concordant results if the permanganate solution is standardised by means of potassium ferrocyanide. This method is preferred to the benzidine hydrochloride method of Cumming (*loc. cit.*). In the determination of the calcium in ferrocyanide solutions by precipitation as oxalate, dilute, boiling solutions of sodium oxalate should be used, ammonium oxalate precipitating an insoluble double salt and oxalic acid precipitating hydroferrocyanic acid.

The solubility in water of sodium and potassium ferrocyanides over the temperature range 24·9—99·7°, and of calcium ferrocyanide over the range 24·9—64·7° has been investigated. At 24·9°, the solubilities in water of these three salts are 17·11, 23·95, and 36·44 g./100 g. of solution, respectively. For sodium ferrocyanide, the result agrees with that of Conroy (A., 1899, i, 2). This salt has a transition point in the region of 81·5° (81·7° from solubility curve, 81·2° by thermometric method, 81·5° by dilatometric method). Neither the potassium nor the calcium salt shows any transition over the range investigated and the transition point of the potassium salt recorded by Etard (A., 1894, ii, 442) is probably due to contamination with the sodium salt. The result for the potassium salt agrees with that of Vallance (A., 1922, i, 724) and Fabris (*ibid.*, 329) except at temperatures above 84°, where Fabris' values are higher. Densities of the saturated solutions are given. J. S. Carter.

Barium dithionate and the solubility of calcium dithionate. F. Ishikawa and G. Kimura (Bull. Inst. Phys. Chem. Res., 1926, **5**, 1—16).—The solubility of barium dithionate ($BaS_2O_6,2H_2O$) and of calcium dithionate ($CaS_2O_6,4H_2O$) in water has been measured between 0° and 90°. The data for barium dithionate expressed in grams of anhydrous salt per 100 g. of solution are 0°, 7·75; 10°, 11·56; 20°, 15·63; 30°, 19·70; 40°, 23·55; 50°, 26·91; 60°, 30·13; 70°, 33·08; 80°, 35·69; 90°, 38·42. The eutectic temperature is −0·64° and the solubility at this temperature 7·55. For calcium dithionate the corresponding data are: 0°, 13·86; 10°, 17·20; 20°, 20·18; 30°, 23·12; 40°, 25·80; 50°, 28·48; 60°, 30·94; 70°, 33·14; 80°, 35·91; 90°, 38·04. The eutectic point corresponds with −2·09°, 13·40. The densities of both series of saturated solutions are recorded. Dehydration of barium dithionate at different temperatures leads directly to the formation of the anhydrous salt; at 90° a very small amount of barium sulphate is formed. The reaction $BaS_2O_6 = BaSO_4 + SO_2$ is irreversible; it proceeds very slowly at 140°, but is complete after 30 min. at 700°.

K. Kashima.

Solubility relations of isomeric organic compounds. VI. Solubility of the nitroanilines in various liquids. A. R. Collett and J. Johnston (J. Physical Chem., 1926, **30**, 70—82; cf. Sidgwick and Rubie, J.C.S., 1921, **119**, 1013).—Solubility data, determined by a modified synthetic method, for *o*-, *m*-, and *p*-nitroaniline in acetone, ethyl acetate, chloroform, benzene, ethyl alcohol, ethyl ether, and carbon tetrachloride over a range of temperatures up to the respective m. p., are presented and discussed. The solubilities in water and 95% ethyl alcohol at 25° and 40° have also been measured. Although the solubility curves are, in general, similar, significant differences as between the isomerides are noted, and these are to be correlated with m. p. and, presumably, the heat of fusion of the isomeride. At temperatures near the m. p., the sequence of solvents, in order of decreasing solubility, is ideal — acetone, ethyl acetate, (nitrobenzene), chloroform, (dibromoacetylene), benzene, alcohol, ether, and carbon tetrachloride. At lower temperatures, however, the sequence is not invariable. Contrary to Mortimer (A., 1923, ii, 299), the solubility of one isomeride cannot be calculated from that of another, except as a rough approximation. It appears that, in a given solvent at a definite temperature, the isomeride with the lowest m. p. is the most soluble, whilst that with the highest m. p. is the least soluble, when the equilibrium is between crystals and solution. Differences in solubility of the solid isomerides may then be ascribed, apparently, to the same factors which cause differences in the m. p. and heats of fusion (see Sidgwick and Callow, J.C.S., 1924, **125**, 529). The solubility curves show that the solvents examined, with the exception of carbon tetrachloride, are equally effective for the separation of the isomerides by recrystallisation, and, on the assumption that the solubility of one isomeride is not greatly affected by the presence of another, the number of recrystallisations necessary for separation can be calculated.

In purifying the nitroanilines by recrystallisation, the successive use of two solvents, *e.g.*, alcohol followed by water, was found to be more effective than the use of one solvent alone. The m. p. of the *o*-nitroaniline used as found from the time–temperature curve was 69·3°, as against 72° found by the ordinary capillary tube method. L. S. Theobald.

Solubility effects. I. Temperature coefficients. E. Oliveri-Mandalà (Gazzetta, 1925, **55**, 759—768).—In view of the low heats of solution, the author considers that the increased solubility of bromine and iodine in water in presence of potassium bromide and potassium iodide, respectively, is not due to chemical combination, or, at any rate, that no great affinity exists between the halogen and the halide, so that the supposed compounds must be highly unstable. In aqueous solution, caffeine yields with sodium benzoate much more stable compounds, the value of the heat of solution being far higher in this case. Ammonia exhibits a tendency to form additive compounds, not only with alkali chlorides, but also with alkali carbonates. Salicylic acid forms highly stable compounds with dextrose in aqueous solution. It is stated that the reaction isochore cannot be utilised for the calculation of the heat of dissolution when such solubility effects come into play. Conversely, the magnitude of the heat of dissolution may not be used as an argument for or against chemical action between solute and dissolution.

T. H. Pope.

Solubility effects. II. Molecular solubility coefficients. E. Oliveri-Mandalà (Gazzetta, 1925, **55**, 769—774; cf. preceding abstract).—Examples

are quoted to show that solubility effects involving both electrolytes and non-electrolytes are not in accordance with the law of mass action. The ratio of the concentration of solute to that of the solvent solution is usually a function of the latter, which function varies in type, not only when the solutes and solvents are chemically similar, but even when the range of concentration considered is varied. Thus, the measurements of Noyes and Seidensticker on the solubility of iodine in dilute potassium iodide solutions (A., 1899, ii, 11) show that the ratio I : KI is independent of the concentration of the iodide, whereas those of Weith and Dossios (Z. Chem., 1869, 379) made with more concentrated potassium iodide solutions indicate that this ratio is an exponential function of the concentration of the iodide.

T. H. POPE.

Solubility effects. III. Quinine hydrochloride and antipyrine. E. OLIVERI-MANDALÀ and E. CARLI (Gazzetta, 1925, **55**, 774—782; cf. preceding abstracts).—In view of the fact that the use of a mixture of basic quinine hydrochloride and antipyrine as a local endothermic and hypodermic anæsthetic is not attended by the secondary effects produced by quinine alone, the authors have investigated, cryoscopically and by a method based on measurement of the solubility coefficient at various temperatures, the formation or non-formation of molecular complexes of the two compounds.

The presence of antipyrine greatly increases the solubility in water of basic quinine hydrochloride, which then fails to give its characteristic colour reactions. The f. p. of concentrated aqueous antipyrine solutions are very slightly lowered by addition of the quinine salt, whereas those of solutions of medium concentration remain unchanged; combination of the two compounds is thus indicated.

The ratio between the solubility of quinine hydrochloride and the concentration of the antipyrine in the solution, *i.e.*, the solubility coefficient, increases slightly as the concentration of the antipyrine is increased, but remains almost constant when the temperature is varied. Thus, the heat of dissolution of the alkaloid is virtually the same in antipyrine solutions as in water, and chemical action between the two compounds is contra-indicated. No explanation is advanced for these opposing results.

T. H. POPE.

Solubility effects. IV. Acetanilide-antipyrine, acetanilide-pyramidone. E. OLIVERI-MANDALÀ and F. FORNI (Gazzetta, 1925, **55**, 783—788; cf. preceding abstracts).—The values of the solubility coefficient indicate that acetanilide, although its solubility in water is increased considerably by the presence of antipyrine, exhibits no tendency to form molecular compounds with the latter. On the other hand, acetanilide and pyramidone appear to form such compounds. T. H. POPE.

Law concerning the "ratio of tangents" to solubility curves. P. MONDAIN-MONVAL (Bull. Soc. chim., 1926, [iv], **39**, 35—40; cf. A., 1923, ii, 635; 1925, ii, 654).—A reply to criticism by Cohen and Bredée (A., 1925, ii, 976). The author's previous experimental results are generally in good agreement with those of Cohen and Bredée, and the latter's criticism that the author's value for the ratio of the solubilities of the two modifications of ammonium nitrate involves an error of calculation, is without justification; on the contrary, the graphical method employed by Cohen and Bredée is inadmissible.

W. HUME-ROTHERY.

Chemistry of gold. V. LEHNER and C. H. KAO (J. Physical Chem., 1926, **30**, 126—129; cf. Lenher, A., 1913, ii, 514, 628).—The distribution of chloroauric acid between water and aliphatic esters has been studied. The results for methyl, ethyl, *iso*propyl, *iso*butyl, and *iso*amyl esters of the fatty acids up to and including butyric acid show that the power of extracting auric chloride from aqueous solution decreases with increase in number of carbon atoms. The relations observed with acidified aqueous solutions indicate that the distribution is not dependent on the mutual solubilities of ester and water. The presence of hydrochloric acid is an important factor in the distribution, the separation of auric chloride increasing to a maximum when 10% of this acid is present; larger quantities of acid have little or no further effect. Ethyl acetate in 10% hydrochloric acid is thus the most effective extraction agent for auric chloride. This was confirmed by the complete removal of gold from the chlorides of twenty of the commoner metals. Owing to the separation of metallic gold, mol. wt. measurements in the various esters were unsuccessful.

L. S. THEOBALD.

Adsorption by an optical method. Fixation by dispersoids of methylene-blue within the disperse phase. A. FODOR and R. RIWLIN (J.C.S., 1926, 102—112).—A spectrophotometric method is outlined whereby the adsorption of dyes by colloidal finely divided adsorbents may be investigated. If b is the transmissive power of x c.c. of dye solution $+x$ c.c. of a sol, a that of x c.c. of sol diluted with x c.c. of water, and c that of x c.c. of dye diluted with x c.c. of water, then $ac=b$, provided there is no interference due to adsorption or reaction. Experiments with dilute aqueous solutions of methylene-blue show that in presence of silica sol or sodium silicate violet solutions result and the minimum transmission is shifted from 637 $\mu\mu$ to 590 $\mu\mu$. This is indicative of compound formation ("chemosorption"). The stability of this compound is largely dependent on the hydrogen-ion concentration of the medium. Using kaolin suspensions, the b transmission curves lie above, and are parallel with, the calculated ac curves, indicating mechanical adsorption ("lyosorption"). The dye is not adsorbed by aluminium hydroxide sol, natural protein (filtered solution of white of an egg in water), casein, albumin, saponin, and gelatin.

J. S. CARTER.

Adhesion forces in solutions. N. SCHILOV and (MISS) S. PEVSNER (Z. physikal. Chem., 1925, **118**, 361—368; cf. A., 1920, ii, 591).—The adsorption of acids and salts by charcoal from binary solvents has been examined. The curves obtained by plotting the adsorption against the composition of the solvent

vary in type according to the nature of the adsorbed substance and the components of the binary solvent. The curves for the adsorption of salts and inorganic acids from mixtures of ethyl alcohol and water exhibit minima; such minima are not obtained, however, when the adsorbed substance is an organic acid. For non-aqueous binary solvents minima are always shown and in some cases the adsorption from the mixed solvents is very small compared with that from the two pure components. A striking instance of this behaviour is afforded by the adsorption of benzoic acid from mixtures of toluene and ethyl alcohol. L. F. GILBERT.

Adsorption and electrical properties of various charcoals. I. OGAWA (Biochem. Z., 1925, **161**, 275—294).—Specimens of charcoal prepared from blood, sugar, naphthalene, gelatin, paraffin, liver, and agar were heated to a red heat in covered nickel crucibles to activate them. It was found that the adsorptive power of such charcoal bears no relation to the amount of ash it contains. When the charcoal is activated, it adsorbs dissolved substances much more strongly than before, and some substances which are not adsorbed before activation are strongly adsorbed afterwards. Activation also alters the electrical properties of charcoal. H. I. COOMBS.

Adsorptive equilibria of binary gaseous mixtures. W. G. PALMER (Proc. Roy. Soc., 1926, **A, 110**, 133—141; cf. A., 1924, ii, 665).—The adsorption films on platinum and tungsten filaments have been investigated by measurement of the voltage necessary to cohere two filaments in contact. The relation between the cohering voltage and the film composition has been determined for mixtures of carbon monoxide and oxygen, and the observed changes in the composition of the adsorption film are said to afford support for the assumptions underlying the method. The data for mixtures of hydrogen and carbon monoxide suggest that these form a complex CO,H_2 which is adsorbed in addition to the other molecular types. Mixtures of hydrogen chloride and oxygen, and of nitrogen and hydrogen, were also examined, the results indicating that nitrogen forms an incomplete surface film. The calculated latent heats of desorption are found to depend largely on the mode of preparation of the surface.

F. G. SOPER.

Adsorption of ions on a mercury surface. W. A. PATRICK and P. W. BACHMAN (J. Physical Chem., 1926, **30**, 134—135).—A preliminary statement of results. When the droplets formed by forcing mercury through chamois skin are allowed to pass through dilute aqueous solutions of mercurous sulphate or acetate, the mercurous ions are adsorbed to a greater extent than the anions. Curves showing the amounts of ions adsorbed with varying initial concentrations of the electrolyte are given.

L. S. THEOBALD.

Kinetic theory of surface films. R. K. SCHOFIELD and E. K. RIDEAL (Proc. Roy. Soc., 1926, **A, 110**, 167—177; cf. A., 1925, ii, 960).—The behaviour of the surface films of the higher fatty acids has been examined by reference to the surface tension–concentration data of Frumkin (A., 1925, ii, 856). By plotting FA/RT against F, where F is the outward force exerted by the film and A is the gram-molecular area, curves have been obtained for the series of aliphatic acids containing from 4 to 10 carbon atoms which resemble the pv/RT–p curves for gases at successively lower temperatures, whilst those for the acids with 12 and 14 carbon atoms resemble the corresponding curves for liquids just below their critical temperatures. At high surface pressures, the graphs are straight and thus obey the relation $F(A-B)=xRT$ analogous to Amagat's equation for highly compressed gases and liquids. B has in each case the common value (24—25 Å. per mol.) previously found for the acids C_4, C_5, and C_6 in accordance with Langmuir's view that the molecules in these films under high compression are vertically oriented. It is found that x decreases with the length of the hydrocarbon chain, indicating an increasing lateral cohesion. At low surface pressure, the films show a behaviour corresponding approximately, but not exactly, with that of fluids, the lack of quantitative agreement being attributed to a varying molecular orientation in the film at low surface pressure. The authors conclude that although the outward force exerted by expanded and gaseous films is essentially kinetic in origin, that exerted by condensed films is due rather to a steady repulsive force exerted by each molecule on its neighbours. F. G. SOPER.

Phenomena occurring at the surface of bubbles in water. T. ALTY (Proc. Roy. Soc., 1926, **A, 110**, 178—190; cf. *ibid.*, 1924, **A, 106**, 315).—The surface tension of water in contact with various gases has been measured by the drop-weight method (Iredale, A., 1923, ii, 379). For slow rates of flow, it is found that the weight of a bubble is independent of the gas used. When the rate of flow is increased until several bubbles emerge per second so that the age of the surface is diminished, the volume of the bubble, after making necessary corrections, depends on the gas used. The gas bubbles, arranged in decreasing order of volume, give the following series: argon, nitrogen, oxygen, ozone, hydrogen, nitric oxide, carbon dioxide. These variations in size are explained in terms of the rates of adsorption of the various gases at a water surface, argon having the slowest and carbon dioxide the fastest rate. In the presence of electrolytes, the differences between the bubble volumes are augmented as is required by the theory.

F. G. SOPER.

Interfacial tension and emulsification. I. Effects of bases, salts, and acids on interfacial tensions between aqueous sodium oleate solutions and benzene. II. Extremely small interfacial tensions produced by solutes. W. D. HARKINS and H. ZOLLMAN (J. Amer. Chem. Soc., 1926, **48**, 69—80).—The interfacial tension has been measured by the drop-weight method. It is found to be the smaller the longer the drop is allowed to hang before falling, but it may rise again after a time. Under initial non-equilibrium conditions (*i.e.*, without previous mixing of the phases), the interfacial tension between water and benzene is lowered considerably by the presence of oleic acid in the benzene

or by sodium oleate in the water. The depression produced by the latter is much intensified by the presence of sodium hydroxide. With initial equilibrium conditions the general order of effects is the same.

The interfacial tension between aqueous sodium oleate solutions and benzene under non-equilibrium conditions is much reduced by oleic acid (in the benzene phase) or by sodium hydroxide, and when the value falls below about 1 dyne/cm. emulsification apparently occurs spontaneously. Salts have a similar but less pronounced effect, but the lowering produced by sodium chloride may be more than overcome by addition of traces of calcium chloride. The thickness of the adsorbed film of sodium oleate at the interface has been calculated. R. CUTHILL.

Influence of hydrogen-ion concentration on the velocity of dialysis. H. MOMMSEN (Z. physikal. Chem., 1925, **118**, 347—356).—The influence of hydrogen-ion concentration on the rate of diffusion of the ions of certain electrolytes through parchment membranes (cf. Terada, A., 1924, ii, 455) cannot be ascribed to variations in the permeability of the membranes, as is shown by the following experimental results. The rates of flow, under pressure, of water, 0·002*N*-sodium hydroxide, and 0·002*N*-hydrochloric acid through parchment are approximately the same. The velocities of dialysis of non-electrolytes (carbamide and grape-sugar) are almost unaffected by the presence of these concentrations of alkali and acid, a slight acceleration being observed in the case of the acid solution. The velocities of dialysis of anions and of cations are accelerated by an increase and a decrease of p_H, respectively. This effect is due probably to alterations in the electrical charges on the membranes. L. F. GILBERT.

Mechanism of ultrafiltration. J. DUCLAUX and J. ERERRA (Kolloid-Z., 1926, **38**, 54—57).—Comparison between the viscosities and the times of flow through ultrafilters of aqueous solutions show that the membranes used (cellulose, cellulose nitrate, and cellulose acetate) act as though composed of a number of capillary tubes, the dimensions and properties of which are independent of the nature of the solutions. The same conclusion is reached for all liquids which do not dissolve or soften the membranes. The structure of the membranes is fibrous and rigid, and is independent of the nature of the liquid which flows through. The irreversible gels of which the membranes are composed are not solvated to any appreciable extent. N. H. HARTSHORNE.

Reversible permeability of membranes and relation to cell metabolism. C. GURCHOT (J. Physical Chem., 1926, **30**, 83—105).—Experiments on membranes of copper ferrocyanide show that coagulation is brought about by low concentrations of methyl alcohol (minimum concentration 1·5%), propyl alcohol, acetic acid, sodium, potassium, and calcium chlorides, the membrane becoming permeable to sugar. More methyl alcohol (2·0%) is required when the sugar and alcohol are on different sides of the membrane than when both are on the same side. A copper ferrocyanide sol is coagulated by aqueous methyl alcohol, but the precipitation of the sol proved to be less sensitive than the test for permeability of the membrane. Alkalis and water peptise the gel formed. The coagulation of arsenious sulphide and sulphur sols required about 0·5% and 0·4% of ethyl alcohol, respectively; the sulphur sol could be flocculated by dextrose and sugar syrups, and also by glycerol solution (0·5%). In the presence of membrane-forming reagents, viz., copper sulphate and potassium ferrocyanide, no evidence of coagulation of the membrane was obtained. Membranes coagulated by methyl and propyl alcohols and by acetic acid showed no reversal when treated with water; with those coagulated by methyl, ethyl, propyl, and amyl alcohols, reversibility was obtained with 0·02*M*-copper sulphate solution, but in the case of ethyl alcohol, 0·20*M*-copper sulphate was necessary for the recovery of the membrane. Membranes of copper ferrocyanide are coagulated by water at 23—24°. The coagulation is due to selective adsorption and not to decrease in surface tension. The ferrocyanide forms a granular membrane and the adsorbed water present between the particles fills up the spaces more or less completely.

The experiments of Barlow (A., 1906, ii, 273), Walden (A., 1893, ii, 203), and Czapek (Ber. Deut. bot. Ges., 1910, **28**, 159) involve nothing more than a coagulation of the membrane. Intermittent permeability in living membranes is probably also a question of reversible coagulation.

Membranes of copper ferrocyanide in gelatin are better prepared at 8° than at the ordinary temperature. L. S. THEOBALD.

Stability of carbon dioxide solutions. A. KLING and A. LASSIEUR (Compt. rend., 1926, **182**, 130—131; cf. *ibid.*, 1925, **181**, 1062).—The opinion has been expressed that the acid reaction of pure water, found by the author to be p_H 5·8, is due to the presence of dissolved carbon dioxide. It is now shown that aqueous solutions of carbon dioxide kept in platinum vessels either open to the air or closed and in presence of barium, calcium, or sodium hydroxide, undergo a fairly rapid decrease of acidity, until the p_H becomes constant, and equal to that of pure water. In presence of traces of ammonia, however, carbon dioxide solutions are stable. L. L. BIRCUMSHAW.

State of ferric salts in solution. N. TANANAEV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 74—75; from Chem. Zentr., 1925, II, 419).—Solutions of ferric salts usually contain more iron than is required by their formulæ, owing to the presence of ferric hydroxide due to hydrolysis. The iron present as hydroxide is not determined by the iodometric method, and the difference between this and the gravimetric method gives the amount of iron present as hydroxide. With increasing hydrolysis, ferric hydroxide is precipitated. G. W. ROBINSON.

Viscosity of ammonium oleate solutions. E. HATSCHEK and R. S. JANE (Kolloid-Z., 1926, **38**, 33—42).—The viscosity of very dilute ammonium oleate solutions, showing a decided shear elasticity, has been measured in a self-recording Couette viscosi-

meter. With fresh sols, *i.e.*, sols not sheared too energetically or for too long a period, the inner cylinder did not achieve a position of rest for a constant angular velocity, but its deflexion increased, often only after many revolutions, up to a distinct maximum and thereafter fluctuated considerably; maxima recurred periodically and often reached after 40—50 revolutions the full value of the first maximum. If a fresh sol were gently sheared or shaken for a short time and then allowed a brief rest, it generally showed a marked increase in the apparent viscosity, which was succeeded by the fluctuations described above, showing that no permanent effect had been produced. Shearing for long periods at high velocities or energetic stirring produced, however, a fundamental change. At low angular velocities, the viscosity was now constant as in the case of normal sols, and over a wide range of velocities was independent of the shear gradient. Further, it was little higher than that of water. At higher velocities, the viscosity increased very suddenly, reaching values many times those measured at the low velocities.

N. H. HARTSHORNE.

Unstable states of solutions of sodium behenate. M. E. LAING (J.C.S., 1925, **127**, 2751—2755).—The stable forms of 0·05—0·5N_w-sodium behenate solutions at the ordinary temperature are solid white curds, but by rapid cooling they can be obtained in the form of mobile liquids. These unstable solutions have been examined microscopically, and measurements of their f. p., hydrogen-ion concentration, and conductivity have been made. The constituents of 0·05N_w-solution at 18° are approximately, acid soap ($Na_2HB\bar{e}_3$) 42%, dissociated soap 5%, neutral colloid 53%. This corresponds with 14% hydrolysis. On keeping, the hydrolysis diminishes to a tenth of this value and white curd begins to separate out. The hydrolysis at 90° is very much less than at 18°. E. E. WALKER.

Nature of solutions of cellulose in cuprammonium hydroxide. S. M. NEALE (J. Text. Inst., 1925, **16**, T 363—369).—The hypothesis is advanced that cuprammonium cellulose solutions belong to the class of colloidal electrolytes. The strong base, cuprammonium hydroxide, forms with the weak acid, cellulose, a soluble basic salt of which the cation is "crystalloidal" and an anion "colloidal." Each cellulose hexose unit is associated with one atom of copper, and thus the anionic micelle consisting of a large number (n) of condensed hexose groups and carrying n negative charges is, together with n hydroxyl anions, equivalent to n bivalent cuprammonium cations. Cellulose neutralises the cuprammonium hydroxide to the extent of using completely the hydroxyl arising from the first stage of the dissociation of this base. Further action is presumably inhibited on account of the weaker dissociation of the second hydroxyl and by the impossibility of the existence of the soluble cellulose complex in any but a highly alkaline medium. The hypothesis is supported by *E.M.F.* and cataphoresis experiments on cuprammonium hydroxide solutions, alone and containing cellulose. Further evidence from the heats of solution and of ionisation of cellulose could not be obtained owing to experimental difficulties, but such evidence was obtained with dextrose and lævulose solutions in cuprammonium hydroxide, pointing to the existence of a highly ionised cuprammonium sugar salt.

A cuprammonium cellulose solution kept saturated with ammonia gradually became less viscous and deposited a bulky, pale-blue precipitate which contained cupric hydroxide and $C_6H_{10}O_5$ in equimolecular proportions. Further, in a cataphoresis experiment using a zinc ammonium hydroxide solution above the cuprammonium cellulose solution at the bottom of the U-tube, the cellulose was deposited in the anode compartment in layers about 1 mm. apart.

J. C. WITHERS.

Elasticity and flow double refraction in sols having non-spherical particles. I, II. H. FREUNDLICH, H. NEUKIRCHER, and H. ZOCHER (Kolloid-Z., 1926, **38**, 43—47; 48—54).—I. In order to characterise the elastic behaviour of sols, Newton's fundamental law of the friction of liquids must be used as a basis. The Couette viscosimeter is considered to be more suitable than the capillary type for the investigation of this question, since the measurement of the dependence of the friction on the velocity gradient is required. The possible relation between elastic behaviour and the direction of flow double refraction in sols having non-spherical particles is discussed.

II. For a series of sols having non-spherical particles (vanadium pentoxide, benzopurpurin, and cotton-yellow) the flow double refraction measured by the so-called "cross angle" has been compared with the viscosity and the flow elasticity. The last two quantities were measured by an apparatus similar to the Couette viscosimeter but reproducing as far as possible the conditions under which the cross angle was determined. The results of Stapelfeldt (A., 1925, ii, 200) with regard to the cross angle were essentially confirmed. The constancy of the cross angle with varying concentration found by Stapelfeldt in the case of vanadium pentoxide sol proved, however, to be true only for small concentrations. At higher concentrations, it increases with the percentage of vanadium pentoxide. The viscosity and flow elasticity of old vanadium pentoxide sols cannot be expressed by Szegvari's equation $W=\eta G+\theta$ (Z. physikal. Chem., 1923, **108**, 175), in which W is the resistance of the liquid, G the velocity of gradient, η the viscosity coefficient, and θ the flow elasticity. θ is not constant, but depends on G. Between the cross angle ψ (or the deformation ϕ deduced from this), on the one hand, and η and θ, on the other, no simple relation could be detected. With vanadium pentoxide sols, there is some degree of parallelism between ψ and θ, but with the dyes a marked alteration in ψ with time is observed, whilst η and θ remain practically constant. N. H. HARTSHORNE.

Polychrome mercury hydrosols. A. GUTBIER (Kolloid-Z., 1926, **38**, 82).—Polemical against Feick (see this vol., 22). N. H. HARTSHORNE.

Migration velocity and charge number of colloidal gold. W. PAULI (Kolloid-Z., 1926, **38**, 22—26).—The charge on gold particles deduced from

measurements of the hydrogen-ion concentration of the highly dialysed sols, and its great dependence on the number of particles invisible under the ultramicroscope (already treated elsewhere; see Fuchs and Pauli, this vol., 22) are discussed in connexion with migration velocity measurements.

N. H. HARTSHORNE.

Antagonistic action of ions in the neutralisation of sols. H. B. WEISER (J. Physical Chem., 1926, **30**, 20—33; cf. Dhar, Ghosh, and Sen, A., 1924, ii, 733, 737, 830; A., 1925, ii, 386, 511, 778; Weiser and Nicholas, A., 1922, ii, 266; Weiser, A., 1922, ii, 262; Weiser and Middleton, A., 1920, ii, 228; Weiser, A., 1924, ii, 309).—The phenomena previously studied by the author are considered in the light of the observations of Dhar and his co-workers. The effect of dilution of sols on their stability towards electrolytes and acclimatisation is briefly discussed, whilst the action of mixed electrolytes is considered in detail. It is emphasised that in the first case precipitation values are determined by the nature of anion, cation, and sol. The " general dilution rule " of Ghosh and Dhar, that the greater the concentration of a sol the greater is the amount of electrolyte necessary for coagulation, irrespective of the valency of the precipitating ion, fails to take all these factors into account. Strong adsorption of the stabilising ions of the precipitating electrolyte is not essential for acclimatisation of sols when strong adsorption of the precipitating ions occurs during fractional agglomeration. It is, however, essential in fractional precipitation by successive dilutions. In either case, acclimatisation is a necessary concomitant of fractional precipitation.

The factors which determine the precipitation concentrations of mixtures of two electrolytes are: (1) the effect of each precipitating ion on the adsorption of the other; (2) the stabilising action of ions having the same charge as the sol, and (3) the relatively greater adsorbability of ions at lower concentrations. Under (1), the precipitation of arsenious sulphide sol by barium chloride in the presence of alkali chlorides has been examined, and the experiments show that the precipitation value of the former is increased by equivalent amounts of alkali chlorides in the order LiCl>NaCl>KCl, a variation which follows from the assumption that the barium ion reduces the adsorption of alkali cations to different degrees (cf. A., 1925, ii, 855). Experiments on the precipitation of the same sol by mixtures of barium and potassium ferrocyanides show that the departure from additive relationships is greater with the ferrocyanides than with the chlorides, a result due to the difference in the adsorbability of the stabilising ions. Further, with the same sol, the cationic antagonism is greater in the presence of the more strongly adsorbed ferrocyanide ion than is the case with the chloride ion, as shown by a greater adsorption of barium from ferrocyanide solution than from chloride solution. This antagonistic action between precipitating ions of like charge is important in raising the critical concentrations above the additive value only when the ions show a marked difference in adsorbability. The critical values for mixtures of two electrolytes may rise above the additive value even when the precipitating ions are identical and antagonism between them cannot exist (Sen, A., 1925, ii, 664, 665). Deviations from additive behaviour with salt pairs having a common precipitating ion results only when there is an appreciable difference in adsorbability of the stabilising ions. This difference determines the magnitude of the deviation. When the factors (1) and (2) above are not too pronounced, the precipitation values may fall below the additive value on account of the relatively greater adsorption of precipitating ions at low concentrations, as is the case with arsenious sulphide sol precipitated by mixtures of cerium and potassium chlorides.

L. S. THEOBALD.

Formation and ionisation of the compounds of caseinogen with alkali. IV. Transport numbers of the compounds of caseinogen with the alkaline-earth elements. D. M. GREENBERG and C. L. A. SCHMIDT (J. Gen. Physiol., 1926, **8**, 271—278; cf. A., 1925, ii, 129).—The values for the transport number of caseinogen in solutions of the alkaline-earth hydroxides are much higher than in solutions of the alkali hydroxides. This supports the view that part of the alkaline-earth element is held by the caseinogen in the form of complex ions. Grounds are given for believing that the complex anions have a definite composition.

C. P. STEWART.

Physical properties of serum on addition of " water-binding " substances. R. FÜRTH and R. PECHHOLD, with a note by R. KELLER (Biochem. Z., 1925, **164**, 9—17).—See A., 1925, ii, 1056.

P. W. CLUTTERBUCK.

Theory of the coagulation of polydisperse systems. H. MÜLLER (Kolloid-Z., 1926, **38**, 1—2).—The view of Wiegner and Galecki that in the coagulation of polydisperse sols the submicrons act as coagulation nuclei for the amicrons receives theoretical confirmation and the following equation is deduced: $N_t+n_t=N_0/(1+t/T_{N_0})[1+\lambda/\{(\lambda V_n+1)(1+t/T_{N_0})^{\lambda}-1\}]$, where N_0 and n_0 are the original numbers of large and small particles, respectively, $V_n=N_0/n_0$, N_t is the number of large particles and complexes containing at least one of these, and n_t the number of small particles and complexes composed only of these, after time t; T_{N_0} is the so-called half coagulation time of the large particles; and $\lambda=(V_r^2+1)/2V_r$, where $V_r=R/r$, R and r being the radii of the large and small particles, respectively. In the special case where N_0 or $n_0=0$, the equation becomes identical with that of Smoluchowski for monodisperse systems.

N. H. HARTSHORNE.

Rapid coagulation of polydisperse systems. G. WIEGNER and P. TUORILA (Kolloid-Z., 1925, **38**, 3—22).—Smoluchowski's coagulation equation has been found to hold for kaolin and gold sols over a wide range of particle radius, varying in the latter case from 3·7 to 97·0 μμ. A new method for following the course of the coagulation, involving continuous counting under the ultramicroscope and not requiring a protective colloid, gave good results. For regulating

the size and uniformity of the particles in the sols studied the Zsigmondy–Westgren "nuclear" method proved satisfactory. Müller's equation for the coagulation of polydisperse (bidisperse) systems (see preceding abstract) has been found to hold in the case of a number of gold sols in which the ratio of the radii of small to large particles varied from 1 : 1·73 to 1 : 33·32. In accordance with the equation, it was found that polydisperse systems coagulate more rapidly than monodisperse systems having the same original particle number. The nuclear action of the large particles postulated by Wiegner and Galecki is thus established. It is necessary for the radius of the large particles to be at least ten times that of the small for the effect to be detectable experimentally with certainty. N. H. HARTSHORNE.

Kinetics of agglutination of red blood-cell suspensions. J. OLIVER and P. SMITH (J. Physical Chem., 1926, **30**, 1—11).—The agglutination of red blood-cell suspensions proceeds at a maximum speed at the isoelectric point, with tervalent salts (Oliver and Barnard, A., 1924, ii, 831). An attempt is now made to apply Smoluchowski's formula (A., 1917, ii, 297) to this "rapid agglutination" of red blood-cells. A 1·5% suspension in 8·5% sucrose solution was prepared from defibrinated rabbit blood, stabilised with sodium hydroxide, and brought to the isoelectric point by addition of aluminium chloride. Agglutination was followed by counting single cells or aggregates of cells. The results are in fair agreement with Smoluchowski's theory and with those for colloids (cf. Westgren and Reitstötter, A., 1918, ii, 301; Ehringhaus and Wintgen, A., 1923, ii, 390). The values of the ratio, radius of sphere of attraction/radius of cell, range from 142·3 to 2513, thereby showing a large difference from the highest value previously obtained, viz., 13·7 (Ehringhaus and Wintgen). This is due to the small number of particles originally present. The absolute rate of agglutination of weak cell suspensions is approximately the same as the rate of coagulation of concentrated colloidal solutions. The greater distance between the blood-cells ($35·4 \times 10^{-4}$ cm.) and their practically negligible Brownian movement must thus be compensated, and the unknown factor causing rapid agglutination is included in a larger sphere of attraction. L. S. THEOBALD.

Accurate characterisation of protective colloids and allied substances. J. VOIGT (Kolloid-Z., 1926, **38**, 73—75).—Experiment shows that certain protective colloids, possibly nearly all, decrease the number of metal particles in hydrosols to an extent which increases with the coarseness of the protective colloid particles. If these are very finely divided, the effect may be reversed. By the addition of certain electrolyte solutions, the process can be made retrograde. At low concentrations a protective colloid may act as a coagulant in certain circumstances. The determination of the particle number in a protective colloid solution after the addition of a stable formol gold sol and of the alteration of this number on addition of electrolyte solutions, together with the determination of the gold number and transition number, furnish a further trustworthy method of characterising protective colloids. The method appears to be capable of useful application to body-fluids. N. H. HARTSHORNE.

Protection of suspensoid colloidal solutions. G. ROSSI and B. CECCHETTI (Gazzetta, 1925, **55**, 900—908).—The precipitating concentrations of potassium iodide, potassium chloride, magnesium chloride, and barium chloride have been determined with a series of arsenic trisulphide sols, and with the same sols containing a fixed ratio of arsenious sulphide to gelatin. With the unstabilised sols, the amount of electrolyte necessary for precipitation increases with the concentration of the sol, but with the stabilised sols the reverse relationship holds. According to the theory of Rossi (A., 1924, ii, 459), emulsoid sols may be regarded as intermediate between true solutions in which the solute is held in solution through its affinity for solvent molecules, and suspensoid sols, in the stabilisation of which the solvent plays no part. The added stability of a protected suspensoid sol is attributed to the mutual adsorption of the suspensoid and emulsoid particles, the latter carrying with them adsorbed or combined solvent molecules. The resulting system will possess a stability maintained by the joint action of the emulsoid substance and the stabilising ions. Further, since it has been shown by Wenz (Z. Biol., 1886, **22**, 1) that the stability of an emulsoid sol decreases with increase in its concentration, the adsorption of emulsoid by suspensoid particles should result in a lowering of the precipitation concentration for a given electrolyte when the degree of adsorption exceeds a certain limiting value. F. G. TRYHORN.

Swelling and dispersion of colloidal substances in ether–alcohol mixtures. E. W. J. MARDLES (J.C.S., 1925, **127**, 2940—2951).—Observations have been made on the swelling and dispersion of cellulose acetate, cellulose nitrate, resins, and other colloids in various ether–alcohol mixtures and in other mixed solvents. Measurements have also been made of the solvent power of mixed solvents and of the viscosity, density, and surface tension of the sols produced. Solvent power is measured either by observing the temperature of precipitation, or the proportion of neutral solvent (*e.g.*, hexane) which must be added to produce precipitation. It is shown that there is a close connexion between swelling and dispersion. Maximum swelling of Zanzibar copal occurs in an ethyl alcohol–ethyl ether mixture containing 70% by volume of the latter. This mixture has also maximum solvent power for the more soluble Kauri and Benguela copals. In several other cases, maximum swelling power of solvents is correlated with maximum solvent power. With increase in solvent power of liquid mixtures for cellulose nitrate, the change in density of the dispersion medium increases and the sols become relatively less viscous. The surface tensions of the organosols are either the same or slightly higher than those of the dispersing media. The bearing of these facts on the causes of the increased solvent action of solvent mixtures is discussed. E. E. WALKER.

Catalysis in micro-heterogeneous systems. I. Decomposition of hydrogen peroxide by colloids. A. GALECKI and (MLLE.) K. BINGER. **II. Decomposition of hydrogen peroxide by the gold hydrosols of Gutbier and Verádi.** A. GALECKI and (MLLE.) I. KRZECZKOWSKA.—See this vol., 251.

Imitations of cell-division and spore-germination with calcium fluosilicate. L. A. HERRERA (Atti R. Accad. Lincei, 1925, [vi], 2, 387—392).—By warming solutions of calcium fluosilicate to about 50°, with or without the addition of formaldehyde, slow coagulation occurs, the silicate coagulum exhibiting a variety of forms, such as those of amœbæ, dividing cells, germinating spores, of from 9 to 80 microns in diameter. It is suggested that these are due to incomplete crystallisation in which a network of invisible crystals of calcium fluoride is superposed on one of calcium silicate. The changes in shape of the coagula are attributed to the combined action of osmotic pressure, convection currents, surface tension, and the diffusion of calcium chloride. F. G. TRYHORN.

Mass action equation for condensed gases, with application to Haber equilibrium data. L. J. GILLESPIE (J. Amer. Chem. Soc., 1926, **48**, 28—33).—From the equation previously derived (A., 1923, ii, 375) for the fugacity of a gas in a mixture, the following general mass action expression for pressure and concentration effects in a mixture of compressed gases at constant temperature has been deduced: $\log K_p=\log K_f(1/2{\cdot}3RT)\Sigma\nu_1\int_0^p(RT/p-v_1/n_1)dp$. Here K_p and K_f are the usual mass action expressions in terms of pressures and fugacities, respectively, ν_1 is the stoicheiometrical coefficient of substance 1 in the reaction and v_1/n_1 its molar volume, and p is the pressure, T the temperature, and R the gas constant. This equation can be reduced to the approximate form $\log K_p=\log K_f+(\Sigma\nu_1A_1)/(2{\cdot}3R^2)p/T^2-(\Sigma\nu_1\beta_1)/(2{\cdot}3R)p/T$, where A and β are constants in the Keyes equation of state. Both equations represent satisfactorily the Haber equilibrium data obtained by the Fixed Nitrogen Research Laboratory (cf. Larson, A., 1924, ii, 331) up to 100 atm. pressure. Verification is thereby afforded of Lewis and Randall's fugacity rule to which the fundamental fugacity equation can be reduced. R. CUTHILL.

Influence of minute traces of water on solution equilibria. I. E. COHEN and W. D. J. VAN DOBBENBURGH (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 702—712).—See this vol., 18.

Ionisation of the strong electrolytes. H. M. DAWSON and J. S. CARTER (Proc. Leeds Phil. Soc., 1925, **1**, [i], 14—16).—The equilibrium represented by $NaCl+I_2=NaClI_2$, was established by saturation of solutions of sodium chloride, of 0·8—5·3N concentration, with iodine at 25°. From a knowledge of the total dissolved iodine, ($[NaClI_2]+[I_2]$), and assuming the validity of the exponential expression $S=S_0e^{-aC}$, representing the dependence of the solubility, S, of iodine on the salt concentration, C, S_0 being the solubility of iodine in pure water and a a constant (Carter, this vol., 236), the value of the mass law expression $[NaCl][I_2]/[NaClI_2]=K$, is calculable. The value of a, all concentrations being expressed in volume terms, is found to be 0·281. Using this, the values of K are found to be constant (0·617—0·621) over the entire range of salt concentration. This value is somewhat larger than that obtained by Jakowkin (A., 1896, ii, 514) using more dilute solutions (0·1—1·0N), but is in good agreement with the value of Rây and Sarkar (J.C.S., 1922, **121**, 1449) for the equilibrium, $HCl+I_2=HClI_2$. The constancy of K cannot be explained on the basis of the Arrhenius hypothesis of incomplete ionisation unless the improbable assumption is made that the chlorine ion has the same combining capacity for iodine as the neutral sodium chloride molecule. The results harmonise more readily with the view that the strong electrolytes are completely ionised in solution. J. S. CARTER.

Hydration of strong electrolytes, the viscosity of their aqueous solutions, and the dilution law. J. N. SUGDEN (J.C.S., 1926, 174—196).—The results of experiments in which acetic acid was distributed between amyl alcohol and solutions of strong electrolytes and of sucrose have been used to calculate the hydration of these dissolved substances. With the exception of the sulphates, where the values of the molecular hydration (H) decrease with dilution, the H values are reasonably constant over the concentration range investigated (in general 0·1—1·0N) and appear to be additive (*e.g.*, the difference between the apparent molecular hydration of a sodium and a potassium salt is independent of the anion). The hydration values of the chlorates and nitrates of potassium are negative. A theory of hydration is outlined according to which the cations only are hydrated, whilst the non-hydrated anions exert a depolymerising action on the solvent, whereby the equilibrium, $(H_2O)_3\rightleftharpoons(H_2O)_2+H_2O\rightleftharpoons3H_2O$, is displaced towards the right. Aqueous solutions of negatively hydrated salts have therefore abnormally large vapour pressures.

The equation of Arrhenius, $\log\eta/\eta_0=\theta c$, connecting the viscosity η of a salt solution of concentration c g.-mol./litre with the viscosity η_0 of the pure solvent, θ being a constant, has been modified and the validity of the semi-empirical equation, $\log\eta/\eta_0=Kc(H-H_0)$, established, H being the salt hydration number, H_0 a zero value determined by the anion, and K a constant.

The hydration theory has been applied to the calculation of the degree of ionisation α as determined from measurements of f.-p. depression. Making the assumptions that the hydration is independent of dilution and has the same value at the f. p. as at 25°, existing data for a number of solutions of strong electrolytes have been shown to conform to the requirements of the dilution law, $(1-\alpha)=k\sqrt[3]{n}$, n being the number of g.-mol. of electrolyte/1000 g. of water and k a constant the value of which is apparently characteristic of the electrolyte over a considerable concentration range. Solutions of sodium chloride and of potassium and barium bromides

deviate somewhat from the requirements of this expression, whilst the values of k for solutions of lithium, magnesium, calcium, copper, and cobalt nitrates decrease continuously with increasing concentration. J. S. CARTER.

Hydrolytic dissociation curves. J. O. W. BARRATT (Biochem. J., 1925, **19**, 875—881).—A theoretical investigation of the hydrolytic dissociation of substances which cannot be obtained in a state of purity is presented. The mathematical treatment of experimental results and various types of curves are discussed. S. S. ZILVA.

Ionisation of ethoxytrimethylammonium hydroxide, trimethylamine oxide, and their derivatives. W. A. NOYES.—See this vol., 154.

Ionic activity product of water in glycerol–water mixtures. J. COLVIN (J.C.S., 1925, **127**, 2788—2792).—Electrometric measurements of the activities of the hydrogen and the hydroxyl ions in aqueous sodium hydroxide solution at 25° have been made in the presence of various quantities of dissolved glycerol, by means of the hydrogen electrode and the Donnan–Allmand electrode (*ibid.*, 1911, **99**, 845), respectively. As the concentration of the glycerol increases from 0 to 40 g. per 100 c.c., the activity of the hydrogen ion increases from $1{\cdot}16\times10^{-12}$ to $7{\cdot}06\times10^{-12}$, and that of the hydroxyl ion drops from $0{\cdot}883\times10^{-2}$ to $0{\cdot}135\times10^{-2}$. Both the dissociation constant of water and the ionic activity product remain almost constant over this range. E. E. WALKER.

Activity of hydrobromic acid in pure aqueous solution and in solutions containing sulphates. R. S. LIVINGSTON (J. Amer. Chem. Soc., 1926, **48**, 45—53; cf. Lewis and Storch, A., 1918, ii, 27; Bates and Kirschman, A., 1920, ii, 88).—The activity of hydrobromic acid in pure aqueous solution at concentrations of 0·08—1·55M, in solutions containing sodium sulphate, and in mixed solutions of potassium bromide and sulphuric acid, has been determined by *E.M.F.* measurements with cells of the type $H_2|HBr(xM)|AgBr|Ag$. The values for solutions containing sulphates agree with those deduced from reaction velocity measurements (A., 1923, ii, 747), being much less than in pure aqueous solution. A method of calculating the activity of strong electrolytes in presence of weak electrolytes is described. R. CUTHILL.

Activity coefficient of lithium hydroxide in water and in aqueous lithium chloride solutions, and dissociation of water in lithium chloride solutions. H. S. HARNED and F. E. SWINDELLS (J. Amer. Chem. Soc., 1926, **48**, 126—135; cf. A., 1925, ii, 397, 538).—The activity coefficient of lithium hydroxide has been determined in pure aqueous solution by means of the cell $H_2|LiOH|Li_xHg|LiOH|H_2$ and in solutions containing lithium chloride by means of the cell $H_2|LiOH,LiCl|Li_xHg|LiOH|H_2$. From measurements on the cell $H_2|HCl,LiCl|AgCl|Ag$, the activity of hydrochloric acid in lithium chloride solutions has been obtained. The results are used to calculate the ionic activity coefficient and the concentration of water in lithium chloride solutions, and show that at concentrations above 0·03M lithium chloride increases the dissociation of water more than sodium and potassium chlorides do. The dissociation reaches a maximum at M-salt concentration. R. CUTHILL.

Equilibrium diagrams of binary systems containing benzoic acid as one component. N. A. PUSHIN and F. WILOWITSCH (Ber., 1925, **58**, [*B*], 2864—2868).—Investigation has been made of the equilibrium diagrams of eight binary systems composed of benzoic acid with naphthalene, *p*-phenylenediamine, diphenylamine, carbamide, acetanilide, benzanilide, ethylurethane, and resorcinol. Benzoic acid forms with naphthalene solid solutions with a maximal concentration of 30 mol.% of benzoic acid. *p*-Phenylenediamine and benzoic acid yield the *compound*, $C_6H_4(NH_2)_2,C_6H_5{\cdot}CO_2H$. The other compounds examined do not form either crystalline compounds or solid solutions with benzoic acid. H. WREN.

Influence of pressure on equilibria in binary systems. II. Urethane–benzene. N. A. PUSHIN (Z. physikal. Chem., 1925, **118**, 447—459; cf. this vol., 126).—The system urethane–benzene has been studied under pressures up to 4050 kg./cm.^{2} The influence of pressure is generally similar to that observed with systems previously investigated by the author, and is very marked in that the eutectic mixture contains 80% of urethane when the pressure is 4050 kg./cm.^{2}, whereas the proportion at atmospheric pressure is only 4·4%. L. F. GILBERT.

Iron–nickel and iron–cobalt equilibrium diagrams. L. GRENET (J. Iron and Steel Inst., 1925, **112**, 267—278).—See A., 1925, ii, 973.

Equilibrium at high temperatures in the iron–carbon–silicon system. M. L. BECKER (J. Iron and Steel Inst., 1925, **112**, 239—253).—See A., 1925, ii, 973.

Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. I. Ternary systems. M. A. HAMID (J.C.S., 1926, 199—205).—The four ternary systems which form the basis of the system water–sodium sulphate–sodium nitrate–potassium sulphate–potassium nitrate have been investigated at 25° and 90°, existing data being revised. The systems water–potassium sulphate–potassium nitrate and water–sodium nitrate–potassium nitrate (Reinders, A., 1914, ii, 549) are of the simplest type. The system water–sodium sulphate–potassium sulphate is complicated by the existence of the double salt $K_3Na(SO_4)_2$, glaserite, which dissolves sodium sulphate to form solid solutions. The only double salt existing in the system water–sodium sulphate–sodium nitrate at 25° is darapskite, $Na_2SO_4,NaNO_3,H_2O$, the formation of the two anhydrous double salts described by Massink (A., 1917, ii, 412) not being observed (cf. Foote, A., 1925, ii, 786). At 90°, the only stable solid phases are the two anhydrous salts. J. S. CARTER.

Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. II. Quaternary system, H_2O-Na_2SO_4-$NaNO_3$-K_2SO_4-KNO_3. M. A. HAMID (J.C.S., 1926, 206—214; cf. preceding abstract).—Investigations of the quaternary system at 25° show that, apart from the individual salts, the only solid phases are glaserite, darapskite, and a compound of uncertain composition, probably a triple or tetragenic salt. Glaserite is the only double salt that occurs at 90°. J. S. CARTER.

Systems potassium chloride-potassium oxalate-water and potassium oxalate-mercuric oxalate-water. N. TRIFONOV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 71—72, 72; from Chem. Zentr., 1925, II, 382).—The solubility of potassium oxalate at 20° is 34·93 g. in 100 g. of water. The solubility of mercuric oxalate is 0·0107 g. in 100 g. of water. The isotherms for the system potassium oxalate–mercuric oxalate–water at 20° show the existence of five breaks corresponding with the simple salts and the three double salts $K_2C_2O_4,HgC_2O_4,2H_2O$, $2K_2C_2O_4,HgC_2O_4,3H_2O$, and $3K_2C_2O_4,HgC_2O_4,4H_2O$. G. W. ROBINSON.

Electrometric and phase-rule study of basic salts of copper. H. T. S. BRITTON (J.C.S., 1925, **127**, 2796—2807).—Basic salts are precipitated on the gradual addition of alkali to solutions of the sulphate, chloride, bromide, or nitrate. The individualities of the basic salts $Cu_4(OH)_6SO_4,H_2O$ and $Cu_4(OH)_6Cl_2,H_2O$ have been established by means of a phase-rule study of the systems CuO-SO_3-H_2O and CuO-HCl-H_2O at 25°. The behaviour of the $Cu|Cu(OH)_2,NaOH$ electrode is erratic, and for this reason Jellinek and Gordon's value of the solubility product of cupric hydroxide (A., 1924, ii, 836) is inaccurate. The basic salts do not blacken on boiling except in the presence of an excess of alkali. Werner's formulation of these substances as the normal salts of a hypothetical hexol-cupric base is shown to be open to objection. E. E. WALKER.

Reaction provinces. I. W. P. JORISSEN (Chem. Weekblad, 1926, **23**, 79—82).—The extent to which reaction occurs between three substances, of which one or more pairs or all three can enter into mutual reaction, may be conveniently represented by means of triangular diagrams, in which the intersections of the sides represent respectively 100% of each constituent. Several cases already investigated are illustrated by this method, which is very convenient for stating concisely explosive limits in mixtures of gases, in systems of two gases with one solid etc. S. I. LEVY.

Dissociation and specific heats of chlorine and hydrogen chloride at high temperatures. K. WOHL and W. KADOW (Z. physikal. Chem., 1925, **118**, 460—474; cf. Z. Elektrochem., 1924, **30**, 36; A., 1924, ii, 600).—Values already obtained for the molecular heat and heat of dissociation of chlorine have been confirmed by a modified method of calculation. The authors have also made a further series of experiments, similar to those previously made but differing in regard to the composition of the explosion mixtures. From these, the dissociation constants of hydrogen chloride between 2055° and 2603° Abs. have been derived, with a maximum error of $\pm 0{\cdot}22$ in log K_{HCl}. The values agree satisfactorily with those derived from the extrapolation of equilibrium data at the ordinary temperature. L. F. GILBERT.

Thermal dissociation of sodium carbide. E. W. GUERNSEY and M. S. SHERMAN (J. Amer. Chem. Soc., 1926, **48**, 140—146).—When sodium carbide is heated, any free sodium formed is present in the gas phase only. The dissociation pressure p has been measured at 600°, 650°, and 700°, and is represented approximately by the equation $\log p = 9059 - 6609/T$, where T is the temperature (Abs.). It reaches the value 760 mm. at about 800°, so that any sodium carbide formed as a step in the fixation of nitrogen as cyanide (A., 1925, ii, 889), for which temperatures above 900° are required, can exist only in the gas phase. Approximate determinations show that the carbide in the gas phase is largely dissociated at 700°. R. CUTHILL.

Electrical conductivities of hydrogen chloride and potassium chloride in water and acetone-water mixtures. T. K. BROWNSON and F. M. CRAY (J.C.S., 1925, **127**, 2923—2935).—The electrical conductivities of hydrogen chloride and potassium chloride have been measured over a wide range of dilutions at 20° and 25° in acetone–water mixtures containing 5—100% of water by volume. A thermionic valve oscillator was used as a source of alternating current, and platinised platinum was used for the electrode, as it was shown that no error was introduced through catalytic action of the platinum on the acetone. The equivalent conductivity of hydrogen chloride at infinite dilution falls sharply to a minimum in the solvent containing about 85% of acetone. At finite dilutions up to about 10,000 the equivalent conductivity falls throughout as the acetone content increases, owing to the superimposed effect of the decreasing degree of ionisation. The equivalent conductivity of potassium chloride at infinite dilution falls to a well-defined minimum in the solvent containing approximately 40% by volume of water, but at other dilutions this is shifted owing to changes in the degree of dissociation and disappears in the more concentrated solutions. The influence of temperature on the degree of dissociation is more marked the higher the acetone content and the greater the concentration of the electrolyte. The Ostwald dilution law does not hold fully in any acetone–water mixture investigated, but the divergences decrease as the proportion of acetone increases. E. E. WALKER.

Electrode capacity and resistance of electrolytes for a wide range of frequencies. B. B. BANERJI (Trans. Faraday Soc., Jan., 1926, advance proof).—The variation of the electrode capacity and the cell resistance with the frequency of the alternating current has been examined in cells of very small capacity, using silver, cadmium, and nickel electrodes in solutions of their respective salts. At constant current intensity, the frequency was varied from 170 to 14,500 cycles per sec., and the observed results agree well with the formula $y=(\alpha+\beta x)/(x+\gamma)$,

where x is the square of the frequency, y the capacity of the cell, and α, β, and γ are constants. The relation may be accounted for by assuming that the electrodes act as condensers, one condenser being due to a Helmholtz double layer with fairly heavy leak and the other to concentration changes by ionic transport with a slight leak. The thickness of the double layer calculated on this assumption from the observed capacity agrees well with the value found by other methods. The observed resistance of the cell varies with the frequency, decreasing in one series from 239 to 130 ohms as the frequency is increased from 170 to 14,500 cycles per sec., but after correction for the extra resistance of the electrodes on the theory of a double condenser effect, a constant electrolytic resistance is obtained, which agrees moderately well with the accepted value. An arrangement is described by which the harmonics can be eliminated from the alternating current generated by a triode valve. F. G. Soper.

Passage of metallic ions through liquid dielectric media. W. Kusnetzov and W. Kudrjavzeva (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 7—8; from Chem. Zentr., 1925, II, 386; cf. this vol., 248).—A current was passed for a long period through a cell consisting of copper|copper sulphate in water|toluene|copper. Although there was an appreciable passage of current, the weight of the electrode in toluene was unchanged. The transport in toluene must therefore have been effected by toluene ions, the toluene being impervious to external ions. The fall of potential was located principally in a layer 0·5 mm. thick at the interface of the phases, where a metallic precipitate was slowly formed due to the neutralisation of the metallic ions by the ions of the dielectric medium. Ultra-violet radiation was without effect on the potential of an amalgamated zinc electrode. G. W. Robinson.

Application of the osmotic theory of Nernst to non-aqueous solutions. A. E. Brodsky (Z. Elektrochem., 1926, **32**, 5—6).—The influence of dilution on the *E.M.F.* of combinations of $Hg|Hg_2Cl_2,KCl$ and $Hg|Hg_2Br_2,KBr$ electrodes and of concentration cells of these electrodes has been studied in 50·01% ethyl alcohol (at 16·5—17·0°), absolute methyl alcohol (at 13·2—13·5°), and water (at 14·5—15°). The results are compared with those calculated from Nernst's osmotic theory and are discussed. N. H. Hartshorne.

Solubility product of mercury halides in water. A. E. Brodsky and J. M. Scherschewer (Z. Elektrochem., 1926, **32**, 1—4).—From measurement of the *E.M.F.* of cells of the type $Hg|Hg_2(NO_3)_2(c_0)|$saturated $KNO_3|KX(c),Hg_2X_2|Hg$, where X is either Cl or Br, the solubility products of mercurous chloride and bromide have been calculated at temperatures varying from 11° to 26·5°. Although the results are not in agreement with those of previous workers, it is claimed that they are accurate because the *E.M.F.* of the cell $Hg|Hg_2Cl_2,KCl|KBr,Hg_2Br_2|Hg$ calculated from them agrees with that observed experimentally by Bugarsky (A., 1897, ii, 307). The solubility product of mercurous iodide is also deduced.
N. H. Hartshorne.

Temperature coefficients of reference electrodes. L. J. Bircher and G. D. Howell (J. Amer. Chem. Soc., 1926, **48**, 34—40).—The method used by Fales and Mudge (A., 1921, ii, 79) has been applied to cells of the type $(Pt)H_2|H_2SO_4(nN),Hg_2SO_4|Hg$, and the following values obtained for the temperature coefficient: $H_2|H_2SO_4(0·1N)$, −0·00027; $H_2|H_2SO_4(N)$, −0·00043; $H_2SO_4(0·1N),Hg_2SO_4|Hg$, +0·00028; $H_2SO_4(N),Hg_2SO_4|Hg$, +0·00030. R. Cuthill.

Hydrogen electrode studies of the precipitation of basic chromates, borates, and carbonates. H. T. S. Britton (J.C.S., 1926, 125—147).—The relations involved in the precipitation of the basic chromates, borates, and carbonates of thorium, aluminium, chromium, beryllium, and zinc, the basic chromates of neodymium, samarium, yttrium, cobalt, and nickel, and the basic carbonates and borates of zirconium, manganese, and magnesium have been examined by a hydrogen electrode titration method. Precipitates are formed at the same p_H as is required for the precipitation of the corresponding hydroxides (A., 1925, ii, 1203, 1204), but delayed precipitation occurs with the borates of zirconium and thorium and the basic carbonate of zirconium. The ability of the precipitant to produce this critical p_H determines the precipitation of these metals as basic salts; in cases where this value is only just attained, precipitation is incomplete and in extreme cases is apparent only as an opalescence. Individual cases are discussed at length, and the conditions for the precipitation of normal salts considered. The action of potassium chromate in precipitating basic salts may be explained from considerations of the dissociation of chromic acid with formation of hydrochromate ions (A., 1924, ii, 704). J. S. Carter.

Measurements with the quinhydrone electrode. K. Linderstrøm-Lang (Compt. rend. Trav. Lab. Carlsberg, 1925, **16**, [3], 1—24).—New determinations of the *E.M.F.* of the cell Pt, quinhydrone, experimental liquid, H_2 (1 atm.), Pt have been made at 18°, with special reference to the disturbing influences of electrolytes and proteins. The extrapolated value $E=0·70475\pm0·00005$ volt is obtained for pure water. The somewhat divergent values previously obtained when electrolytes are present are attributable to the salting-out effect on quinol and benzoquinone. The depressing influence of potassium chloride and sodium chloride, although slightly greater than that calculated from solubility measurements, is due to this cause, divergences being attributed to experimental error. The influence of ammonium sulphate is in the opposite direction, measurements of *P.D.* and of solubility being recorded in each of the three cases. Results for acid casein, egg-albumin, and serum-albumin are also given, special difficulties in obtaining constant *P.D.*, which are partly attributed to electrode poisoning, being found in the latter case. The casein error in acid solution is small and independent of hydrogen-ion concentration, whilst in alkaline solution a constant *P.D.* is not obtained unless measured immediately after adding the quinhydrone. Egg-albumin and especially serum-albumin give larger deviations, which vary with concentration of protein and of hydrogen ions. The effects are opposite in

sign in the two cases, the serum-albumin error being positive, like that of ammonium sulphate. The alteration in *P.D.* is, in general, approximately proportional to the concentration of the substance producing it. Correction tables are given for hydrochloric acid and the substances mentioned above, by means of which the various disturbing factors may be compensated. The correction appears as an additive term Q in the formula for p_H, viz., $p_H=[(0{\cdot}36675-E_K)/0{\cdot}0577]+Q$, where E_K is the *E.M.F.* (corr.) of the element Pt, quinhydrone, experimental liquid| 3·5*N*-KCl|0·1*N*-KCl, calomel electrode at 18°.

C. H. D. Clark.

Potential distribution in a layer of a liquid dielectric medium. W. Kusnetzov (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 6; from Chem. Zentr., 1925, II, 385—386).—The fall of potential between two parallel flat electrodes is linear. In castor oil, toluene, oil of turpentine, liquid "vaseline," and petroleum the fall of potential is confined to the vicinity of the electrodes, so that the potential is constant in the body of the medium. The *P.D.* used was 55—8200 volts with electrodes at a distance of 16—31 mm. G. W. Robinson.

Influence of acetonitrile on the electroendosmotic movement of liquids. O. Arnd (Biochem. Z., 1926, **166**, 414—423).—The electrokinetic potential ζ is dependent on the non-electrolyte content of the solution. With increasing concentration of acetonitrile (up to $M/8$) in $M/1000$-potassium chloride, ζ decreases from 50·6 to 34·7; with further increase of the concentration (up to M), it rises slightly to a limiting value (37·1). This change is due not merely to the size of the dielectric constant of the non-electrolyte, but also to its chemical constitution and its ease of absorption (cf. A., 1922, ii, 342).

P. W. Clutterbuck.

Passivity of zinc dust in the alkaline reduction of nitro-compounds. V. A. Izmailski and V. N. Kolpenski (Russian J. Chem. Ind., 1925, **1**, No. 4, 31—32).—The temporary passivity of zinc dust employed to reduce nitro-compounds may be prevented by the preliminary treatment of the zinc with alkali hydroxide. The phenomenon is due to the occlusion on the surface of the metal of molecules of a gas, evidently hydrogen, possibly with formation of zinc hydride. T. H. Pope.

Electrolysis of oxides dissolved in boric acid or in borates. Andrieux (Compt. rend., 1926, **182**, 126—127).—The electrolyte was fused in a carbon crucible serving as an electrode, the other being a hollow, water-cooled, carbon or iron rod, which could be lowered vertically into the molten electrolyte. In the case of anhydrous borax, the electrolyte was maintained at 900°, and the iron cathode cooled below 880°, the b. p. of sodium. On withdrawing the cathode slowly from the fused mass, it was found to be coated with (1) a layer of pure sodium, (2) a layer of sodium mixed with boron, (3) a thin layer of boron, and (4) a layer of solidified electrolyte. If the borax contained oxides such as alumina or calcined beryllia, reduction of the electrolyte by sodium was almost completely prevented, whilst by raising the temperature above the b. p. of sodium, boron only was obtained.

L. L. Bircumshaw.

Electrolytic deposition of carbonaceous iron from its complex compounds with organic acids. H. Schmidt (Z. Elektrochem., 1926, **32**, 33—41).—The electrolytic deposition of carbon along with the iron from solutions of complex citrates, tartrates, succinates, oxalates, formates, acetates, and carbonates of this metal has been studied. It is in all cases a similar process, and is dependent on the cathode potential, or the cathodic current density, and on the percentage current yield of the iron. The carbon is present chiefly in a form decomposable by dilute acids with evolution of gaseous carbon compounds. Neither decomposition voltage experiments nor analyses of the electrolyte surrounding the cathode after long electrolysis have shown the presence of unknown ions, *e.g.*, ionised carbon, or of decomposition products other than a slight reduction observed with the oxalate and formate solutions, and formic acid detected in the succinate solution. The observations are discussed. N. H. Hartshorne.

Mercury cathodes in electrolytic oxidation processes. I. Stscherbakov (Z. Elektrochem., 1925, **31**, 617; cf. A., 1925, ii, 979).—The auxiliary iron cathode required in preparing chloroform electrolytically must be confined within a diaphragm. Alternatively, an unprotected platinum cathode may be used if a little chromate be added to the electrolyte. The mercury cathode method lends itself well to the preparation of perchromates. In all cases, considerably higher current densities than those previously mentioned may be applied. W. A. Caspari.

Cathodic pulverisation of alloys. J. Mazur (Bull. Acad. Polonaise, 1925, A, 81—92).—A study of the effect of cathodic pulverisation on pure metals and on alloys of different types shows that this is the same as that obtained by the action of an acid on the polished metal. Layers of deposit, when produced on surfaces of quartz, mica, and platinum, possess a crystalline and cellular structure. Although crystals are not produced from electrolytic copper under ordinary conditions, these are obtained when pulverisation takes place at the temperature of liquid air. Alloys of cadmium and bismuth, which do not form mixed crystals, give deposits the composition of which differs from that of the original alloy. The composition of the deposit is said to depend on the area of each metal exposed on the cathodic surface. The mechanism of transport is discussed, and the author concludes that the electric field causes vaporisation of the metal, which then condenses on cooler parts of the apparatus, the crystals forming and growing on the new support, mechanical disintegration of the surface being a different phenomenon. Photomicrographs of cathodic surfaces after pulverisation and of the deposited layers are reproduced in support of the contentions raised. C. H. D. Clark.

Limits of inflammability of mixtures of methane and air. M. J. Burgess and R. V. Wheeler.—See B., 1926, 114.

Influence of water vapour and hydrogen chloride on the velocity of decomposition of ammonia. A. SCHMIDT.—See B., 1926, 87.

Absorption of hydrogen in potassium vapour arcs. R. D. RUSK (Phil. Mag., 1926, [vii], **1**, 97—109).—The rate of absorption of hydrogen in the potassium vapour arc at 200° and at initial pressures of about 1 mm. has been obtained as a function of the arc potential. The experimental tube contained a coated platinum filament, which served as cathode, a nickel anode, and a side tube with constrictions for filling with potassium. The rate of absorption of the hydrogen was obtained from observations of the change in pressure, measured by means of a McLeod gauge. Careful purification of the potassium was essential. The thermal effect of the filament caused some absorption of hydrogen, for which, where necessary, a correction was applied. No absorption due to the arc occurred at potentials less than 16 volts, but for higher voltages the rate of absorption increased rapidly with increasing potential. Experiments at a high constant voltage and at temperatures from 40° to 180° gave an increasing rate of absorption roughly proportional to the vapour density of the potassium. The absorption is due to the formation of an active type of hydrogen which combines with the potassium to give potassium hydride. This active hydrogen, which is not formed at less than 16 volts, is probably atomic hydrogen, produced from charged molecules by secondary collisions. The absorption of hydrogen by potassium at higher temperatures, in the absence of the arc, is due to the presence of atomic hydrogen produced by ordinary thermal dissociation.

A. B. MANNING.

Unimolecularity of the inversion process. S. W. PENNYCUICK (J. Amer. Chem. Soc., 1926, **48**, 6—19).—The use of accurate methods of determining zero time readings in the inversion of sucrose and the taking into account of mutarotation effects (A., 1924, i, 1287) show that the velocity coefficient calculated on the assumption of a unimolecular reaction increases slowly with the time. The very large increases observed by Fales and Morrell (A., 1922, ii, 832), using strong acids as catalysts, are probably due to experimental error. F. p. experiments give qualitatively similar results. It is suggested that the catalytic action of acids is due to hydrogen ions increasing the number of active water molecules. The observed increase in velocity coefficient is ascribed to increase in the activity of the hydrogen ions during inversion (cf. Taylor and Bomford, A., 1924, i, 1286), and to removal of water by the reaction. Accordingly, the relation $dx/dt=k$ [sucrose molecules per molecule of water] [$H^{\cdot}$ activity] is proposed. R. CUTHILL.

Action of boric acid on alkali carbonates in solution. B. L. VANZETTI (Gazzetta, 1925, **55**, 939—944; cf. A., 1925, ii, 421).—Quantitative measurements of the action of boric acid on a boiling solution of sodium carbonate show that the reaction proceeds almost to completion if the carbon dioxide is removed by a current of hydrogen. The velocity of the reaction is practically equal to that of the analogous reaction between arsenious acid and sodium carbonate, the velocity coefficients calculated for a unimolecular reaction being about 8·0 in each case. It is suggested that the reaction proceeds according to the equations $H_3BO_3+HCO_3'=H_2BO_3'+H_2CO_3$; $H_2CO_3=H_2O+CO_2$. The equality of the velocities of the reactions with boric and arsenious acids is thus attributable to the equality of their ionisation constants. F. G. TRYHORN.

Influence of carbon rings on the velocity of reactions involving their side-chains. I. Hydrolysis of cyclic and open-chain malonic esters. R. GANE and C. K. INGOLD (J.C.S., 1926, 10—17).—Variation in the angle between two valencies of a carbon atom affects the readiness with which groups attached to these valencies interact (Beesley, Ingold, and Thorpe, *ibid.*, 1915, **107**, 1080—1106, and later papers; Ingold, *ibid.*, 1921, **119**, 305—329, and later); the smaller the angle, the more readily interaction takes place. That the independent action of these groups on some external reagents carries with it a decreasing tendency to reaction is proved by determinations of the relative rates of hydrolysis by alkalis of a series of cyclic malonic esters. Points connecting the logarithms of the initial velocities of hydrolysis, under identical conditions of temperature and concentration, and the calculated angle between the valencies of the carbon atom in question, lie on a smooth curve, both for the cyclic malonic esters and the *gem*-dimethyl ester. The indicated value of 105·3° for the angle between the valencies of the central carbon atom joined to the carbethoxyl groups in the *gem*-dimethyl ester is unexpectedly low.

The rates of hydrolysis of some open-chain tautomeric malonic esters were also observed in view of the theory of amide formation by the action of aqueous ammonia on esters advanced by Fischer and Dilthey (A., 1902, i, 269; cf. Ingold, Sako, and Thorpe, J.C.S., 1922, **121**, 1177), in which a process, possibly auxiliary only, involving a tautomeric hydrogen atom is formulated instead of a direct action by ammonia on the carbethoxyl group, influenced possibly by spatial conditions. The initial rates of hydrolysis of the tautomeric malonic esters (monomethyl, monoethyl, mono-*n*-propyl) were, however, found to be more rapid than the steric theory allows, and although the influence of the various alkyl groups was observed, the operation of an additional mechanism involving a tautomeric hydrogen atom is considered probable. Ethyl *iso*propylmalonate hydrolyses more slowly, whilst ethyl malonate hydrolyses extremely rapidly.

W. M. COLLES.

Atmospheric oxidation. II. Kinetics of oxidation with sodium ferro-pyrophosphate. J. H. C. SMITH and H. A. SPOEHR (J. Amer. Chem. Soc., 1926, **48**, 107—112; cf. *ibid.*, 236).—Velocity measurements show that the oxidation of sodium ferro-pyrophosphate or of potassium arsenite in presence of this substance as catalyst is a process of autoxidation (cf. Manchot, A., 1901, ii, 549). The catalysed oxidation of sodium sulphite seems to involve a purely catalytic effect in addition.

R. CUTHILL.

Catalysis. A. MITTASCH (Ber., 1926, **59**, [*B*], 13—36).—A lecture delivered before the German Chemical Society. H. WREN.

Dynamics of surface action in closed vessels. F. H. CONSTABLE (Nature, 1926, **117**, 230—231).—An extension to the dynamics of catalytic decomposition in closed vessels of the theoretical treatment describing the effect of diluent gases and vapours on the initial stages of catalytic action (A., 1925, ii, 983). The decomposition of nitrous oxide and ammonia by platinum, and the dehydrogenation of ethyl alcohol by copper in closed vessels give results in agreement with the general relation derived; the relation is obtained without assuming that the surface is saturated. A. A. ELDRIDGE.

Catalytic combustion. II. Union of carbon monoxide and oxygen in contact with nickel, copper, and their oxides. W. A. BONE and G. W. ANDREW (Proc. Roy. Soc., 1925, **A**, **110**, 16—34).—After treatment with carbon monoxide, nickel becomes covered with a highly reactive surface film of nickel carbonyl, or possibly oxycarbonyl, which is unaltered by prolonged treatment in a vacuum at 375°. Copper forms a similar surface film, which is, however, very unreactive. Experiments with nickel oxide at 150° showed that the catalytic effect was unattended by any appreciable reduction of the oxide, and even in the absence of oxygen the reduction was negligible. The oxidising effect of the surface is due to an activated oxygen film, and the same conclusion was reached using copper oxide at 165°. It is concluded that, certainly for copper and probably also for nickel, the real catalytic combination does not necessarily involve any intermediate oxide or carbonyl formation, but only the occlusion of the respective gases. The evidence in the case of the oxides is regarded as conclusively against the theory of alternating reductions and re-oxidations of the surface.

F. G. SOPER.

Immobile groups of atoms with strong specific external fields as the cause of catalytic activity. F. H. CONSTABLE (Proc. Roy. Soc., 1926, **A**, **110**, 283—301; cf. A., 1925, ii, 311, 804, 881).—Copper surfaces prepared by electrolytic deposition, by reduction of ammoniacal solutions of copper, or by hammering or polishing copper foil or gauze, were inactive as catalysts in the decomposition of ethyl alcohol at temperatures up to 370°. Active surfaces were produced by the rapid condensation of copper vapour, by the violent agitation of the atoms in an inactive surface at 820° (by passage of ammonia), by the reduction of cuprous or cupric oxide, or by the thermal decomposition of organic copper salts in a rapid stream of indifferent gas. The reaction velocity was determined over a range of temperatures between 200° and 300° for the active surfaces, and the heat of activation calculated. With the exception of metal activated by ammonia, and copper heated in a stream of alcohol above 280°, when the surface is rapidly poisoned by the reaction products, all these preparations showed very nearly the same surface activity and the same temperature coefficient of activity. The activity is assumed to be due to the existence of groups of atoms in the surface in a state of strain. The external field of force of such a group produces such strains in the adsorbed molecules that chemical reaction occurs at a measurable rate. In electrodeposition, or in the chemical deposition of copper from solution, the basic space lattice is already present and the slow arrival of the copper atoms enables them to fit into the regular structure, making the external field and consequently the catalytic activity small. A. B. MANNING.

Catalytic activation of titania. W. A. RUDISILL and C. J. ENGELDER (J. Physical Chem., 1926, **30**, 106—113; cf. Bischoff and Adkins, A., 1925, ii, 568).—The factors which influence the activity of titania catalysts in the decomposition of ethyl alcohol have been examined. These catalysts differ widely in their specificity towards the two reactions $C_2H_5{\cdot}OH \longrightarrow H_2+CH_3{\cdot}CHO$ and $C_2H_5{\cdot}OH \longrightarrow C_2H_4+H_2O$, and the treatment which they undergo during their preparation has a marked effect on the extent and nature of the decomposition. The pre-heated vapour of ethyl alcohol was passed at a uniform rate over the catalyst heated at 350°, and the volume and composition of the gas evolved were determined. The catalysts were prepared from titanium potassium oxalate as the starting point, with variations in the procedure for obtaining the oxide, after a first precipitation of titanium hydroxide with ammonia. The activity of the catalyst decreases with an increase in the temperature of ignition of the hydroxide, after 350°, and there is a decrease in the production of ethylene. The duration of ignition is of small importance, for heating beyond a period of 1 hr. has little effect, and a period of 2 hrs. is quite sufficient for the preparation of an efficient catalyst.

Small proportions of carbon monoxide and dioxide are always produced, probably from secondary decompositions. The invariable formation of ethane, in amounts up to 36·9%, is also significant.

The character of the anion present during the precipitation of the titanium hydroxide has an important bearing on the activity. The catalysts prepared from sulphate and chloride solutions, and by hydrolysis, are the most active, particularly the last-named. Samples prepared from the sulphate, and by hydrolysis, give the highest percentage of ethylene (dehydration of the alcohol) and the lowest percentage of hydrogen. Reprecipitation increases activity, as appears with the catalysts derived from the oxalate direct, when the activity is low, giving also the lowest percentage of ethylene and the highest of ethane. Results with preparations from the sulphate showed that thorough washing of the precipitated hydroxide is necessary if an active and lasting catalyst is to be obtained.

An expected increase in activity accompanies an increase in the degree of sub-division, but a finer-sized contact mass favours the decomposition of the alcohol by dehydration as against dehydrogenation. During comparisons of the relative stability of the various catalysts, those prepared from the sulphate and by hydrolysis showed the greatest activity with prolonged use. The former (ignition temperature 300°) remained very active after 10 hrs.' continuous

use. The activity of some of the other preparations depreciated slowly under these conditions.

L. S. THEOBALD.

Catalysis in micro-heterogeneous systems. I. Decomposition of hydrogen peroxide by colloids. A. GALECKI and (MLLE.) K. BINCER (Bull. Acad. Polonaise, 1925, **A**, 93—111).—The activity of various sols in catalysing the decomposition of hydrogen peroxide is studied quantitatively in relation to methods of sol formation, the influence of alkali, and the sizes of particles. The velocity coefficients and times of half change are recorded under widely varying conditions. The sols examined fall into two groups, classed as "active" and "inactive." The inactive catalysts show protective action on the active catalysts. Of the active class, gold sols prepared by Zsigmondy's formaldehyde method cause more rapid decomposition in alkaline than in neutral solution, and show, in general, a fairly sharp optimum concentration of alkali. On the other hand, gold sols prepared by Doerinckel's method (A., 1909, ii, 896) do not catalyse in neutral solution, and are classed as inactive. It is shown that they arrest the decomposition by active gold sols in neutral solution. Other members of the inactive protective group of the albumin type show inappreciable activity in neutral solution, and, in alkaline solution, are markedly less efficient than active gold sols of the same concentration. The protective effect is less marked in alkaline than in neutral solution (cf. Gróh, A., 1915, ii, 239). The effect of size of particle is studied by preparing approximately uniform sols by Westgren's condensation method. A linear relationship is found between surface and activity, as measured by the velocity constant. Sols prepared by the Gutbier–Verádi method at higher temperatures show the peculiar behaviour recorded by Rusznyák (see A., 1914, ii, 42, and following abstract).

C. H. D. CLARK.

Catalysis in micro-heterogeneous systems. II. Decomposition of hydrogen peroxide by the gold hydrosols of Gutbier and Verádi. A. GALECKI and (MLLE.) I. KRZECZKOVSKA (Bull. Acad. Polonaise, 1925, **A**, 111—127).—The observation of Rusznyák that gold hydrosols prepared at higher temperatures by the Gutbier–Verádi method have smaller catalytic activity in decomposing hydrogen peroxide, although the active surface is greater than when the sols are prepared at lower temperatures, has been investigated. It is found that the gold sols fall into two classes in relation to activity, namely, those prepared (1) below and (2) above 50°. The first class show normal behaviour, but the second exhibit the recorded abnormalities. In alkaline solution, sols of the second class have no optimum concentration of alkali, and the velocity temperature coefficient shows a maximum between 50° and 60°. That two definite groups exist is confirmed by ultra-microscopical observations, by Ostwald viscosity measurements at 25°, and by approximate determinations of the mobility of the sol particles in an electric field. Sols prepared by the above method at about 70° appear to behave exceptionally, and to show behaviour characteristic of the first class. It is concluded that activity does not depend only on the active surface of catalyst, but also on the nature of that surface, as affected by its method of formation.

C. H. D. CLARK.

Catalytic formation of petroleum hydrocarbons from fats. J. MARCUSSON and W. BAUERSCHÄFER.—See B., 1926, 117.

Catalytic decomposition of hydrogen peroxide in a bromine-bromide solution. III. Interpretation of rate measurements as a function of the activity product of hydrobromic acid. R. S. LIVINGSTON (J. Amer. Chem. Soc., 1926, **48**, 53—58; cf. A., 1923, ii, 747).—By means of the author's new activity data (this vol., 245) it has been shown that the steady-state rate in the above reaction in all solutions (including those containing sulphates) of ionic strength less than unity is given by the empirical equation $-d[H_2O_2]/dt=0{\cdot}043[H_2O_2][H^{\cdot}][Br']\gamma^2$, where γ is the activity coefficient of hydrobromic acid. The steady-state function (A., 1923, ii, 473) assumes a much more constant value if activities are substituted for the concentrations of the electrolytes involved.

R. CUTHILL.

Catalysis by silver ion of oxidation of chromic salts by persulphuric acid. Existence of tervalent silver compounds. D. M. YOST (J. Amer. Chem. Soc., 1926, **48**, 152—164; cf. Marshall, A., 1901, ii, 156).—The rate of this reaction at 25° and 35° is given by the equation $-d[S_2O_8'']/dt=k[S_2O_8''][Ag^{\cdot}]$. It therefore appears probable that the rate of the whole process is determined by the velocity of the slow reaction $S_2O_8''+Ag^{\cdot}=Ag^{\cdot\cdot\cdot}+2SO_4''$, this being followed by the rapid reaction $3Ag^{\cdot\cdot\cdot}+2Cr^{\cdot\cdot\cdot}+7H_2O=Cr_2O_7''+3Ag^{\cdot}+14H^{\cdot}$. In support of this view, the black precipitate produced when a solution of a silver salt and persulphuric acid are mixed in absence of a reducing agent has been examined. This substance has powerful oxidising properties, readily oxidising a chromic salt to chromate, but appears to be a higher oxide, not a peroxide, and analysis and measurements of its oxidising power indicate that it is an oxide or basic sulphate of tervalent silver (cf. Austin, J.C.S., 1911, **99**, 262).

R. CUTHILL.

Method of obtaining iodine, based on electrolysis in alkaline solution. L. PISARSHEVSKI and S. TELNI.—See B., 1926, 88.

Electrolysis of lead chloride. R. SAXON (Chem. News, 1926, **132**, 102—103).—No metallic lead is obtained by the electrolysis of hot aqueous solutions of lead chloride; addition of sucrose, which increases the solubility of lead chloride, results in a deposit of very finely divided metal which does not adhere to the cathode.

A. R. POWELL.

Electrolytic production of heavy metals from fused electrolytes. I. Iron. F. SAUERWALD and G. NEUENDORFF.—See B., 1926, 131.

Rusting of iron. W. KISTIAKOVSKI.—See B., 1926, 131.

Electrolytic deposition of metals. I. Theory of the mechanism. P. K. FRÖLICH and G. L. CLARK.—See B., 1926, 131.

Electrolytic deposition of metals. II. X-Ray investigation of electrolytic nickel. G. L. CLARK and P. K. FRÖLICH.—See B., 1926, 131.

Chemical effects produced by resonance radiation. H. S. TAYLOR, A. L. MARSHALL, and J. R. BATES (Nature, 1926, **117**, 267).—Hydrogen and oxygen, with the concentration of mercury vapour obtained by bubbling the gases through liquid mercury at the ordinary temperature, combine rapidly in the presence of the resonance radiation from the cooled mercury arc (cf. Hirst and Rideal, this vol., 34), hydrogen peroxide being a prior product of reaction, particularly at high rates of gas flow. Mercuric oxide is also formed. No evidence could be adduced to assign any of the photosensitised process to a liquid mercury surface, variation in the rate of reaction at such a surface being ascribed entirely to variations in the concentration of mercury vapour caused by removal as mercuric oxide and irregular renewal due to skin effects. Improvements in technique have been effected. A. A. ELDRIDGE.

Photosensitisation by optically excited mercury atoms. The hydrogen–oxygen reaction. A. L. MARSHALL (J. Physical Chem., 1926, **30**, 34—46; cf. Taylor and Marshall, A., 1925, ii, 1078).—A more detailed examination of the reaction between hydrogen and oxygen has been made in a quartz reaction system, the only light of any intensity being the resonance line, 2536 Å., of the cold mercury arc. The gases were prepared electrolytically, passed over heated palladised asbestos, and dried over phosphorus pentoxide. Experiments at 50°, with gas mixtures ranging in composition from 406 mm. hydrogen and 148 mm. oxygen to 572 mm. of the former and 156 mm. of the latter, gave reactions of the same speed, the fall in pressure being 24·7 mm. per min. The pressure–time curves show an initial break at a point corresponding with saturation with water vapour, and then become linear. Curves of a different character are obtained when oxygen is in excess, the rate of combination decreasing rapidly as the reaction proceeds. The results with mixtures containing 2 vols. of hydrogen to 1 vol. of oxygen over the temperature range 25—70° indicate that the temperature coefficient obtained is an involved quantity, depending, at least, on two factors, viz., the increased vapour pressure of mercury at the higher temperatures giving an increased light absorption, and the increased yield per quantum absorbed. The close agreement of the values obtained at 60° and 70° seems to indicate that the true temperature coefficient will be found nearly equal to unity. At times, considerable amounts of mercuric oxide are formed, especially at 70° with excess of oxygen, and this accounts for some of the variability found in the rate between successive experiments; similarly with the gradual deterioration of the mercury arc. In later experiments, with 2 vols. of hydrogen to 1 vol. of oxygen, the rate of reaction is constant throughout, the final pressure in every case being the vapour pressure of water at the temperature (50—70°) of the experiment.

The results obtained at present favour the kinetic equation $d[H_2O]/dt = K_2 . [H_2]/\{[H_2]+[O_2]\}$. From energy considerations, it is probable that a " chain reaction " is involved, and several possible mechanisms, unsupported by thermal data, however, are advanced.

Previous kinetic and photochemical studies of gas reactions are summarised. L. S. THEOBALD.

Photochemical formation of hydrogen chloride. G. KORNFELD and H. MÜLLER (Z. physikal. Chem., 1925, **118**, 476).—Corrigenda to a previous paper (A., 1925, ii, 984). L. F. GILBERT.

Photochemical synthesis of hydrochloric acid. J. CATHALA (J. Chim. phys., 1926, **23**, 78—95).—The reaction scheme has been stated previously by the author (A., 1925, ii, 812). It is applied to explain the results of Cochn and Tramm (A., 1923, ii, 206) on the photosynthesis of carbonyl chloride and sulphuryl chloride. A. E. MITCHELL.

Energy changes in photochemical reactions in presence of iodine. B. K. MUKERJI and N. R. DHAR (Z. Elektrochem., 1925, **31**, 621—625).—The reactions between iodine on the one hand and potassium formate, potassium oxalate, ferrous sulphate, and sodium nitrite on the other are accelerated principally by light of 3160—4600 Å. The energy absorbed by 1 mol. of iodine per second is 0·1, 28, 15, and 49 quanta, respectively. If the reactions were unimolecular, they would accord with Einstein's law of photochemical equivalence. The authors find, however, that the reactions are bimolecular, and conclude that Einstein's law is not obeyed, probably because the reactions are exothermic. In such cases, the large amounts of energy liberated and its effects on activation introduce complications which render a simple law inapplicable. W. A. CASPARI.

Reactions in the presence of charcoal. C. SANDONNINI (Atti R. Accad. Lincei, 1925, [vi], **2**, 427—432).—Boiling 0·1*N*-oxalic acid solution is not measurably decomposed by exposure for 3 hrs. to a carbon arc, but 10—12% decomposition is produced in the presence of 0·01% of an uranium salt. This value is reduced to 6—7% by the addition of some low-temperature poplar charcoal, activated by steam at 850°. The decomposition of slightly alkaline solutions of potassium *p*-bromobenzenesulphonate was determined during 4 hr. periods of darkness and of illumination (*a*) in the absence of catalysts, (*b*) in the presence of charcoal, (*c*) in the presence of copper, and (*d*) in the presence of both charcoal and copper. Without catalysts, no decomposition occurred in the dark, and less than 2% in the light. In the dark from 0·65% to 0·95% decomposition was produced in the presence of charcoal, and, with illumination, from 2·28% to 3·21%. The corresponding values in the presence of copper were 3·78% to 5·26%, and 5·83% to 7·79%, and in the presence of both copper and charcoal, from 10·71% to 23·70% decomposition in the dark, and from 14·29% to 26·28% in the light. F. G. TRYHORN.

Properties of potassium mercuric oxalate. N. TRIFONOV (Mit. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 72; from Chem. Zentr., 1925, II, 382).—Potassium mercuric oxalate is decomposed by water

and by light. It may be heated at about 110° without decomposition. G. W. ROBINSON.

Decomposition of potassium ferrocyanide by light. G. ROSSI and C. BOCCHI (Gazzetta, 1925, **55**, 876—883).—The influence of various factors in the decomposition of potassium ferrocyanide by exposure to light has been investigated by determining the alkalinity of the solutions of the salt after exposure to sunlight or the light of an arc lamp. Equilibrium is reached by a 0·25% solution after exposure for 30 min. to an arc lamp. By varying the concentration of the salt, it was found that, with exposures of 60 min., the percentage decomposition decreased from 0·23% to 0·10% as the concentration of the salt decreased from 7·67 to 3·07 g. per 100 c.c. of solution. A further decrease in concentration of the salt to 1·53 g. resulted in a rise in the decomposition to 0·40%. By using solutions of the ferrocyanide containing various amounts of potassium hydroxide, it was shown that the presence of the latter, up to a certain amount, facilitated the decomposition, but with potassium hydroxide in excess of this amount the percentage decomposition decreased to that shown by a neutral solution. The reversibility of the reaction was investigated by alternately exposing to light, and keeping in the dark, a solution of the salt. Complete reversibility was shown after the first exposure, but with successive equal exposures the amount of decomposition increased, and the reversibility of the reaction decreased. Fluorescent substances are without influence on the reaction, and the decomposition is not due to a rise in temperature of the solution. No explanation is offered to account for these observations. F. G. TRYHORN.

Photochemistry of photographic films. F. WEIGERT.—See B., 1926, 109.

Photochemistry of photographic films. J. EGGERT and W. NODDACK.—See B., 1926, 109.

Measurement of radiation intensities by photographic methods. R. A. HOUSTOUN (Nature, 1926, **117**, 159; cf. Toy, this vol., 135).—The use of a ground quartz diffusing screen, with the application of the inverse square law, is preferable to the use of neutral absorbing screens.
A. A. ELDRIDGE.

Photo-oxidation of organic compounds by chromates. J. PLOTNIKOV (Z. Elektrochem., 1926, **32**, 13—15).—An introductory description of researches in progress (see following abstract) on the photo-oxidation of organic substances by chromates and dichromates. In the oxidation of ethyl and methyl alcohols, the precipitation of insoluble decomposition products of the dichromate used interferes with the free infiltration of light, and better yields of aldehyde are obtained with an apparatus in which the precipitate is continuously removed by filtration. Aqueous solutions of the following dyes in the presence of potassium dichromate are not affected by light: trypan-blue, induline, dahlia, aniline-green, malachite-green, naphthol-green, iodine-green, nigrosin, trypan-red, erythrosin, indigo-carmine-blue, gentian-violet, guinea-green-B and -G, brilliant-safranine, aurantia, safranine, lition-carmine, carmine II, rose Bengal, rhodamine-B, Hofmann-violet, methyl-violet, crystal-violet, cresyl-fast-violet, whilst ethyl-green, cyanin, and naphthalene-blue change both in the light and in the dark very quickly, especially on boiling. Nile-blue and cresyl-blue 2 B.S., however, are stable in the dark even on boiling, but in the light they change fairly quickly to bright red, fluorescent substances.
N. H. HARTSHORNE.

Photochemical oxidation of methyl and ethyl alcohols by potassium dichromate. M. SCHWARZ (Z. Elektrochem., 1926, **32**, 15—17).—The oxidation of methyl and ethyl alcohols in the presence of potassium dichromate powder in sunlight has been studied. The oxidation results in the formation of aldehydes only. The molecular ratio of the yield to the quantity of dichromate reduced increases with the time of exposure, and reaches, usually after 12—24 hrs., a value approximating to 2. With large quantities of dichromate there is a falling off in the yield of aldehyde, which is probably due to the screening effect of the precipitates formed and the dichromate powder itself. With methyl alcohol, the latter is reduced to chromic hydroxide and with ethyl alcohol to a brown powder of unknown composition. The reaction velocity is greater in methyl than in ethyl alcohol, especially with larger proportions of dichromate. N. H. HARTSHORNE.

Photochemical oxidation of leuco-bases. B. H. CARROLL (J. Physical Chem., 1926, **30**, 130—133; cf. Gros, A., 1901, ii, 433; Konig, Z. angew. Chem., 1904, **17**, 1633; Eder, Sitzungsber. Akad. Wiss. Wien, 1919, **128**, IIa).—The photo-oxidation of the leuco-bases of malachite-green, brilliant-green, "light-green" (from benzylethylaniline and benzaldehyde) and "furfural-green" (from dimethylaniline and furfuraldehyde) has been studied. Only dyes of the triphenylmethane and xanthen series appear to form stable, photo-sensitive leuco-bases. Incorporation of the bases in collodion films not only provides a practical form for photographic use, but also accelerates the photo-oxidation (Konig, *loc. cit.*). The absorption spectra were slightly displaced towards the longer wave-lengths, the maxima for the above dyes being at 624 μμ, 628 μμ, 628 μμ, 634 μμ, and 480 μμ, respectively. About forty compounds were tried as sensitisers, and all four bases were affected similarly by any one base. In general, the most photosensitive combination oxidised the most rapidly in the dark. Nothing was found, however, which gave a stable plate of practicable speed. Bases accelerate, and free acids retard the oxidation, both in the light and in the dark, the heterocyclic and aliphatic amines being more efficient than the aromatic in this respect. The nitric esters are the only oxidising agents which accelerate the light reaction to a greater extent than the dark. For the four bases examined, the higher the mol. wt. of the group attached to the amino-nitrogen atom the greater the stability. From the curves given showing the relation between exposure and density in the case of light-green sensitised by mannitol hexanitrate, quinoline, and a mixture of the two, the amount of dye formed in a given time is proportional to the intensity of the light. No induc-

tion period is indicated, and the sensitivity of the plates increased after drying. The results are briefly discussed. L. S. THEOBALD.

Effect of light on the permeability of lecithin. L. B. BECKING and M. I. GREGERSEN (Proc. Soc. Exp. Biol. Med., 1924, **22**, 130—133).—Lecithin-collodion membranes were prepared by pouring a 5% solution of lecithin and 5% of collodion in ether over glass plates. The rate of diffusion of potassium chloride through the membrane was determined by the change in electrical conductivity of distilled water by the electrolyte. Exposure to light for 5 min. caused an increase in electrical conductivity, followed by a decrease. The membranes lost their sensitivity to light after 6 or 7 days. CHEMICAL ABSTRACTS.

Action of radon on mixtures containing ammonia and an oxide of carbon. K. C. BAILEY (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 165—168).—Carbon monoxide and ammonia may react in two ways: $CO+NH_3 \rightarrow H_2O+HCN$ or $CO+NH_3 \rightarrow H_2+HOCN$. A mixture of these gases was subjected to the action of radon for 13 days. No cyanide was detected, but ammonium cyanate and carbamide (dixanthylcarbamide test) were found to be formed. Radon therefore causes the synthesis of cyanic acid. A small amount of ammonium cyanate and carbamide (determined nephelometrically) resulted from the interaction of carbon dioxide and ammonia in the presence of radon. R. A. MORTON.

Hydrogen. II. Solid metal-hydrogen compounds. G. F. HÜTTIG (Z. angew. Chem., 1926, **39**, 67—75; cf. A., 1925, ii, 702).—The tendency of hydrogen to yield gaseous compounds with the halogens, the oxygen, nitrogen, and carbon groups of elements, and with boron (elements forming a compact area of the periodic classification) is greatest for the halogen group; these hydrides dissociate into the elements at high temperatures. Metallic or alloy-like hydrides are formed to the maximum extent by the nickel–palladium–platinum group, and are also formed by iron, cobalt, and copper. In these cases, the weight of hydrogen absorbed by the metal varies continuously with the temperature and pressure, and the products can scarcely be regarded as chemical compounds. The absorption by palladium is much higher than that of the other metals; it is probable that hydrogen is combined both chemically and osmotically (in solution), there being an equilibrium between these two forms. At low temperatures, most of the hydrogen is combined chemically. Aluminium, gallium, indium, thallium, silver, and gold, and the beryllium group, which lie between those forming gaseous hydrides and those forming metallic hydrides, show no tendency to combine with hydrogen. The tendency to form salt-like hydrides in which hydrogen functions as an electronegative element is a maximum for the alkaline-earth metals and lithium, and is also shown by zirconium, thorium, cerium, praseodymium, sodium, potassium, rubidium, cæsium, and actinium. These hydrides are usually formulated as stoicheiometric compounds, but the actual hydrogen content is generally appreciably less than is thus indicated. They also have appreciable decomposition pressures, which increase with rising temperature. It is suggested that this peculiarity of hydrogen, in forming a range of solid solutions extending from a pure metal to a stoicheiometric compound, is due to its great mobility. In all compounds at temperatures above 0° Abs. the atoms are capable of motion about their mean positions. If the atoms of one element of a binary compound are much more mobile than those of the other, the condition is approached in which the former move freely, as in the case of osmotic diffusion through a solution. There is then no sharp distinction between a solid solution and a compound. A. GEAKE.

Reactions of the type $Cl_2+2KOH=KCl+KClO+H_2O$. F. W. BERGSTROM (J. Physical Chem., 1926, **30**, 12—19; cf. A., 1923, ii, 31; 1925, ii, 231, 315, 885, 1083).—The action of solutions of ammonio-bases on elements more electronegative than nickel has been examined. The elements react with solutions of potassamide, and, to a lesser extent, with other ammonio-bases, provided that the alkali-metal salts of the element are soluble in ammonia. The initial reaction is of the type $Cl_2+2KOH=KCl+KClO+H_2O$. Iodine reacts rapidly with potassamide at −33°, according to the equation $6I+6KNH_2=6KI+4NH_3+N_2$. Sulphur readily reacts with the amides of lithium, potassium, calcium, barium, and magnesium; and selenium with those of lithium, sodium, barium, and calcium (slowly). With potassamide at −33° or the ordinary temperature, selenium forms, initially, a white precipitate containing an explosive substance; excess of selenium then yields highly-coloured solutions, containing polyselenides and a soluble, non-explosive, potassium salt of an ammonio-acid containing this element. Tellurium reacts fairly readily with potassium and sodium amides at the ordinary temperature, but slowly at −33°. Arsenic and antimony, at the ordinary temperature, with potassamide slowly give red solutions; with bismuth, the reaction is very slow. Red and yellow phosphorus both react with potassamide and red phosphorus with sodamide. With the latter, and with dilute solutions of potassamide, tin gives red solutions. The equation is $10Sn+6M^INH_2=2(SnNM^I,2NH_3)+M^I_4Sn_8$. Dissolution by lithium amide is very slow; with calcium and barium amides, there is no effect at the ordinary temperature. In the more concentrated solutions of potassamide, the formation over the metal of a passive coating, removable by ammonium chloride, prevents reaction. The curves of solubility of tin in the amides plotted against concentration indicate the formation of the compounds Na_4Sn_8 or K_4Sn_8, respectively.

Sodium and *potassium ammoniostannites* were prepared as white solids, very soluble in liquid ammonia, by the action of (1) mercury on the product of the reaction of tin with the respective amides and (2) the amides on excess of tin amalgam, and in the case of the potassium salt, the action of the amide on stannous chloride. The constitution may be represented by the formulæ $Sn(NH_2)_2,K(\text{or Na})NH_2$; $SnNK(\text{or Na}),2NH_3$ or $K(\text{or Na})[Sn(NH_2)_3]$.

Lead behaved towards potassamide in an erratic manner; either a green solution containing poly-

plumbide and, presumably, ammonioplumbite was slowly formed or there was no action, as was the case with sodamide. A solution of potassamide (0·6*N*) did not attack gold, copper, or germanium, and mercury was attacked with extreme slowness. Amalgams of lead, bismuth, or silver were unaffected; those of copper and gold were attacked very slowly, and that of tin more rapidly. L. S. THEOBALD.

Reaction between cupric copper and iodide, and between cuprous iodide and iodine. I. M. KOLTHOFF (Rec. trav. chim., 1926, **45**, 153—161).—The reversible reaction between cupric copper and iodide may be represented $Cu^{\cdot\cdot}+2I' \rightleftharpoons CuI+0{\cdot}5I_2$, the ions reacting, and not the molecules, in contradiction to the work of Herschkovitsch (A., 1925, ii, 904). The value of $K'=[Cu^{\cdot\cdot}][I']^2/\sqrt{I_2}$, in which the concentrations are put equal to the concentrations of the components, is calculated from the data of Shaffer and Hartmann (A., 1921, ii, 417), and increases with increasing electrolyte concentration, a mean value being 4×10^{-4}. Introducing terms for the activity of the ions, the true constant $K=1{\cdot}8\times10^{-4}$. If the cupric-ion concentration is kept low by great dilution or by the addition of oxalate or other complex-forming salts, the reaction is reversed and cuprous salts may be quantitatively oxidised by iodine. At 18°, the solubility of iodine in water corresponds with $1{\cdot}09\times10^{-3}M$, and the activity of cupric ions in solutions of electrolytes is calculated from solubility measurements. The tri-iodide constant $K_{I_3'}=[I'][I_2]/[I_3']$ is $1{\cdot}10\times10^{-3}$ at 18° and is practically unaffected by the presence of 0·1*N*-electrolytes. W. HUME-ROTHERY.

Preparation of sodium aurothiosulphate. K. L. MCCLUSKEY and L. EICHELBERGER (J. Amer. Chem. Soc., 1926, **48**, 136—139; cf. Fordos and Gélis, Ann. Chim. Phys., 1845, **13**, 394).—This salt, which appears to contain gold in the aurous state, has been prepared by adding a solution of sodium thiosulphate to a solution of cæsium chloroaurate or sodium chloroaurite (Diemer, A., 1913, ii, 515). It is somewhat unstable, but may be preserved under anhydrous ether at 0° in the dark. R. CUTHILL.

Magnesium hydrogen halides. R. M. PICKENS (Science, 1925, **62**, 226).—Catalytic reduction of magnesium triphenylmethyl chloride yields an indication of the formation of magnesium hydrogen chloride. A. A. ELDRIDGE.

Fluorides and double fluorides of aluminium. M. TOSTERUD (J. Amer. Chem. Soc., 1926, **48**, 1—5).—The compound stated by Mazzuchelli (A., 1907, ii, 549) to be $Al_2F_6,17H_2O$ is really $Al_2F_6,18H_2O$. This hydrate decomposes at the ordinary temperature, forming $Al_2F_6,7H_2O$, but if heated at a high temperature in a closed system gives the anhydrous salt. Baud's double salt, $Al_2F_6,6KF$ (A., 1904, ii, 176), actually has the formula $Al_2F_6,4KF$, and an analogous *rubidium* compound, $Al_2F_6,4RbF$, has been isolated. The conductivity of mixed solutions of aluminium fluoride and alkali fluorides is at a minimum at points corresponding with the composition of the known double salts. R. CUTHILL.

Hydrolysis of aluminium sulphate. A. J. PELLING.—See B., 1926, 125.

Pseudo-alums. R. M. CAVEN and T. C. MITCHELL (J. Royal Tech. Coll., 1925, [2], 26—33).—See A., 1925, ii, 396.

Double sulphates of the rare-earth metals and the alkali metals. IV. Double sulphates of neodymium and sodium. F. ZAMBONINI and G. CAROBBI (Atti R. Accad. Lincei, 1925, [vi], **2**, 374—377; cf. A., 1925, ii, 222, 579; this vol., 137).—The existence of the following *compounds* is indicated by the determination of the 25° isotherm of the system $Nd_2(SO_4)_3$–Na_2SO_4–H_2O. $Nd_2(SO_4)_3,Na_2SO_4,2H_2O$, stable in contact with solutions containing up to 0·3% of neodymium sulphate, and from 0·5% to 5·0% of sodium sulphate; $4Nd_2(SO_4)_3,5Na_2SO_4,8H_2O$, stable in contact with solutions containing from 5·5% to 9·0% of sodium sulphate; $3Nd_2(SO_4)_3,4Na_2SO_4,6H_2O$ and $2Nd_2(SO_4)_3,3Na_2SO_4,5H_2O$, stable in contact with solutions containing, respectively, from 14·0% to 9·0%, and from 15·0% to 17·0%, of sodium sulphate. F. G. TRYHORN.

Stannous chloroiodide, bromoiodide, and chlorobromide. T. KARANTASSIS (Compt. rend., 1926, **182**, 134—136).—Stannous chloroiodide is obtained by dissolving iodine in a solution of stannous chloride and hydrochloric acid, and reducing the red liquid by addition of excess of tin: $2SnCl_2+4I=SnCl_4+SnI_4$; $SnI_4+Sn=2SnI_2$ and $SnCl_4+Sn=2SnCl_2$; $2SnCl_2+2SnI_2=4SnClI$. If the original solution contains excess of iodine, red crystals of stannous iodide are first deposited, which are slowly converted in the cold into white needles of the chloroiodide. With a large excess of stannous chloride, white crystals of the chloroiodide are deposited at once. The existence of the chloroiodide is further confirmed by thermal analysis of mixtures of the chloride and iodide. A solution of the bromoiodide is obtained in an analogous manner. The pale yellow needles deposited in presence of an excess of stannous bromide consist of a solid solution of the iodide in the bromoiodide. Thermal analysis confirms the existence of mixed crystals with a tendency to form the bromoiodide. Stannous chlorobromide does not appear to exist as a stable salt. On thermal analysis of mixtures of chloride and bromide, a eutectic is found, f. p. 213°, with 62·8 mol. of stannous bromide, a considerable dilution of the mixture occurring on further addition of stannous chloride. L. L. BIRCUMSHAW.

Action of sodium hypophosphite on stannous chloride. A. TERNI and C. PADOVANI (Atti R. Accad. Lincei, 1925, [vi], **2**, 501—505).—The addition of stannous chloride, either as solid or in very concentrated solution, to a concentrated solution of sodium hypophosphite produces a voluminous white precipitate of a strongly reducing substance, the analysis of which corresponds with the formula $SnCl_4,Sn(H_2PO_2)_4,3H_2O$. When heated, the substance is dehydrated at 140°, and decomposes, with a characteristic reddening and the evolution of phosphine, at 190°. If the heating is stopped immediately the red colour appears and the mass

extracted with concentrated hydrochloric acid, a bright red residue remains, which has very strong reducing properties and a composition approximating closely to that of phosphorus suboxide, P_4O.
F. G. TRYHORN.

New double salt of ammonium nitrate and sulphate. L. WÖHLER and W. SCHÄFFER (Z. anorg. Chem., 1925, **149**, 389—394).—A double *salt*, NH_4HSO_4,NH_4NO_3, is formed from ammonium nitrate and concentrated sulphuric acid, or from a concentrated aqueous solution of ammonium sulphate and nitrate and sulphuric acid. It is very hygroscopic and readily soluble in water, and melts at 87°. The solubility was determined over the range 20—60°, and the solubility isotherm at 25° was worked out for the system NH_4NO_3–NH_4HSO_4–H_2O, to which sufficient sulphuric acid was added to prevent decomposition of the hydrogen sulphate. A. GEAKE.

Phosphorus. I. Colourless phosphorus. L. WOLF and K. RISTAU (Z. anorg. Chem., 1925, **149**, 403—412).—Colourless phosphorus can be obtained pure only in a darkened room and in the absence of oxygen and moisture. Apparatus and procedures are described for its preparation under these conditions in an atmosphere of nitrogen either by fractional distillation or by fractional crystallisation from benzene. It is a colourless, transparent mass or a white, finely crystalline product, which melts to a perfectly clear and colourless liquid. It is stable under the above conditions, but rapidly becomes yellow in light. A. GEAKE.

Production of arsenic subsulphide. Reduction of certain arsenic compounds by sodium hyposulphite. W. FARMER and J. B. FIRTH (J.C.S., 1926, 119—125).—Sodium hyposulphite reduces arsenic compounds at the ordinary temperature in neutral or acid solution, forming immediately a dark brown product, which after repeated extraction with colourless ammonium sulphide leaves an insoluble residue of sulphide of arsenic containing, in the case of tervalent arsenic, 12·7% of sulphur corresponding with the formula As_3S (cf. Scott, *ibid.*, 1900, **77**, 651). The products obtained by the reduction of tervalent and quinquevalent arsenic compounds under acidic, neutral, or alkaline conditions at various temperatures by different concentrations of sodium hyposulphite have been studied in detail. In moderately acid solution, tervalent arsenic compounds such as the oxide and the normal sodium and potassium arsenites yield precipitates consisting of arsenic subsulphide mixed with small amounts of arsenic trisulphide; quinquevalent arsenic compounds yield products which approximate to As_2S_3,As_3S. In neutral solution only quinquevalent arsenic compounds yielded products containing arsenic subsulphide, tervalent arsenic compounds giving precipitates containing only 6—7% S. In alkaline solution, reduction occurs only at the b. p., and no arsenic subsulphide is formed, the largest amount of sulphur in the product being 11%. In strongly acid solutions, the precipitate is chiefly arsenic trisulphide. The precipitation is not quantitative. In neutral solutions, 99·24% of tervalent arsenic compounds and 57·25% of quinquevalent arsenic compounds were precipitated by 10% sodium hyposulphite.
W. M. COLLES.

Action of hydrogen sulphide on a neutral solution of potassium permanganate. H. B. DUNNICLIFF and S. D. NIJHAWAN (J.C.S., 1926, 1—7).—The first products of the reaction between hydrogen sulphide and potassium permanganate in dilute (1%) solution are: (*a*) colloidal hydrated manganese dioxide, which rapidly coagulates into a gelatinous precipitate, (*b*) sulphur, (*c*) potassium sulphate, and (*d*) potassium dithionate. Some potassium thiosulphate is formed simultaneously by the action of hydrogen sulphide on (*d*). No sulphide, sulphite, tri-, tetra-, or penta-thionate, or colloidal sulphur is found in solution. When excess of hydrogen sulphide is passed into the solution, the hydrated manganese dioxide is converted into colloidal manganous sulphide, which rapidly coagulates. The potassium dithionate is reduced to potassium sulphate and thiosulphate, with the separation of sulphur partly in the colloidal state. The complete reaction is represented by the equation $10KMnO_4+22H_2S=3K_2SO_4+10MnS+2K_2S_2O_3+22H_2O+5S$. The various stages of the reaction have been investigated quantitatively. The reaction is alkaline throughout, due to adsorption of the anions of the potassium salts by the hydrated manganese dioxide and manganous sulphide. W. M. COLLES.

Polysulphides and polyselenides of lithium, sodium, and potassium. F. W. BERGSTROM (J. Amer. Chem. Soc., 1926, **48**, 146—151).—These metals dissolved in liquid ammonia react rapidly with sulphur, forming white precipitates of the monosulphides, which combine with sulphur to form light yellow or orange disulphides. These are readily soluble in ammonia, and addition of sulphur to the solutions gives red solutions of higher sulphides. The reaction between sulphur and sodium or potassium is found to be more complex than stated by Hugot (A., 1899, ii, 650). The mode of formation of polyselenides is very similar, but since the highest selenides obtained contained 5·0—5·8 atoms of selenium for 2 atoms of alkali metal, Hugot evidently failed to attain equilibrium in his experiments. R. CUTHILL.

Sulphur chloride and sulphur. G. BRUNI (Z. anorg. Chem., 1925, **149**, 387—388; cf. A., 1924, ii, 672).—Priority is claimed for the discovery of the existence of polythionyl chlorides, *e.g.*, S_4Cl_2 (cf. A., 1919, ii, 281). A. GEAKE.

Hydrolysis of sulphur monochloride. H. L. OLIN (J. Amer. Chem. Soc., 1926, **48**, 167—168).—The first stage of this process is probably to be represented: $S_2Cl_2+2H_2O=2HCl+H_2S+SO_2$ (cf. Carius, Annalen, 1858, **106**, 291). R. CUTHILL.

Action of sulphur monochloride on silica. P. BUDNIKOV and E. SCHILOV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 64—65; from Chem. Zentr., 1925, II, 388).—By the action of 40 g. of sulphur monochloride on 5 g. of silica for 1 hr. at 1000°, about 40% of the silica was converted into silicon tetrachloride. G. W. ROBINSON.

Stability and decomposition products of thiosulphuric acid. E. H. RIESENFELD and E. GRÜNTHAL (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, 6, No. 9, 1—36).—Experiments in which known amounts of hydrochloric acid and sodium thiosulphate, and sulphuric acid and barium thiosulphate, were allowed to react in closed vessels at constant temperature, the composition of the solution being determined after various time intervals, show that the thiosulphuric acid is not entirely decomposed. Under favourable conditions—low acidity and an initially low concentration of thiosulphate—the presence of thiosulphate ion may be demonstrated after 8 months. The decomposition of thiosulphuric acid is influenced by the acidity of the medium, in strongly acid solutions sulphur and sulphurous acid being the principal reaction products, together with some pentathionic acid. In dilute acid solutions (0·1*N*), some of the sulphur remains in colloidal solution. Pentathionic acid reacts to form trithionic and finally sulphuric acids. No tetrathionic acid was observed. The appearance and subsequent disappearance of a yellow colour are due to the formation of a hitherto unknown sulphur compound derived from the oxide S_2O_3, about 40% of the total sulphur being present in these solutions as the hydrate of this oxide.

The primary decomposition of thiosulphuric acid is represented by the equation $H_2S_2O_3=H_2SO_3+S$. The appearance of pentathionic acid is due to the reactivity of the freshly-formed colloidal sulphur, $5S+5SO_2+2H_2O=2H_2S_5O_6$, the pentathionic acid reacting with sulphurous acid to form some trithionic acid and more thiosulphuric acid, $S_5O_6''+2SO_3''=S_3O_6''+2S_2O_3''$. Trithionic acid slowly decomposes to give a mixture of thiosulphuric and sulphuric acids, $S_3O_6''+H_2O=SO_4''+S_2O_3''+2H^{\cdot}$.

On addition of copper sulphate to sodium thiosulphate solutions, in neutral solution a yellow precipitate and in hydrochloric acid solution a white precipitate of a sodium cuprous thiosulphate of varying composition is obtained. The precipitate decomposes on keeping to form copper sulphide. In the absence of sulphides this reaction affords an excellent qualitative test for the detection of thiosulphates, being about ten times as sensitive as the usual hydrochloric acid reaction. Polythionates do not give this reaction. J. S. CARTER.

Processes of reduction, oxidation, and autoxidation. W. TRAUBE and W. LANGE [and, in part, R. STAHN, R. JUSTH, and P. BAUMGARTEN] (Ber., 1925, 58, [*B*], 2773—2790).—I. Reducing action of chromous compounds. Chromous salts, which are stable in aqueous solution, have the power of decomposing water in the presence of acids, with slow liberation of hydrogen and formation of chromic salts. The reaction can be greatly accelerated by the addition of a suitable catalyst, notably a metal of the platinum group, or of a hydrogen acceptor. Among chromous compounds, the hydroxide is particularly active, either in the presence of alkalis or in neutral solution. Such solutions are conveniently prepared by the electrolytic reduction of chromic chloride or, less frequently, by sulphate solutions and subsequent addition of the calculated quantity of standard alkali hydroxide or ammonia. If the alkali is added gradually to the solution of the chromous salt containing the substance to be reduced, the latter is always present in excess with regard to the chromous hydroxide, and reduction is readily effected even of substances which under other conditions afford relatively stable chromous salts. Thus oxalic, hydrocyanic, and thiocyanic acids are converted into glycollic acid, methylamine, and hydrogen sulphide and methylamine, respectively. Azides and azoimide instantaneously yield nitrogen and ammonia. Chloroacetic acid is converted into acetic acid, whilst benzaldehyde yields benzyl alcohol.

II. Decomposition of water by ferrous hydroxide or carbonate in the presence of palladium. The action of the platinum metals towards chromous salts and water does not extend to the manganous and stannous salts, which, under these conditions, do not decompose water at 100°. Evolution of hydrogen is not observed when palladium chloride is added to a boiling solution of ferrous sulphate, even after addition of an excess of alkali hydroxide. If, however, sodium hydroxide is added to a boiling solution of ferrous sulphate in quantity rather less than is required for complete precipitation of ferrous hydroxide and the solution is boiled after addition of palladium chloride, hydrogen is slowly evolved and triferric tetroxide is produced. Sodium hydroxide may be replaced by sodium carbonate. The process differs in principle from that observed with chromous salts, since decomposition of the water is not instantaneous and depends distinctly on the amount of palladium. The action with iron salts is not therefore purely catalytic, and it is probable that its incidence is to be ascribed to the simultaneous exothermal production of palladium hydride. If this is the case, the persistence of the change must be due to a subsequent partial dissociation of the hydride into its components, with evolution of hydrogen.

III. Behaviour of carbon monoxide towards water in the presence of palladium. In the presence of finely-divided palladium and absence of air, carbon monoxide is oxidised by water to carbon dioxide, with simultaneous production of palladium hydride. Wieland (A., 1912, ii, 347) has assumed the primary action to consist in the addition of water to carbon monoxide, with formation of formic acid, which is subsequently decomposed into carbon dioxide and hydrogen. The hypothesis is based on the experimental isolation of small amounts of barium formate, which, however, might arise from the reduction of carbon dioxide by palladium hydride (cf. Wieland, *loc. cit.*). The authors have therefore attempted to arrange the experimental conditions in such a manner as to remove formic acid, if produced by hydration of carbon monoxide, from the dehydrogenating action of palladium, using for this reason alkaline solutions containing a sufficient amount of ethyl alcohol; the presence of alcohol or sodium hydroxide has no influence on the " oxygen-free combustion " of carbon monoxide. Under these conditions, carbonate is immediately formed in the solution, and therefore must be produced directly from carbon monoxide; its production is accompanied by increase in the hydrogen content of the palladium. Sodium formate added

before the experiment, is found unchanged in amount at its conclusion. The production of carbonate is invariably less, of hydrogen greater than corresponds with the volume of carbon monoxide absorbed. This is caused by the very slow action of palladium on ethyl alcohol, from which hydrogen is withdrawn, with production of acetaldehyde, which, however, never leads to that of recognisable amounts of carbon dioxide. On the other hand, carbon monoxide is absorbed to a very appreciable extent by palladium. Since combustion of carbon monoxide does not take place through formic acid, it must be assumed that the change is due to the decomposition of water in the manner described for ferrous hydroxide and carbonate.

IV. Autoxidation of aliphatic amino- and polyhydroxy-compounds containing copper in complex union. Solutions of ammonia, amines, aliphatic amino-acids, and aliphatic polyhydroxy-compounds absorb atmospheric oxygen and undergo profound oxidation only in the presence of copper and in solutions of definite hydroxyl-ion concentration. Free oxygen cannot be replaced by combined oxygen, except in the case of the most powerful oxidising agents; thus nitrite is immediately produced when ammoniacal solutions of copper oxide are exposed to air, whereas chlorate, chromate, or nitrate does not produce this effect in the absence of air at 36—40°. Replacement of the alkali or barium hydroxide by tetraethylammonium hydroxide in the autoxidation of glycerol or mannitol in the presence of copper affects the course of the change in such a manner that formic acid is the sole isolable product, the production of carbon dioxide or oxalic acid could not be detected. Formic acid is also obtained by the similar oxidation of glycine. H. WREN.

Action of hydrogen fluoride on compounds of selenium and tellurium. I. Selenium dioxide. E. B. R. PRIDEAUX and J. O'N. MILLOTT (J.C.S., 1926, 167—174).—Selenium dioxide rapidly absorbs anhydrous hydrogen fluoride, forming colourless liquids in which it is very soluble. Liquids containing up to 75% of hydrogen fluoride are obtained by prolonged action. No volatile selenium compounds are formed. The products, which contained usually 40—50% of hydrogen fluoride, fume in air and evolve hydrogen fluoride at the ordinary temperature and also selenium dioxide at higher temperatures. After distilling off the excess of hydrogen fluoride up to 100°, the residue has the composition SeO_2,5HF. The solid which freezes from the residue at −17° to −18° has the same composition.

W. M. COLLES.

Green colour of tungsten trioxide. N. H. SMITH and H. S. LUKENS (Chem. News, 1926, **132**, 33—35).—The green colour which sometimes develops when tungstic acid is ignited is due to the presence of sodium salts. The intensity of the colour is roughly proportional to the amount of sodium salt present; thus 0·05% of sodium chloride imparts a faint greenish-yellow colour to the oxide, 0·16% a pale green colour, and 0·74% a deep green colour. The green oxides do not become yellow even after prolonged heating in oxygen. Pure tungsten trioxide is only slightly discoloured by exposure to bright sunlight and the discoloration is only superficial, whereas the green colour due to sodium salt is the same throughout the particle. To obtain a yellow oxide from sodium tungstate, the cold solution of the latter should be treated with one-third its bulk of concentrated hydrochloric or nitric acid and the mixture heated to boiling to convert the tungstic acid into the bright yellow, granular form which does not adsorb sodium salts. The use of a smaller proportion of acid results in a more or less flocculent and paler yellow precipitate from which all the sodium salt cannot be removed by washing.

A. R. POWELL.

Tungsto-vanado-arsenates. II. G. CANNERI (Gazzetta, 1925, **55**, 883—894; cf. A., 1924, ii, 117).—It was suggested that the heterotriarsenates are members of three limiting series represented, respectively, by the compounds

(1) $(NH_4)_6H[As(W_2O_7)_4(V_2O_6)_2],nH_2O$,
(2) $(NH_4)_6H[As(W_2O_7)_3(V_2O_6)_3],25H_2O$,
(3) $(NH_4)_6H[As(W_2O_7)_2(V_2O_6)_4],25H_2O$.

The colour of these compounds increases in intensity with increasing number of V_2O_6 groups in the complex anion. An attempt has been made to determine the reproducibility of salts of the above types, by the crystallisation at constant temperatures of solutions of various amounts of ammonium tungstate in solutions containing a given ratio of As_2O_5 : NH_4VO_3. The differing compositions of the heterotriarsenates obtained from solutions containing the ratio As_2O_5 : NH_4VO_3=3 : 2 suggest that they are members of a series of mixed crystals of salts of the type (1). From solutions in which the ratio As_2O_5 : NH_4VO_3 was, respectively, 3 : 4 and 1 : 2, salts were obtained approximating in composition to type (2) in the former case, and to both types (2) and (3) in the latter. In no case was the reproducibility satisfactory.

F. G. TRYHORN.

Hypochlorous acid and the alkali hypochlorites. G. MÜLLER (Z. anorg. Chem., 1925, **149**, 401—402).—The conclusion of Dietzel and Schlemmer (A., 1925, ii, 892) that chlorine and sodium hydroxide do not react quantitatively in accordance with the equation $2NaOH+Cl_2=NaOCl+NaCl+H_2O$ is due to an error in calculation. A. GEAKE.

Presence of dvi-manganese (element 75) in manganese salts. V. DOLEJŠEK and J. HEYROVSKÝ (Chem. Listy, 1926, **20**, 4—12).—When a solution of a manganese salt is electrolysed using a mercury dropping cathode and the applied *E.M.F.* is plotted against the current intensity, a sharp change in the direction of the curve takes place at an *E.M.F.* of 1 volt, followed by a less noticeable change at about 1·2 volts. The first is due to an element, present to the extent of 1 in 40,000, which, when concentrated into a product containing it to the extent of 1 in 50, yields the following lines in the *X*-ray spectrograph, which correspond with those of element 75 (dvi-manganese): $L\alpha_1$, 1430 *X.*; $L\beta_1$, 1253·3 *X.*; $L\beta_2$, 1204·3 *X.*; and $L\gamma_1$, 1059 *X.* The second is believed to be due to eka-manganese. Products containing

1—2% of dvi-manganese may be obtained by placing a piece of platinum foil in contact with manganese amalgam under a concentrated solution of a manganese salt; after several days, the deposit on the platinum is collected and dissolved in hydrochloric acid, the solution, after removal of the heavy metals, is evaporated to dryness, the residue dissolved in water, and iron, cobalt, nickel, and zinc are removed as usual. Concentrates of dvi-manganese may also be obtained by bubbling air into strong solutions of manganese salts, by the incomplete reduction of permanganates (which are relatively rich in dvi-manganese), by treating a permanganate solution with a barium salt, and by heating pyrolusite with hydrochloric acid, dvi-manganese chlorides being evolved with the chlorine. Dvi-manganese appears to be an active catalyst for oxidation reactions; its presence accelerates the oxidation of the lower oxides of manganese, nickel, and iron in the air. The higher oxides and chlorides are very volatile and the lower oxide forms salts resembling those of zinc and manganese. The authors do not approve of the name "rhenium" for this element, as the chemical properties of the substance discovered by them, as well as the lines in the *X*-ray spectrum, do not agree with those observed by the discoverers of rhenium.

A. R. Powell.

Reduction of ferric oxide by hydrogen. H. Kamura (J. Iron and Steel Inst., 1925, **112**, 279—298).—See A., 1925, ii, 981.

Ferro- and ferri-cyanides. N. Tarugi (Gazzetta, 1925, **55**, 951—975).—An analysis has been made of six specimens of "blue" obtained, respectively, (*a*) by the action of 3 mols. of potassium ferrocyanide on 4 mols. of a ferric salt in neutral solution, (*b*) by the action of potassium ferricyanide on excess of a ferrous salt; by the action of potassium ferricyanide on a ferric salt and hydrogen peroxide, (*c*) in neutral solution at 0°, (*d*) in acid solution at 0°, (*e*) at the ordinary temperature, and (*f*) by the action of potassium ferricyanide on a ferric salt and hydrazine. In every case the products contained oxygen, in amount varying from 0·45% to 2·14%. This oxygen is present as a result of the formation of a per-acid by the oxidation of the ferrocyanide by the ferric salt. The stages suggested for this reaction are, respectively, $4FeCl_3+2H_2O=4FeCl_2+4HCl+O_2$, and $4FeCl_2+3K_4Fe(CN)_6+O_2+2HCl=Fe_7(CN)_{18}K_2(OH)_2+10KCl$. This action is similar to that postulated by Baudisch and Bass (A., 1922, i, 993) as a second phase in the decomposition of potassium ferrocyanide by light in the presence of oxygen. The per-acid is assigned the annexed formula. Ordinary Prussian-blue is regarded as the ferrous salt of this acid. Considerable evidence is reported for the existence of salts of this acid. Empirical and structural formulæ are suggested for the "blues" prepared by the above methods and their relationship to this acid is discussed. The "blues" obtained at the ordinary temperature in the presence of hydrogen peroxide or hydrazine are ascribed the empirical formulæ

$$Fe_{12}(CN)_{30}HKO_2,25H_2O,$$

and $Fe_{12}(CN)_{34}K_2O,18H_2O$. These, it is suggested, are formed by the partial reduction of the "blue" obtained by the action of ferrous salts on potassium ferricyanide under normal conditions.

F. G. Tryhorn.

Sulphito-amminocobaltates. E. H. Riesenfeld [with W. Petrich] (Medd. K. Vetenskapsakad. Nobel-Inst., 1925, **6**, No. 6, 1—21).—The sulphito-group in the sulphito-amminocobaltates in general behaves as a univalent radical, occupying only one co-ordination position. In those compounds in which all the co-ordination positions are not filled, *e.g.*, as in $NH_4[(SO_3)_2Co(NH_3)_2]$, either the co-ordination number changes from 6 to 4, involving a change from a hexahedral orientation of groups round the cobalt atom to a tetrahedral arrangement, or the sulphito-group occupies two co-ordination positions. Assuming the former view, only one salt of the above constitution should exist, whereas assuming the latter, *cis-* and *trans*-modifications should exist, of which the *cis*-form should be capable of further resolution into two optically active forms. Actually only a single salt was obtained, and attempts at resolution by fractional crystallisation of the strychnine salt were unsuccessful; the failure of attempts to replace the two ammonia groups by one ethylenediamine molecule and the fact that replacement of the sulphito-groups by two oxalato-groups results in the formation of ammonium diamminodioxalatocobaltate (Riesenfeld and Klement, A., 1922, ii, 853) are taken as sufficient evidence that the substance is the *trans*-compound and that the hexahedral arrangement persists, the sulphito-group occupying two co-ordination positions.

The preparation of the following compounds is described: *Pentammino-monosulphitocobaltic sulphite*, $[Co(NH_3)_5SO_3]_2SO_3,2H_2O$, dark brown prisms. Pentammino-monochlorocobaltic chloride, $[Co(NH_3)_5Cl]Cl_2,3H_2O$. *Ammonium tetrammino*-trans-*disulphitocobaltate*, $(NH_4)[Co(NH_3)_4(SO_3)_2]$, yellow hexagonal plates. *Ammonium diethylenediamino*-trans-*disulphitocobaltate*, $NH_4[Co\ en_2\ (SO_3)_2]$, yellow, quadrangular plates; *strychnine* salt, $C_{21}H_{22}N_2O_2,H[CO\ en_2\ (SO_3)_2],2H_2O$, $[\alpha]_G=-30°$, $[M]_G=-219°$. *Ammonium dipropylene-diamino*-trans-*disulphitocobaltate*, $NH_4[Co\ pn_2\ (SO_3)_2]$. *Ammonium* trans-*diammino*-*disulphitocobaltate*, $NH_4[Co(NH_3)_2(SO_3)_2]$, *strychnine* salt, $C_{21}H_{22}N_2O_2,H[Co(NH_3)_2(SO_3)_2],2H_2O$, $[\alpha]_G=-70°$, $[M]_G=-437°$. *Ammonium triammino-trisulphitocobaltate*, $(NH_4)_3[Co(NH_3)_3(SO_3)_3]$. *Cobaltic triamminotrisulphitocobaltate*, $Co[Co(NH_3)_3(SO_3)_3]$.

J. S. Carter.

Binary bromides and iodides of platinum. L. Wöhler and F. Müller (Z. anorg. Chem., 1925, **149**, 377—386).—Pure platinum tetrabromide is obtained by heating bromoplatinic acid in a current of bromine at 300°. At 370°, further loss of bromine takes place with formation of the *tribromide*, and at 405—410° the dibromide is formed. The dibromide is difficult to prepare, as it is stable over a temperature

range of only 5°. The corresponding iodine compounds are also difficult to prepare from the tetraiodide because they are stable only over narrow ranges of temperature. By heating platinum with iodine in a sealed tube, the tetraiodide is formed at 240—300°, and the *tri-iodide* at 350—400°. The di-iodide is obtained with difficulty at a higher temperature.

A. GEAKE.

Formation and decomposition of the complex sodium chlorides of platinum and iridium. L. WÖHLER and P. BALZ (Z. anorg. Chem., 1925, **149**, 353—358).—When sodium chloroplatinate and chloroiridate are heated, the chlorine contents fall continuously with rising temperature until they correspond with the chloroplatinite and chloroiridite, respectively. The same curves are obtained when platinum and iridium are chlorinated with sodium chloride and chlorine. Similarly, the chlorine contents vary continuously with the composition. At higher temperatures, metallic platinum and iridium are formed. No evidence was obtained of the formation of complex chlorides of tervalent or univalent platinum, or of bivalent or univalent iridium. Below 660°, sodium chloroplatinate is obtained, and above 800° only the chloroplatinite. Sodium chloroiridate is obtained below 570° and is completely decomposed at 800°. Sodium chloroiridate may be determined by titration with sodium thiosulphate.

A. GEAKE.

Preparation of beryllium chloride by the action of carbonyl chloride on beryllium oxide. C. MATIGNON and J. CATHALA (Compt. rend., 1925, **181**, 1066—1068).—Beryllium chloride may be prepared most conveniently by heating the oxide in a current of carbonyl chloride. By working under specified conditions, data have been obtained enabling the velocity of reaction at different temperatures to be studied empirically. If the speed of the stream of carbonyl chloride is doubled, the reaction velocity increases by an amount which varies with the temperature. The chlorination increases rapidly with rise of temperature. J. GRANT.

Sodium pyroborate monohydrate. M. RAKUSIN and A. NESMEJANOV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 52—54; from Chem. Zentr., 1925, II, 388).—Sodium pyroborate monohydrate is prepared by heating borax to constant weight at 180°. G. W. ROBINSON.

Purification of phosphoric oxide. G. I. FINCH and R. P. FRASER (J.C.S., 1926, 117—119).—Modifications in the apparatus devised by Finch and Peto (*ibid.*, 1922, **121**, 692) are described. In 1 hr. 500 g. of impure phosphoric oxide can be distilled in a current of oxygen flowing through a red-hot iron tube with a 70—80% yield of pure oxide free from lower oxides and organic matter and possessing a minimum vapour pressure (cf. Smits and Rutgers, *ibid.*, 1924, **125**, 2573), and very voluminous.

W. M. COLLES.

Formation of ozone from air under pressure. H. VON WARTENBERG and M. TREPPENHAUER (Z. Elektrochem., 1925, **31**, 633—636).—Experiments on dry air compressed to 2—5 atm. with 50-cycle alternating current at 15,000—22,500 volts show that there is a slight rise in the yield of ozone per unit time up to 2 atm., followed by a rapid and continuous decline. The current efficiency shows a similar maximum at 2 atm. Higher voltages than those mentioned caused sparking. Compressed ozonised air may be produced more efficiently by ozonising first and compressing afterwards.

W. A. CASPARI.

Ozonisation with high-frequency current. H. VON WARTENBERG and M. TREPPENHAUER (Z. Elektrochem., 1925, **31**, 636—640).—The yield of ozone is not materially affected by increasing the frequency up to 300,000 cycles. At very low rates of flow of the air or oxygen, however, increasing frequency reduces the yield very considerably. Experiments on ammonia synthesis in the same apparatus showed a similar relation between frequency and rate of flow. W. A. CASPARI.

Determination of coloured gases by means of the photoelectric cell. H. and A. COPAUX.—See B., 1926, 125.

Crucible methods of analysis. J. D. M. SMITH (Chem. News, 1926, **132**, 65—72).—A more detailed account of the use of the crucible previously described (this vol., 41).

Deflexion potentiometer. H. BIENFAIT (Rec. trav. chim., 1926, **45**, 166—168; cf. Goode, A., 1922, ii, 307).—A description of an apparatus for electrometric titrations or more accurate potential measurements. A single triode valve is used, and the accuracy obtained is 0·5 millivolt with a range of 1 volt. The potential is calculated from direct readings on a millivoltmeter and need not be checked by compensation. The arrangement resembles the original apparatus of Goode (*loc. cit.*), but is more accurate owing to arrangements to allow for changes in the potential of the battery and storage cell. It is much more simple than the later improved apparatus of Goode (A., 1925, ii, 1196).

W. HUME-ROTHERY.

Chromic acid method for the determination of small amounts of bromine. P. L. HIBBARD (Ind. Eng. Chem., 1926, **18**, 57—60).—Bromine may be satisfactorily determined in amounts from 0·1 to 10 mg. by liberating with chromic anhydride and sulphuric acid, and drawing the gas in a current of air into a solution of potassium iodide, the liberated iodine being determined as it is set free by standard thiosulphate solution. Organic matter is previously removed by means of sodium peroxide, the temperature being kept as low as possible. Any iodine present must either be removed or accounted for, and if large amounts of chlorine are present it is necessary to carry out a double separation, whereby the small proportion of chlorine carried over the first time becomes negligible the second time. The presence of a little chloride seems to be advantageous, but when more than traces of chlorine are present the oxidising mixture should not be allowed to become warm. Nitrate or nitric acid must not be

present in sufficient amount to allow of the concentration becoming higher than *N*. D. G. HEWER.

Determination of dissolved oxygen in water in presence of nitrite. M. E. STAS.—See B., 1926, 110.

Determination of sulphites and of ferrous iron. W. D. BONNER and D. M. YOST (Ind. Eng. Chem., 1926, **18**, 55—56).—The iodine method for determining sulphites was taken as the standard, after comparison with gravimetric determinations, and other methods were compared with it. Potassium permanganate is unsuitable owing to formation of dithionic acid. Hypochlorite, dichromate, and bromate solutions all gave poor results, but bromine may be used for quantitative work. Potassium iodate was the most satisfactory reagent used, and its solution is more stable than that of either iodine or bromine, but it should be initially acid. Ferrous iron may be determined by adding its solution to one of disodium phosphate containing hypochlorous acid, whereby the iron is precipitated as ferric phosphate, and the excess of hypochlorous acid found by adding potassium iodide to the mixture and determining the liberated iodine. The tribromide method for ferrous iron was found to be inaccurate. D. G. HEWER.

Volumetric determination of sulphates by means of barium chloride and potassium stearate. H. ATKINSON (Analyst, 1926, **51**, 81—82).—In connexion with the method previously described (this vol., 38), it is pointed out that the presence of relatively large amounts (1% and upwards) of neutral salts appreciably affects the end-point, sodium and potassium chlorides depressing the barium chloride titration and potassium nitrate increasing it; with large amounts of neutral salts, the potassium stearate is salted out and the method fails. Phosphates interfere with the stearate reaction, but may be removed by boiling the solution with an excess of aluminium chloride. The resulting solution has an acid reaction to the indicator, and dilute sodium hydroxide is therefore added until the colour changes to yellow. On cooling, the liquid becomes greenish-yellow and its sulphate content may then be determined by the barium chloride-potassium stearate method. A. R. POWELL.

Electrometric determination of tellurium in presence of ferric iron, selenium, and copper. W. T. SCHRENK and B. L. BROWNING (J. Amer. Chem. Soc., 1926, **48**, 139—140).—An adaptation of the method of Lenher and Wakefield (A., 1923, ii, 576) to avoid the use of a spot-plate indicator.

R. CUTHILL.

Use of liquid amalgams in volumetric analysis. III. Determination of phosphoric acid by using lead amalgam. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1925, **14**, 569—576).—See A., 1925, ii, 1201.

Determination of arsenic and silver in silver arsenobenzenes. U. CAZZANI.—See B., 1926, 107.

Assay of potassium chlorate. LEHN AND FINK INC.—See B., 1926, 87.

S

Perchloric acid as an analytical reagent. Determination of potassium. J. H. YOE (Ann. Chim. Analyt., 1926, [ii], **8**, 1—3; cf. A., 1925, ii, 902).—Since Smith and Ross (A., 1925, ii, 437) have shown that it is not possible completely to dry the potassium perchlorate, and that potassium perchlorate crystallised from acid solution occludes perchloric acid, the author's method requires modification.

D. G. HEWER.

Determination of rubidium and cæsium. W. STRECKER and F. O. DIAZ (Z. anal. Chem., 1925, **67**, 321—341).—Rubidium and cæsium may be precipitated quantitatively as perchlorates by the following method. The solution is evaporated with an excess of perchloric acid until fumes of the latter are evolved and, after cooling, 10—15 c.c. of alcohol containing 0·3% of perchloric acid are stirred into the pasty residue. The precipitate is collected in a glass crucible with a porous bottom of sintered glass, washed with a 0·3% alcoholic solution of perchloric acid, dried at 150°, and weighed. As a test of the purity of the precipitate, a weighed amount is mixed with twice its weight of hydrazine sulphate and four times its weight of sodium carbonate and the mixture is fused for 10 min. The residue is dissolved in water and the chloride formed determined by titration with silver nitrate. The precipitate formed by the addition of sodium cobaltinitrite to a solution of a rubidium salt varies in composition between $NaRb_2Co(NO_2)_6$ and $Na_2RbCo(NO_2)_6$, according to the conditions of precipitation, so that this method is not applicable to the gravimetric determination of rubidium. The cæsium salt, on the contrary, has the composition $Cs_3Co(NO_2)_6,H_2O$ when precipitated at 80°. Both rubidium and cæsium may be weighed as the chlorostannates, which are obtained as follows: the concentrated solution of the chlorides of the two metals is treated with a mixture of 1 part of concentrated hydrochloric acid and 2 parts of alcohol. If potassium is present, it is almost completely precipitated as chloride at this stage. The solution is filtered, if necessary, and the precipitate washed with absolute alcohol. The filtrate is heated to boiling and treated with a hot alcoholic solution of stannic chloride. After keeping for 4 hrs., the white, crystalline precipitate of rubidium and/or cæsium chlorostannate is collected, washed with absolute alcohol, dried at 110°, and weighed. The filtrate contains the remainder of the potassium, which may be recovered as perchlorate in the usual way after evaporation to dryness and removal of the excess tin. The weighed chlorostannate precipitate is dissolved in a hot solution of tartaric acid, the tin removed with hydrogen sulphide, the filtrate evaporated to dryness, and the residue ignited to destroy the tartaric acid. The resulting chlorides are roughly weighed and dissolved in the smallest possible quantity of water with an equal weight of sodium or, preferably, ferric chloride. The solution is mixed with 50 c.c. of glacial acetic acid per g. of chlorides, heated nearly to boiling, and treated with a solution of antimony trichloride in glacial acetic acid. After setting aside over-night, the precipitated cæsium complex chloride (having a composition between $3CsCl,2SbCl_3,FeCl_3$

and $3CsCl,2SbCl_3,0{\cdot}5FeCl_3$) is collected in a glass crucible with a porous bottom of sintered glass, washed with a 5—10% solution of antimony trichloride in glacial acetic acid, and dissolved in hydrochloric acid. The solution is treated with perchloric acid and alcohol to obtain cæsium perchlorate for weighing; it is unnecessary to remove the antimony before adding the perchloric acid. Rubidium, if desired, may be recovered from the acetic acid filtrate by evaporation to dryness, removal of the antimony by hydrogen sulphide, and subsequent precipitaton of the rubidium with perchloric acid.

A. R. POWELL.

Sensitivity of certain reagents with strontium and calcium ions. D. RAQUET (Ann. Chim. Analyt., 1926, [ii], **8**, 3—10).—Strontium may be detected (*a*) alone or (*b*) in the presence of calcium in the following proportions: with calcium sulphate, (*a*) 1 part in 5,000 parts, (*b*) 1 in 10 (expressed as strontium corresponding with calcium); with 0·25% ammonium sulphate, (*a*) 1 in 10,000, (*b*) 1 in 10; with 0·33% sodium sulphite, (*a*) 1 in 5000, and in the presence of alcohol, (*a*) 1 in 25,000, (*b*) 1 in 100; with calcium chromate, (*a*) 1 in 300, (*b*) 1 in 15; with potassium chromate in alcohol, (*a*) 1 in 20,000, (*b*) 1 in 15; with Caron and Raquet's reagent (100 g. of ammonium chromate dissolved in water and 70—75 c.c. of ammonia solution, and then 50 c.c. of glacial acetic acid added, and the whole made up to 1000 c.c.) (*a*) 1 in 15,000, (*b*) 1 in 100. To detect calcium in the presence of other members of the group, an excess of Caron and Raquet's reagent is added, the barium chromate filtered off, and ammonia added to the filtrate until a yellow colour is obtained; 1 vol. of 60% alcohol is then added, and any strontium chromate filtered off. The calcium can then be detected (1 part in 10,000 parts) by the addition of potassium ferrocyanide. In a 1 in 10 solution of strontium chloride, 1 part of calcium for 100 parts of strontium can be detected.

D. G. HEWER.

Separation of lead and silver. G. VORTMANN and O. HECHT (Z. anal. Chem., 1925, **67**, 276—281).—The nitrate solution of the two metals is treated with tartaric acid equal to 15—20 times the weight of the metals present, and ammonia is added in slight excess. The lead may now be precipitated by the addition of a 10% solution of ammonium phosphate, and the precipitate collected, washed with 0·2% ammonium nitrate solution, ignited gently, and weighed as lead phosphate. Alternatively, the silver may be precipitated by the addition of an excess of 10% potassium iodide solution to the boiling liquid and the precipitate collected in a Gooch crucible, washed with very dilute ammonium nitrate solution, dilute nitric acid, and hot water in succession, dried at 130°, and weighed as silver iodide.

A. R. POWELL.

Determination of thallium. W. STRECKER and P. DE LA PEÑA (Z. anal. Chem., 1925, **67**, 256—269).—Thallium gives a brick-red, granular precipitate which settles and filters readily when a solution of a thallium salt is treated at 80° with an excess of an acetic acid solution of sodium cobaltinitrite, produced by mixing equal volumes of solutions containing (*a*) 57·2 g. of cobalt nitrate and 100 c.c. of acetic acid per litre, and (*b*) 360 g. of sodium nitrite per litre. Precipitation is quantitative and the precipitate may be dried at 100—110° and weighed as $NaTl_2Co(NO_2)_6$ for the determination of thallium. The precipitation of thallium as a metallic sponge is attended with difficulties, owing to the ease with which the metal oxidises and the trouble of removing the excess of the precipitant. Good results are obtained, however, if the solution is boiled with magnesium turnings in a flask fitted with a Bunsen valve and the excess of magnesium removed by shaking or warming gently with a large volume of ammonium chloride solution. When effervescence ceases, the sponge is allowed to settle and the clear liquor decanted off; the sponge is washed several times with recently boiled water, and its weight may be determined by measuring the volume of hydrogen evolved when it is dissolved in hydrochloric acid, by transferring it by means of a nickel spatula to a porcelain boat and heating for 40 min. in a current of hydrogen at 200—210°, or by bringing it into contact with a small globule of Wood's metal melted under hot water and determining the increase in weight of the alloy. Thallium may be determined volumetrically by adding slowly to the cold solution of the thallium salt a standard solution of potassium iodide (8·138 g. per litre) until no further precipitate forms, followed by a further 10 c.c. in excess, filtering off the yellow thallous iodide, and determining the excess of potassium iodide in the filtrate by a modification of the method of Fresenius. The iodine is liberated by addition of a few drops of concentrated sulphuric acid saturated with nitrous acid vapours and extracted from the solution by shaking with xylene. The xylene layer is separated, washed, and titrated with thiosulphate.

A. R. POWELL.

Electrolytic separation of copper from cadmium. A. JÍLEK and J. LUKAS (Chem. Listy, 1926, **20**, 18—21).—Copper may be deposited free from cadmium by electrolysis of a nitrate solution containing 15 c.c. of concentrated nitric acid, 6 g. of tartaric acid, and 15 g. of 40% hydrofluoric acid in a volume of 100—150 c.c. A rotating anode and the usual platinum dish cathode are used with a current of 1 amp. at 4 volts. If the copper present is less than 1% of the cadmium, the deposit must be redissolved in nitric acid and the process repeated, or the proportion of hydrofluoric acid may be increased to 20 g. in the first electrolysis.

A. R. POWELL.

Titration of mercury with potassium cyanide, lead with arsenate, and iron with thiosulphate. K. JELLINEK and J. CZERWINSKI (Z. anorg. Chem., 1925, **149**, 359—376).—When mercuric chloride is titrated with potassium cyanide containing alkali (cf. Jellinek and Krebs, A., 1923, ii, 871; Jellinek and Kühn, A., 1924, ii, 695; Rupp, Wegner, and Maihs, A., 1925, ii, 716), the reaction goes to completion and quantitative results may be obtained under suitable conditions. It is recommended to add mercuric chloride to hot potassium cyanide until the red colour of phenolphthalein is destroyed; a small, known amount of hydrochloric acid is then added to destroy hydrogen carbonate, and the titration completed with

sodium hydroxide until the red colour reappears. The potassium cyanide and alkali are then equivalent to the mercuric chloride and acid.

According to Rupp (*loc. cit.*), the result obtained by the titration of lead nitrate with alkali arsenate (cf. Jellinek and Kühn, *loc. cit.*) depends on the absolute amount of lead taken. This is probably due to the use of potassium arsenate; when sodium arsenate is used, the result is independent of the weight or concentration of lead nitrate, and is only slightly sensitive to acids.

When ferric chloride is titrated with sodium thiosulphate (cf. Jellinek and Vinogradov, A., 1924, ii, 703), more than the stoicheiometric proportion of thiosulphate is required (cf. Rupp, *loc. cit.*). Under carefully controlled conditions, a correction can be applied and a quantitative result obtained.

A. Geake.

Confirmatory test for aluminium. H. W. Estill and R. L. Nugent (J. Amer. Chem. Soc., 1926, **48**, 168—169).—To the solution is added sufficient of an alcoholic extract of dried alkanet root to make it ruby-red, then 3—5 c.c. more 6*N*-ammonium hydroxide solution than is necessary to change the red colour to blue, and the whole kept for 5 min. If aluminium is present, a purple lake rises to the surface, the solution being decolorised.

R. Cuthill.

Analysis of materials containing a mixture of metallic iron and iron oxides. H. C. M. Ingeberg.—See B., 1926, 130.

Application of the reaction between ferric salts and iodides to the determination of ferrous and ferric iron. N. Tananaev (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 72—73; from Chem. Zentr., 1925, II, 418—419).—The solution of a ferric salt is treated with a fivefold excess of potassium iodide and then with an excess of sodium thiosulphate. The thiosulphate is then titrated with iodine solution. In the case of a ferrous salt, the solution is treated with potassium sodium tartrate, sodium hydrogen carbonate, and excess of iodine, whereby the ferrous salt is quantitatively oxidised. The excess of iodine is titrated with sodium thiosulphate solution in an atmosphere of carbon dioxide. G. W. Robinson.

Detection of iron, manganese, and chromium without the use of nitric acid. G. G. Longinescu and E. Petrescu (Bull. Chim. pur. appl., 1924, **27**, 1—3 pp.; from Chem. Zentr., 1925, II, 487—488).—The sulphides of the hydrogen sulphide group are dissolved in 4% hydrochloric acid. The insoluble residue is removed by filtration and the hydrogen sulphide by boiling, a portion of the solution being tested for iron. After addition of concentrated ferric chloride solution, the metals present are precipitated as hydroxides by addition of sodium hydroxide solution, aluminium and zinc remaining in solution as aluminates and zincates, respectively. Chromium is detected in a small amount of the precipitate by boiling with a little (2 c.c.) sodium hypochlorite solution, whereby a yellow coloration due to sodium chromate is obtained. Manganese may be detected in another portion of the precipitate by boiling for a few minutes with 10 c.c. of sodium hypochlorite solution, when a pink coloration due to sodium permanganate is obtained, changing to green after filtration. With excess of sodium hypochlorite, sodium ferrate may be formed, but the violet coloration due to it disappears on acidifying with acetic acid. The preliminary addition of ferric chloride facilitates the separation of the hydroxides.

G. W. Robinson.

Use of uranous sulphate in volumetric analysis. G. Vortmann and F. Binder (Z. anal. Chem., 1925, **67**, 269—276).—Uranous sulphate acts as a mild reducing agent and at the same time gives a solution that is stable in the air and is not oxidised by hydrogen peroxide or by iodine. Ferric salts are readily reduced on warming to ferrous, whilst sexavalent molybdenum is unaffected. The solution of uranous sulphate is prepared by warming a solution of 50 g. of uranyl sulphate in 200 c.c. of water and 50 c.c. of sulphuric acid with granulated zinc on the water-bath for 40 min.; the solution is filtered and diluted to 0·1*M* for use. Iron is determined by adding hydrochloric acid and 10 drops of 10% potassium thiocyanate solution to the ferric chloride solution, heating to 60°, and titrating with uranous sulphate until the red colour disappears. The oxidising power of a sample of manganese dioxide is determined by heating it with hydrochloric acid and an excess of uranous sulphate in an atmosphere of carbon dioxide and titrating the excess with a standard solution of ferric chloride. A similar procedure serves for the determination of chloric acid and of chromic acid. Manganese dioxide and nitric acid may be determined indirectly by allowing them to oxidise ferrous sulphate in acid solution and then titrating the ferric salt formed with uranous sulphate. A. R. Powell.

Separation of iron and aluminium from zirconium. R. Lessnig (Z. anal. Chem., 1925, **67**, 341—352).—The solution of the chlorides or nitrates of the three elements is treated with 2 g. of ammonium chloride and with dilute ammonia until the precipitated hydroxides just flocculate; 100 c.c. of a cold saturated solution of ammonium carbonate are added, and the solution is diluted to 400 c.c., heated gently over a small flame to 70—80°, and maintained at that temperature for 10 min. or until the precipitate flocculates. The zirconium hydroxide first precipitated redissolves in the ammonium carbonate, leaving the iron and aluminium hydroxides in a dense, readily filtered form. For complete separation, the precipitate is collected, washed with hot water, redissolved in hydrochloric acid, and the process repeated. The combined filtrates are boiled to decompose the ammonium carbonate, acidified with hydrochloric acid, evaporated to about 200 c.c., and treated with ammonia (free from carbonate) at 50° to obtain zirconium hydroxide, which is collected, washed with hot water, ignited wet at 1000°, and weighed as ZrO_2. Thorium, if present, accompanies the zirconium and must subsequently be separated by means of oxalic acid. The presence of titanium interferes with the separation, part of the titanium remaining with the zirconium and the remainder accompanying the iron. A. R. Powell.

Reaction of cobalt. L. MINDALEV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 57—59; from Chem. Zentr., 1925, II, 419).—Solutions of cobaltous salts give with potassium ferrocyanide in the presence of ammonia a red coloration, which is perceptible even with 0·00005*N*-solutions. Nickel does not interfere with the reaction, provided the ratio of cobalt to nickel is not less than 1 : 200. In order to avoid the effect of the blue nickel ammonium compound, the solution, after addition of ammonia, is diluted until faintly blue and the potassium ferrocyanide solution is added. When concentrated solutions are precipitated with potassium ferrocyanide, the presence of cobalt is shown by the red colour of the precipitate and of the filtrate.

G. W. ROBINSON.

Determination of bismuth and its separation from lead and other metals by hydrolysis. L. MOSER and W. MAXYMOWICZ (Z. anal. Chem., 1925, **67**, 248—256).—For the separation of bismuth from zinc, copper, cadmium, and lead, the nitrate solution, which must contain only small amounts of chlorides or ammonium salts, is treated with a dilute solution of sodium carbonate until a slight permanent turbidity remains. This is discharged with a few drops of nitric acid, 2 g. of sodium bromate are added, and the solution is heated to boiling, more nitric acid being added if a precipitate forms. A 10% solution of sodium bromide is then added slowly, while boiling is continued until no further precipitate forms and the bulk of the liberated bromine is expelled. The basic bismuth bromide thus produced is usually contaminated with a little lead if that metal is present in the original solution; it should therefore be redissolved in dilute nitric acid and precipitation repeated as before. Alternatively, the nitric acid solution of the precipitate is nearly neutralised with sodium carbonate, avoiding a precipitate, and the bismuth precipitated as phosphate by the addition of ammonium phosphate. The bromate–bromide hydrolysis of bismuth salts provides a delicate test for the presence of bismuth in a solution, a marked turbidity being obtained in solutions in which hydrogen sulphide produces little or no coloration.

A. R. POWELL.

Production of thin Wollaston wires. R. SUHRMANN and K. CLUSIUS (Physikal. Z., 1925, **26**, 913).—A thin piece of platinum foil is mounted on a glass frame and three fragments of shellac are fastened on to the foil. The wire is imbedded in the shellac and the whole immersed in potassium cyanide. Satisfactory wires 0·002 mm. thick are obtained on electrolysis.

R. A. MORTON.

Laboratory pump for the circulation of gases. W. FRANCIS.—See B., 1926, 111.

Silica to glass and to metal joints. L. J. BUTTOLPH (J. Opt. Soc. Amer., 1925, **11**, 549—557).—The various methods which have been proposed for the making of metal in-leads through silica are discussed. Among them are (*a*) a ground-in tapered "invar" pin, mercury-sealed, for temperatures up to 200° only; (*b*) a platinum tube sealed, either directly or with a flux, into the silica; (*c*) a tungsten wire, which is sealed into a silica capillary, and the joint made air-tight with either mercury or lead; (*d*) molybdenum or tungsten wires, which may be sealed directly into silica, in a vacuum, if of diameter not exceeding 0·001 in. Glass to silica seals may be made by the usual graded joint, or by a joint in which silver chloride is used as a cement.

S. BARRATT.

Gallium-in-quartz thermometer graduated to 1000°. S. BOYER.—See B., 1926, 79.

Measurement of very low temperatures. XXXIII. Comparison of the constant volume hydrogen and helium thermometers with various zero-point pressures. F. P. G. A. J. VAN AGT and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 693—700).—Data already obtained (cf. p. 234) are used to compare the hydrogen and helium thermometer scales with each other and with different zero-point pressures, the corresponding temperatures on the Centigrade scale being calculated and tabulated. The differences between the hydrogen and helium scales, for the same density, increase with decreasing temperature, but at each temperature they decrease to zero proportionately with the zero-point pressure.

J. W. BAKER.

Simple heating apparatus. H. TER MEULEN (Chem. Weekblad, 1926, **23**, 113).—Heating may be very economically and efficiently effected by use of a small asbestos box, having a small opening for the gas flame in the bottom, and two or more larger openings in the cover for crucibles, dishes, etc. The flame is prevented from impinging directly on the vessels to be heated by a small piece of bent asbestos placed above it.

S. I. LEVY.

Light filter for polarimetry. N. SCHOORL (Chem. Weekblad, 1926, **23**, 113—114; cf. this vol., 142).—The filter previously described is accurate to 0·1° in rotations of 10—15°, but should not be used for higher rotations. It does not give a monochromatic light, but the black point coincides with that given by sodium light within these limits.

S. I. LEVY.

Distillation of mercury containing gold. E. H. RIESENFELD and W. HAASE (Ber., 1925, **58**, [*B*], 2828—2834).—Two forms of apparatus are described for the distillation of mercury containing gold. The first consists of a Wetzel flask connected to a removable receiver from which a thick-walled rubber tube leads to a Volmer–Langmuir combination. Between the two parts is placed a vessel cooled with liquid air, which prevents mercury vapour from the pump diffusing back to the distillate. Distillation takes place at the rate of about 150 g. per hour; the temperature of the mercury vapour in the upper part of the flask is 70—80°, the pressure being therefore less than 0·1 mm. of mercury. The second form consists of a large flask connected with a mercury reservoir. The vapours pass from the flask through a porous glass filter placed parallel to the vertical axis of the flask. Under these conditions it is considered that spurting is impossible. Partly completed experiments establish definitely that gold volatilises with mercury during the distillation of auriferous mercury. Hence, a valid proof of the

conversion of mercury into gold has not been established (cf. Miethe and Stammreich, A., 1924, ii, 874; also Naturwiss., 1924, **12**, 597, 1211).

The determination of minute amounts of gold in mercury is effected by dissolving a large quantity of the sample in nitric acid (1 : 4) until only 1—2 c.c. remains. It is essential that the warm mixture should be agitated continuously, so that mercurous nitrate is present in the solution, whereby any dissolved gold compound is reduced to the metal which passes back to the mercury. The residual amalgam is dissolved in dilute nitric acid in a specially designed quartz filter and the residual gold is ignited and weighed on a micro-balance. H. WREN.

Dewar flasks in physical chemistry laboratory exercises. A. C. GRUBB (Ind. Eng. Chem., 1926, **18**, 163).—Errors in the determination of heats of neutralisation may be considerably lessened by using a Dewar flask as calorimeter with an inner tube containing one of the reagents in a thin bulb blown at the end. At the right moment the bulb is broken by means of the projecting end of the glass stirrer, and the maximum temperature change quickly ascertained. Only one thermometer is necessary.

D. G. HEWER.

Pipettes for potash work. C. M. BIBLE (Ind. Eng. Chem., 1926, **18**, 143).—When making frequent determinations of potassium as chloroplatinate the use of pipettes transferring 19·38 c.c. for 20% K_2O and above, 38·76 c.c. for 4—20%, and 58·14 c.c. for less than 4% is convenient. D. G. HEWER.

Alchemical nomenclature. E. J. HOLMYARD (Nature, 1926, **117**, 155—156).—The Arabic alchemical names for iron, copper, tin, lead, mercury, sal ammoniac, and sulphur, as given in the Dresden and British Museum manuscripts (cf. Wiedemann and Ruska, Sitzungsber. Phys.-Med. Soz. Erlangen, 1924, **56**, 17), are compared and discussed.

A. A. ELDRIDGE.

Mineralogical Chemistry.

Iron coloration in rocks and minerals. G. R. MACCARTHY (J. Elisha Mitchell Sci. Soc., 1925, **41**, 135—137).—Ferrous compounds occurring in rocks and soils are nearly or quite colourless; ferric compounds are brown, red, or yellow. Hydrated ferroso-ferric compounds are blue; the black colour of certain iron minerals may be due to dehydration of ferroso-ferric compounds. Mixtures of ferroso-ferric and ferric compounds are purple or green, with large and small proportions, respectively, of the latter.

CHEMICAL ABSTRACTS.

Deposition of native copper from ascending solutions. R. C. WELLS (U.S. Geol. Surv. Bull., 1925, No. 778, 1—69).—An attempt to derive a satisfactory theory to account for the deposition of native copper, with special reference to the Lake Superior district. A large number of experiments have been carried out to examine the probable equilibrium and solubility relationships involved in the dissolution, transportation, and, finally, precipitation of copper. From the results of these experiments and from considerations of existing data, four possibilities are suggested: (i) hot rising solutions carrying cuprous sulphate are gradually cooled, thereby depositing the metal; (ii) solutions of cuprous chloride in concentrated brines deposit the metal on dilution; (iii) hot acid solutions carrying cuprous sulphide meet with ferric oxide, when a number of rather complex reactions occur involving the formation of ferrous, cuprous, and cupric salts and the deposition of metallic copper, either at once or upon subsequent cooling or dilution; (iv) the fourth theory is to some extent the opposite of the preceding, in that it involves the reduction of copper compounds by ferrous iron. The first two theories ignore the specific nature of the gangue or the rocks encountered.

J. S. CARTER.

Micas from the limestone contact at Mansjö Mtn., Sweden. H. VON ECKERMANN (Tsch. Min. Petr. Mitt., 1925, **38**, 277—287).—Analyses, with density and optical determinations, are given of a biotite (I) and four phlogopites (II—V) collected from different points in the contact-zone of pegmatite intrusive into eulysite and limestone. The ratios deduced from the analyses are as follows and lead to no general formula:

	H_2O.	K_2O.	Al_2O_3.	(Fe,Mg)O.	SiO_2.	Sp. gr.
I.	1·90	1·01	1·94	5·12	6	3·085
II.	1·74	1·04	1·18	6·41	6	2·831
III.	2·12	1·10	1·24	6·10	6	2·819
IV.	1·55	0·78	1·35	5·84	6	2·869
V.	1·95	0·98	1·33	7·00	6	2·737

The results are discussed in connexion with the metamorphic reaction $Fe_3O_4+CO \rightleftharpoons 3FeO+CO_2$. The "oxidation degree" (ratio Fe_2O_3/FeO) varies in the five analyses from 0·0425 to 6·9100.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.
I.	34·03	2·74	18·46	2·01	21·54	8·06	0·50
II.	40·95	—	13·14	0·85	1·71	28·03	0·40
III.	40·80	0·05	13·16	1·84	2·16	26·72	0·46
IV.	40·47	2·44	14·66	2·42	0·65	26·64	0·50
V.*	39·41	0·29	13·44	2·27	0·15	29·18	1·87

	Na_2O.	K_2O.	Li_2O.	F.	H_2O.	Total.
I.	0·34	8·88	0·04	0·25	3·29	100·03
II.	0·96	10·25	—	3·15	2·06	100·17
III.	2·44	7·95	—	2·89	2·95	100·20
IV.	0·67	7·57	0·11	2·44	2·09	100·61
V.*	0·58	7·59	0·20	1·55	2·33	99·65

* Also BaO 1·28, Cl 0·21.

L. J. SPENCER.

Calcite in regular growth on ankerite and chalybite. A. DE KLERK and V. GOLDSCHMIDT (Tsch. Min. Petr. Mitt., 1925, **38**, 159—164).—Specimens from the Simplon tunnel show small crystals of clear calcite in regular growth on yellowish-white

ankerite and on chalybite. The ankerite has angle ρ 43° 54′, *d* 3·06, ε 1·5264, ω 1·7194, and gave analysis I. This agrees with the formula $Ca_2Mg(Fe,Mn)C_4O_{12}$, suggesting that the formula of dolomite should be $2CaMgC_2O_6$, and that of calcite $4CaCO_3$ or $Ca_4C_4O_{12}$. The crystals of calcite gave analysis II.

	$CaCO_3$.	$MgCO_3$.	$FeCO_3$.	$MnCO_3$.	Insol.
I.	50·81	22·65	24·44	1·10	0·43
II.	97·55	0·38	0·88	—	—

L. J. SPENCER.

Andesine from Trifail, Yugoslavia. A. HIMMELBAUER (Tsch. Min. Petr. Mitt., 1925, **38**, 610—623).—A detailed crystallographic description is given of small crystals of andesine found singly in lignite and clay at Trifail (formerly in southern Styria). They are clear and colourless, but enclose some brown glass. Analysis by N. Sahlbom gave

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.
57·30	26·87	0·82	0·06	8·64

Na_2O.	K_2O.	H_2O (at 105°).	Total.
6·02	0·62	0·12	100·45

also MnO trace, but no TiO_2 or BaO. Deducting impurities, this corresponds with $Ab_{53·7}An_{42·7}Or_{3·6}$. *d* 2·675. New crystallographic elements are deduced. The angle (010) : (001)=86° 4′, although lying between the corresponding angle of albite and anorthite, varies somewhat from previous values, the difference being perhaps due to the presence of the orthoclase molecule. L. J. SPENCER.

Hornblendes from Lower Austria. A. MARCHET (Tsch. Min. Petr. Mitt., 1925, **38**, 494—507).—The hornblendes occurring as constituents of the crystalline schists, mostly amphibolites, of the Waldviertel in Lower Austria (A., 1925, ii, 997) are grouped as : (1) pale-coloured hornblendes with relatively low refraction; (2) green hornblendes; and (3) brown hornblendes. Optical data were determined for eighteen of these, but only two could be isolated satisfactorily for chemical analysis, these being green hornblendes from amphibolites. From analysis I, 0·66% sphene and 0·08% pyrite have been deducted; and from II, 2·06% magnetite. The composition of some others was calculated from the analyses of the rocks. For the green hornblendes it is shown that with increasing ferrous oxide, and corresponding decrease in magnesia, there is an increase in refractive index and decrease in the optic axial angle. The brown hornblendes do not fall into this series.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.
I.	42·80	1·59	11·31	4·13	14·61	0·17
II.	42·78	2·93	12·32	1·54	14·15	0·15

	MgO.	CaO.	Na_2O.	K_2O.	H_2O.
I.	8·81	13·88	1·11	1·08	0·51
II.	9·42	13·12	1·63	1·25	0·71

			I.	II.		Brown.	
a′ on (110)	...	1·660	1·666	1·672	1·671	1·680	1·673	1·652
$2V_a$	.....	86°	78°	70°	66°	46½°	85¾°	87½°
FeO	.....	10·7	11·4	14·6	14·2	15·0	10·6	11·5
MgO	.....	11·7	10·2	8·8	9·4	4·6	11·0	9·6

L. J. SPENCER.

Crystallographic investigation of tscheffkinite. A. K. BOLDYREV (Bull. Russ. Acad. Sci., 1924, 257—288).—The results of chemical, crystallographic, and etching investigation of crystals of tscheffkinite from the Ilmensky Mountains of the Ural range indicate that the habit, the combination of faces, and the corresponding angles are similar to those of crystals of orthite, but the differences are sufficiently great to show that the two minerals are not isomorphous, but morphotropic. The composition of tscheffkinite is $Ce_2CaSi_3O_{10}$, whereas that of orthite may be represented by $Al_2CaSi_3O_{10},AlCaHO_3$.

T. H. POPE.

Chemical composition of tscheffkinite. L. E. KAUFMAN (Bull. Russ. Acad. Sci., 1924, 315—320).—The results of analysis of tscheffkinite from the Ilmensky Mountains are :

SiO_2.	ThO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Y_2O_3.	Ce_2O_3.	La_2O_3 etc.
19·22	0·80	17·22	3·86	4·56	1·25	18·58	22·70

FeO.	MnO.	CaO.	H_2O.	K_2O.	Na_2O.	Total.
7·24	1·34	3·34	0·67	0·37	0·42	101·57

These results correspond with the formula,

$$(Ca,Fe)_2(Ce_2,Al_2,Fe_2)_2(Si,Ti)_4O_{16},SiO_2.$$

T. H. POPE.

[Swedenborgite], a new mineral from Långban. G. AMINOFF (Z. Kryst., 1924, **60**, 262—274).—The mineral, named " swedenborgite," contains

Sb_2O_5.	P_2O_5.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
54·17	0·23	34·72	0·94	0·52	8·50	0·21	0·39	99·68

corresponding with the formula $Na_2O,2Al_2O_3,Sb_2O_5$ The crystals are hexagonal, c=1·6309; uniaxial, negative, ω=1·7724, ε=1·7700. CHEMICAL ABSTRACTS.

Synthesis and modes of occurrence of scapolites. W. EITEL (Tsch. Min. Petr. Mitt., 1925, **38**, 1—38).—A review is given of the modes of occurrence of scapolite minerals and of their possible genesis. They are most frequently found in contact-metamorphic limestones or where limestone has been assimilated by igneous magmas, with evidence in some cases of pneumatolytic action. Attempts to synthetise these minerals have sometimes resulted in the formation of meionite or of products resembling this, but marialite has not been obtained artificially. The complex system Na_2CO_3–$CaCO_3$–$Na_2Al_2Si_2O_8$ (nepheline)–$CaAl_2Si_2O_8$ (anorthite) has been studied by fusing in an atmosphere of carbon dioxide under pressure various mixtures of calcium carbonate, sodium carbonate, silica, and alumina (or nepheline and anorthite). With nepheline and carbonates, cancrinite was obtained. Anorthite with calcite yielded a product resembling gehlenite, and with calcium and sodium carbonates a substance resembling meionite. Meionite was also obtained from a fusion of albite and calcium carbonate. L. J. SPENCER.

Some iron-alkali-amphiboles. J. MOROZEWICZ (Tsch. Min. Petr. Mitt., 1925, **38**, 210—222).—The alkali-rocks of the Mariupol district, on the Sea of Azov in Ukraine, contain amphiboles of peculiar types. *Taramite* (anal. I—II) occurs as short-prismatic, bluish-black crystals in dykes of mariupolite intersecting the alkali-granite of the Wali-tarama valley. *Fluotaramite* (anal. III—V) occurs as long-acicular, greenish-black crystals in dykes of syenite-pegmatite. In both the plane of the optic axes is

perpendicular to the plane of symmetry, but of different orientation. The pleochroism is intense. Taramite is remarkable in being readily and completely decomposed by hot hydrochloric acid. It is further remarkable in being low in silica and high in iron; the water is also high, although the mineral is perfectly fresh. The densities of the materials analysed are 3·4761, 3·4389, 3·2308, 3·3176, and 3·2671, respectively; and the m. p. 1080°, 1050°, 1080°, 1000°, and 1085° (±10°), respectively. Metasilicate formulæ, on the same lines as the general formula of Penfield and Stanley (A., 1907, ii, 102), are given for each analysis. For

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.
I.	37·51	0·73	8·50	11·41	23·21	1·70	0·56
II.	38·81	1·07	9·23	11·94	21·72	0·64	0·47
III.	52·59	0·91	1·64	7·69	11·80	0·60	9·32
IV.	50·62	1·03	1·67	12·40	8·63	5·35	5·70
V.	50·00	0·46	3·46	10·36	12·46	0·36	8·27

	CaO.	Na_2O.	K_2O.	F.	H_2O (+105°).	H_2O (−105°).	Total (less O for F).
I.	7·91	3·79	2·10	0·14	2·32	0·33	100·15
II.	6·87	4·76	2·24	0·13	2·19	0·18	100·25
III.	3·41	6·79	2·06	2·05	1·44	0·34	99·78
IV.	0·50	8·05	2·94	2·40	1·32	0·23	99·83
V.	3·55	6·15	2·14	1·75	1·64	0·21	100·07

example, from analysis I, 22·50 mol.% $[(OH,F)_2R_2O]^{II}SiO_3$, 8·60 $[Na_2(Mg,Fe)R_2O_4]^{II}SiO_3$, 5·64 $[(OH,F)_2Mg_2]^{II}SiO_3$, 63·26 $M^{II}SiO_3$, where R=Al, Fe^{III}, and M=Fe^{II}, Mn^{II}, Mg, Ca, K_2, Na_2, H_2. In fluotaramite the glaucophane–riebeckite molecule $Na_2R_2(SiO_3)_4$ is present in large amount; for example, from analysis V, 20·00 mol.% $[(OH,F)_2Mg_2]^{II}SiO_3$, 36·30 $Na_2R_2(SiO_3)_4$, 43·70 $Me^{II}SiO_3$. Taramite shows some analogies to hastingsite, and fluotaramite to crossite. L. J. SPENCER.

Composition of pitchblendes. G. KIRSCH (Tsch. Min. Petr. Mitt., 1925, **38**, 223—228).—The amounts of UO_3, UO_2, PbO, ThO_2 shown in published analyses of pitchblende are tabulated; and the ratio UO_2/UO_3 (also of UO_2+ThO_2/UO_3) is deduced for the original mineral after making allowance for the transformation $2UO_2 \rightarrow PbO+UO_3$. The ratios then range from 11·45 for the purest crystallised mineral from Branchville, Connecticut, to 0·4 for a pitchblende from Australia (1·00 from Joachimsthal). It is suggested that there are here two distinct minerals—one an oxide (UO_2) and the other an oxygen salt (uranate U_2O_5 or U_3O_8), but that they are now in part represented by "radioactive transformation pseudomorphs." For the original cubic oxide the name ulrichite is proposed, bröggerite and cleveite being regarded as altered varieties containing thorium or rare-earths. The massive uranate, pitchblende, which sometimes shows nodular surfaces, is cryptocrystalline and perhaps orthorhombic. L. J. SPENCER.

Variation of ozone in the atmosphere. H. BUISSON and C. JAUSSERAN (Compt. rend., 1926, **182**, 232—234).—Previous determinations of the mean amount of ozone in the atmosphere (A., 1925, ii, 627) have been repeated with the view of recording daily variations. Experiments extending over 9 weeks show a difference between the two extreme values amounting to 15% of that previously obtained. This value (0·3 cm., expressed as the thickness of a layer of pure ozone) has been confirmed by a method in which the absorption of sunlight by ozone is expressed as a function of the sun's altitude. These variations cannot be correlated with atmospheric changes. J. GRANT.

Nitrogen compounds in rain and snow. F. T. SHUTT and B. HEDLEY (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 1—10).—The results of investigations carried out at the Dominion Experimental Farm, Ottawa, are summarised. During the period 1907—1924 every fall of rain and snow was analysed, the determinations comprising nitrogen present as free ammonia, albuminoid ammonia, and as nitrates and nitrites. Snow is decidedly poorer in nitrogen compounds than rain. It is shown that rain and snow supply annually, per acre, nitrogen in available forms equivalent to an application per acre of 44 lb. of commercial sodium nitrate. J. S. CARTER.

Organic Chemistry.

Catalytic formation of petroleum hydrocarbons from fats. J. MARCUSSON and W. BAUERSCHÄFER.—See B., 1926, 117.

Action of anhydrous aluminium chloride on nonane and on *cyclo*pentane. M. V. COX (Bull. Soc. chim., 1925, [iv], **37**, 1549—1553).—When nonane is heated for 8 hrs. with 30% of anhydrous aluminium chloride, the resulting butane corresponds with a yield of 1 mol. for each mol. of nonane (cf. Grignard and Stratford, A., 1924, i, 841). Pentene is formed simultaneously; this is transformed into *cyclo*pentane under the influence of the chloride. Under the conditions of experiment, *cyclo*pentane is stable in presence of aluminium chloride. H. J. EVANS.

Detection and determination of gaseous olefines. I. Action on olefines of chlorine dissolved in carbon tetrachloride. V. SOROKIN and A. BELIKOV (Russian J. Chem. Ind., 1925, **1**, [3], 28—29).—Even when bubbled slowly through a 14·5% solution of chlorine in carbon tetrachloride, ethylene, propylene, and *iso*butylene are not absorbed quantitatively, whereas the absorption of butadiene is almost quantitative, the error being 2·5—5%. Thus this method of determining butadiene gives appreciably more accurate results than the bromination method. Under the above conditions, propylene yields a mixture of αβ-dichloropropane, with a product, b. p. 142—148°, which was not investigated further, and *iso*butylene gives αβ-dichloro-β-methylpropane and αγ-di-

chloro-β-methylpropene (cf. Pogorshelski, A., 1905, i, 165). T. H. POPE.

Preparation of ethyl chloride from ethylene. CHEM. FABR. VORM. WEILER-TER MEER.—See B., 1926, 108.

Preparation of αα-trichloro- and ααα-tetrachloro-ethane. H. J. PRINS (Rec. trav. chim., 1926, **45**, 80—81).—αα-Trichloroethane and ααα-tetrachloroethane are obtained in 73% and 64% yields, respectively, by passing dry chlorine into *s*-dichloroethane in the presence of anhydrous aluminium chloride at 20—40°. J. W. BAKER.

Action of sulphuric and nitric acids on dichloro- and chloro-methyl ether. J. HOUBEN and E. PFANKUCH (Ber., 1926, **59**, [*B*], 86—89).—Chloromethyl ether is converted by nitric and sulphuric acids into nitromethoxymethyl nitrate, b. p. 48°/15 mm., d^{12} 1·5005, $n_D^{12\cdot4}$ 1·43276, which is hydrolysed by alcoholic sodium ethoxide to an equimolecular mixture of sodium nitrite and nitrate, without production of nitromethane; the substance is identical with that obtained by Moreschi (Atti R. Accad. Lincei, 1922, [v], **28**, 277) from dichloromethyl ether. Its production is invariably accompanied by that of *nitronitroxymethylal*, $NO_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}NO_2$, b. p. 88—89°/9 mm., which, under conditions which have not been standardised, may become the main product of the change. Both compounds are violently explosive. H. WREN.

Dehydration of aqueous alcohol. J. BARBAUDY.—See B., 1926, 107.

Magnesium alkoxides and their applications in the synthesis of alcohols. II. *iso*Butyl and *iso*amyl alcohols. A. TERENTIEV (Bull. Soc. chim., 1925, [iv], **37**, 1553—1557; cf. A., 1925, i, 110).—Condensation of *iso*butyl alcohol with magnesium *iso*butoxide, prepared by the action of magnesium on the alcohol, results in the formation of di*iso*propyl ketone, *iso*butyl butyrate, *iso*butaldehyde, *iso*butylene, and hydrogen, together with an octyl alcohol, b. p. 164—167°, d_4^{20} 0·8232, n_D^{20} 1·4236, to which the formula $CHMe_2{\cdot}CH_2{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$ is assigned, and an octyl *iso*butyrate, b. p. 199—202°/747 mm., d_4^{20} 0·8545, n_D^{20} 1·4208. The author adopts the views put forward by Tischtschenko and Grigorieff (A., 1907, i, 284) as regards the mechanism of the reactions which occur.

[With A. BOLOTINE.]—Similar experiments with amyl alcohol and magnesium show that the reaction follows a normal course, di*iso*amyl alcohol being formed. H. J. EVANS.

Ketonic scission of tertiary alcohols. V. GRIGNARD and F. CHAMBRET (Compt. rend., 1926, **182**, 299—302; cf. A., 1923, i, 739; 1925, i, 111).—Tertiary alcohols containing an unsaturated linking attached to the alcoholic carbon atom are readily dehydrated on heating at atmospheric pressure; when heated in a vacuum there is little dehydration, but a hydrocarbon and a ketone are formed: $CR'R''R'''{\cdot}OH = R'{\cdot}CO{\cdot}R'' + R'''H$. Saturated tertiary alcohols and those containing an unsaturated linking in a position other than adjacent to the hydroxyl group are less readily dehydrated, but when heated at 400—500° in a vacuum in the presence of glass wool yields of 20—90% of ketones are formed. From the results detailed below, it is found that groups split off as hydrocarbons from tertiary alcohols in the following order of increasing readiness: Ph < Me < ·CH:CHR = ·CH_2·CH_2·CH:CHR < benzyl and aliphatic groups other than those mentioned < ·CH_2·CH:CHR. β-Phenyl-Δ$^{\epsilon}$-hepten-β-ol yields acetophenone, β-benzyl-Δ$^{\epsilon}$-hepten-β-ol gives Δ$^{\epsilon}$-hepten-β-one, δ-methyl-Δ$^{\alpha}$-hepten-δ-ol gives methyl propyl ketone, δ-benzyl-Δ$^{\alpha}$-penten-δ-ol gives phenylacetone, δ-phenyl-Δ$^{\alpha}$-penten-δ-ol gives acetophenone, δ-methyl-Δ$^{\beta}$-octen-δ-ol gives methyl butyl ketone, δ-benzyl-Δ$^{\beta}$-penten-δ-ol gives benzyl methyl ketone, δ-phenyl-Δ$^{\beta}$-penten-δ-ol gives acetophenone, ε-methyl-Δ$^{\alpha}$-nonen-ε-ol gives allylacetone, ε-benzyl-Δ$^{\alpha}$-hexen-ε-ol gives Δ$^{\alpha}$-hexen-ε-one, ε-phenyl-Δ$^{\alpha}$-hexen-ε-ol gives acetophenone, ζ-methyl-Δ$^{\beta}$-decen-ζ-ol gives Δ$^{\beta}$-hepten-ζ-one, ζ-benzyl-Δ -hepten-ζ-ol gives Δ$^{\beta}$-hepten-ζ-one, ζ-phenyl-Δ$^{\beta}$-hepten-ζ-ol gives acetophenone, ε-methylnonan-ε-ol gives methyl butyl ketone, β-phenylpropan-β-ol gives acetophenone, β-benzylpropan-β-ol gives acetone, δ-ethyloctan-δ-ol gives a mixture of ketones, ζ-methyl-Δ$^{\delta}$-nonen-ζ-ol, and βδ-dimethyl-Δ$^{\epsilon}$-nonen-δ-ol give butylideneacetone. Δ$^{\epsilon}$-*Hepten*-β-*one*, m. p. 70—72°, gradually changing into a *dimeride*, m. p. 100—103°, is prepared by condensation of heptaldehyde and acetone in presence of sodium hydroxide solution. The preparation of many of the alcohols is described by Chambret (Diss., Lyon, 1925). L. F. HEWITT.

Preparation of ethylene glycol from ethylene oxide. CHEM. FABR. KALK.—See B., 1926, 108.

Higher fatty acids of arachis oil. W. D. COHEN.—See B., 1926, 98.

Saturated acids of highest m. p. from arachis oil [lignoceric and hexacosoic acids]. D. HOLDE and N. N. GODBOLE (Ber., 1926, **59**, [*B*], 36—40).—Arachis oil is hydrolysed and crude arachidic acid is isolated from the free fatty acids by crystallisation from acetone and alcohol. The crude acid is distilled under diminished pressure, and the residue, after repeated crystallisation from benzene followed by fractional precipitation with lithium acetate in the presence of chloroform and alcohol, yields a hexacosoic acid, $C_{26}H_{52}O_2$, m. p. 79°, possibly identical with cerotic acid from beeswax (cf. Kiesel, A., 1925, i, 1035). The presence of this acid has not been suspected previously and accounts for the difficulties involved in the isolation of homogeneous lignoceric acid and the wide discrepancies with regard to the physical constants of the latter (cf. Meyer, Brod, and Soyka, A., 1913, i, 1151; Heiduschka and Pyriki, A., 1925, i, 229). The distillates from the crude arachidic acid (above) are converted into their methyl esters, which are fractionated in a high vacuum. The least volatile portion, b. p. 204—211°/0·4—0·5 mm., m. p. 55·7—56·5°, is hydrolysed and the resulting fatty acid is crystallised repeatedly from benzene and, finally, fractionally precipitated with lithium acetate, whereby lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80·5—81°, is isolated.

H. WREN.

Additive products of iodine bromide and hypoiodous acid with unsaturated compounds. II. D. HOLDE and A. GORGAS (Ber., 1926, **59**, [*B*], 113—115; cf. A., 1925, i, 882).—The yields of iodobromo-acids obtained by Hanus' method for the determination of the iodine number of unsaturated acids approach the theoretical values much more closely when chloroform is replaced by glacial acetic acid. Erucic acid thus affords bromoiodobehenic acid, m. p. 37—38°, in 97% yield; *calcium bromoiodobehenate* has m. p. 136° (decomp.) after darkening at 120°. *Calcium dibromodi-iodostearate*, m. p. 115° (decomp.) after darkening at 100°, is described. *Calcium iodohydroxystearate*, m. p. 190—194° (decomp.), *calcium iodohydroxybehenate*, m. p. 184—188° (decomp.), and *calcium di-iododihydroxystearate* have been prepared. H. WREN.

Synthesis of some *cis*-ethylenic compounds. M. BOURGUEL and J. YVON (Compt. rend., 1926, **182**, 224—225; cf. A., 1925, i, 883).—Δ^{α}-Pentinenoic acid when hydrogenated in presence of colloidal palladium yields a Δ^{α}-*pentenoic acid*, b. p. 88—88·5°/15 mm., 184—185°/760 mm. Δ^{α}-Hexinenoic acid when reduced in presence of colloidal palladium yields a Δ^{α}-*hexenoic acid*, b. p. 101·5—102·5°/15 mm., 201—202°/760 mm. Since these acids are different from the stereoisomeric acids already known, and these latter probably have the *trans*-configuration (Auwers, A., 1923, i, 746), it is probable that the acids here described have the *cis*-configuration, a conclusion which is in agreement with the b. p. of members of the crotonic and *iso*crotonic acid series. Reduction of phenylacetylenol in presence of colloidal palladium yields an *allocinnamyl alcohol*, b. p. 120·5°/13 mm. (*phenylurethane*, m. p. 89·5°), thus differing from ordinary cinnamyl alcohol. Support is thus found for the generalisation that partial reduction of acetylenic compounds yields *cis*-ethylenic derivatives. L. F. HEWITT.

Fractional dissolution in alcohol of zinc salts of liquid acids derived from linseed oil. G. AGDE (J. pr. Chem., 1926, [ii], **112**, 37—56).—The contention of Erdmann (A., 1911, i, 832) that linoleic acid can be isolated by the fractional extraction with alcohol of the basic zinc salts of the liquid acids obtained by the hydrolysis of linseed oil is not confirmed. Experiments are described involving the use of linseed oil from five different sources and the preparation by a variety of methods of the supposed basic zinc salts of the liquid acids. Although from the later fractions a product is obtained which has the iodine value of α-linoleic acid, this product is shown to be a mixture of linolenic, linoleic, and oleic acids. Analysis of the mixed zinc salts shows that they must be normal and not basic salts (cf. Erdmann, *loc. cit.*). Detailed investigation of the various fractions leads to the conclusion that a separation of the liquid acids cannot be based on the fractional extraction of the zinc salts. R. W. WEST.

Octadecenoic acids. A. GRÜN and W. CZERNY (Ber., 1926, **59**, [*B*], 54—63; cf. Thoms and Deckert, A., 1921, i, 219).—Ethyl λ-hydroxystearate, m. p. 51—51·3° (Thoms and Deckert, m. p. 44°), is most conveniently prepared by incomplete hydrogenation of castor oil in presence of a nickel catalyst at 80°, conversion of the mixture of glycerides into the corresponding ethyl esters, and crystallisation of the latter from light petroleum and acetone. It is converted by β-naphthalenesulphonic acid at 220° (cf. Grün and Ulbrich, A., 1920, i, 518) into a mixture of the stereoisomeric *ethyl* Δ^{λ}-*octadecenoates*, b. p. 184°/0·8 mm., which is also obtained by treating λ-hydroxystearic acid successively with thionyl chloride and ethyl alcohol, followed by repeated distillation of the product under diminished pressure. The crude ester is hydrolysed by alcoholic potassium hydroxide and the liberated acids are separated by crystallisation from light petroleum into Δ^{λ}-*octadecenoic acid* (elaïdic acid form), m. p. 39·7—40·1°, b. p. 196°/1·5 mm., and Δ^{λ}-*octadecenoic acid* (oleic acid form), m. p. 9·8—10·4°, b. p. 196°/1·5 mm. (after purification by the lead salt method). The liquid acid is partly isomerised by treatment with nitric acid (*d* 1·4) and mercury at 25° to the solid acid. Octadecenoic acid is transformed by bromine in the presence of light petroleum into λμ-*dibromooctadecanoic acid*, which could not be caused to crystallise; it is converted by alcoholic potassium hydroxide into *bromo-octadecenoic acid* containing a little octadecinenoic acid. *Ethyl* λμ-*dibromo-octadecanoate* readily loses 1 mol. of hydrogen bromide under the influence of alcoholic potassium hydroxide, affording *ethyl* λ(or μ)-*bromo*-Δ^{λ}-*octadecenoate*, b. p. 193—195°/0·8 mm., whereas drastic treatment with the reagent converts it into Δ^{λ}-*octadecinenoic acid*, m. p. 34·2°. Oxidation of the acetylenic acid by potassium permanganate in alkaline solution affords decane-ακ-dicarboxylic, nonane-αι-dicarboxylic, sebacic, and hexoic acids; heptoic acid does not appear to be formed. Successive oxidation with permanganate and sodium dichromate and sulphuric acid gives decane-ακ-dicarboxylic, hexoic, and valeric acids. Removal of the elements of water from λ-hydroxystearic acid by β-naphthalenesulphonic acid occurs therefore exclusively in such manner as to form the Δ^{λ}-unsaturated acid; the isomeric Δ^{κ}-acid is not formed. H. WREN.

Detection of unsaponifiable matter in marine animal oils. D. HOLDE and A. GORGAS.—See B., 1926, 98.

Oils of chaulmoogra group. E. ANDRÉ.—See B., 1926, 98.

Influence of phosphates on the oxidation of butyric acid with hydrogen peroxide. E. J. WITZEMANN (J. Amer. Chem. Soc., 1926, **48**, 202—208; cf. A., 1922, i, 6).—The oxidation of butyric acid, as the potassium salt, in aqueous solution by hydrogen peroxide at the ordinary temperature in presence of alkali phosphates has been studied. In presence of potassium dihydrogen phosphate, 80·8% of the butyric acid was unoxidised at the end of 10 days, and in presence of sodium dihydrogen phosphate, 83·6% was unoxidised in 19 days. In presence of dipotassium hydrogen phosphate and disodium hydrogen phosphate, 27·9% and 50·4% of the butyric acid was unchanged in 6 and 19 days, respectively.

The dialkali phosphates are thus much more powerful catalysts for this oxidation than the monoalkali salts. The products of the oxidation were acetic acid, acetone, and carbon dioxide, the proportion of acetone in the product being greater in the presence of the monoalkali phosphates. F. G. WILLSON.

Simultaneous oxidation of dextrose and butyric acid. E. J. WITZEMANN (J. Amer. Chem. Soc., 1926, **48**, 208—210; cf. preceding abstract).—When dextrose and potassium butyrate are treated, in the same solution, with hydrogen peroxide in presence of sodium or potassium hydrogen phosphate, the oxidation of the butyrate (*loc. cit.*) is not influenced by the presence of dextrose, the oxidation of the two substances proceeding independently. The amount of acetone produced from the butyrate was also unchanged, no antiketogenetic effect, analogous to that ascribed to the oxidation of dextrose in the body, being observed. F. G. WILLSON.

Oxidation of α- and β-hydroxybutyric acids with hydrogen peroxide. E. J. WITZEMANN (J. Amer. Chem. Soc., 1926, **48**, 211—222).—*l*-β-Hydroxybutyric acid is practically unoxidised by hydrogen peroxide in 5 days at 37° in dilute aqueous solution in presence of mono- and di-sodium or potassium phosphates, whilst *dl*-α-hydroxybutyric acid undergoes considerable oxidation under these conditions. The consumption of permanganate in the determination of these compounds in aqueous solution indicates that the two acids are both oxidised according to the equation $C_4H_8O_3+5O=CH_3{\cdot}CO_2H+2CO_2+2H_2O$. Whilst lactic acid is oxidised by permanganate in neutral solution with formation, almost exclusively, of acetic acid, the analogous production of propionic acid from α-hydroxybutyric acid was observed in one case only, this acid being generally oxidised by neutral permanganate with loss of two carbon atoms and formation of acetic acid. Propionic acid was also not observed as a product of the action of hydrogen peroxide on α-hydroxybutyric acid. The shortening of the carbon chain by two carbon atoms in the oxidation of the hydroxybutyric acids is ascribed to an enolisation, favoured by increasing concentration of alkali, analogous to that previously observed in the case of pyruvic acid (cf. Witzemann, A., 1920, i, 138). This is in accordance with the greater ease with which α-ketobutyric acid, as compared with the β-derivative (acetoacetic acid), is oxidised with loss of two carbon atoms, as the methylene group in the former contains a more mobile hydrogen than that in the latter. The above results indicate that α-hydroxy- and α-keto-aliphatic acids are to be considered as normal intermediates in oxidative metabolism. F. G. WILLSON.

Hydrogen peroxide as an oxidising agent in acid solution. III. W. H. HATCHER and G. W. HOLDEN (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 11—19).—Glyoxylic acid is most conveniently prepared by the electrolysis of a cold concentrated solution of oxalic acid (Tafel and Friedrichs, A., 1904, i, 849). Any sulphuric acid from the anode liquid is removed by the addition of small quantities of barium oxide, barium acetate being then added to precipitate barium glyoxylate. Treatment with sulphuric acid and evaporation in a vacuum yields the acid, monoclinic, m. p. 98°. The sparingly soluble calcium, silver, and mercurous salts are largely hydrated. The silver salt darkens on exposure to light.

Glyoxylic acid may be titrated with alkali (using phenolphthalein) or potassium permanganate in presence of sulphuric acid. In the latter case, it is inadvisable to heat the solution. The titrated solution contains carbonic and formic acids. Since the volume of *N*-permanganate solution required is exactly double that of the *N*-alkali, the presence of glycollic or oxalic acids may be detected by the ratio of the two titrations.

The bimolecular reaction with hydrogen peroxide in aqueous solution proceeds according to the equation, $CHO{\cdot}CO_2H+H_2O_2=CO_2+H{\cdot}CO_2H+H_2O$. In no case was any oxalic acid detected amongst the reaction products. The rate of reaction is increased in presence of mineral acids. The sodium salt is extremely reactive towards hydrogen peroxide. J. S. CARTER.

Isomeric esters of *p*-phenoxybenzoylacrylic acid. G. P. RICE (J. Amer. Chem. Soc., 1926, **48**, 269—274; cf. A., 1924, i, 1314).—Bromination of *methyl* p-*phenoxybenzoylpropionate*, m. p. 59°, b. p. 252°/16 mm., with subsequent elimination of hydrogen bromide, affords *methyl* p-*phenoxybenzoylacrylate*, as the stable, yellow modification, m. p. 93°. The latter is converted, by exposure to sunlight in saturated benzene solution, into the labile, colourless *isomeride*, m. p. 83°, the reverse change being effected by adding a trace of iodine to the benzene solution. When the yellow modification is exposed as a thin layer of solid to sunlight, it is rapidly converted into a colourless *polymeride*, $C_{34}H_{28}O_8$, m. p. 167°. Treatment of either form of the ester with 2 mols. of semicarbazide hydrochloride in methyl alcohol in presence of sodium acetate affords *methyl* α-*semicarbazido*-β-p-*phenoxybenzoylpropionate*, m. p. 184°, whilst the similar application of 1 mol. of semicarbazide to the yellow isomeride in more dilute methyl-alcoholic solution yields two isomeric *semicarbazones* of the unsaturated ester, m. p. 141° and 150°, after softening in both cases at 75°, respectively. *Ethyl* p-*phenoxybenzoylpropionate*, b. p. 255°/15 mm., affords analogously the yellow form of *ethyl* p-*phenoxybenzoylacrylate*, m. p. 46° [*dibromide*, m. p. 78° (decomp.)]. The colourless *isomeride*, obtained as in the case of the methyl ester, is a liquid. *Ethyl* α-*semicarbazido*-β-p-*phenoxybenzoylpropionate*, m. p. 178°, and two isomeric *semicarbazones* of *ethyl* p-*phenoxybenzoylacrylate*, colourless, m. p. 156°, and yellow, m. p. 85°, are described. p-*Phenoxybenzoylacrylic acid*, m. p. 121°, is produced by condensation of maleic anhydride with diphenyl ether in presence of aluminium chloride. Bromination in glacial acetic acid affords a *dibromide*, m. p. 156° (decomp.), whilst in chloroform an isomeric *dibromide*, m. p. 116—119° (decomp.), is obtained. *p*-Phenoxybenzoylacrylic acid is not changed by exposure to sunlight in benzene solution. The solid material is also unchanged similarly in cold weather, but in hot weather becomes coated with a carrot-

coloured layer. Its esters are not hydrolysed by 10% sodium carbonate solution. When the yellow esters are boiled with concentrated hydrochloric acid for 3 hrs., an acid, probably *α-hydroxy-β-p-phenoxybenzoylpropionic acid*, m. p. 120°, is obtained.

F. G. WILLSON.

Ether-substituted derivatives of ethyl malonate and barbituric acid. A. J. HILL and D. T. KEACH (J. Amer. Chem. Soc., 1926, **48**, 257—262).—The following chloromethyl ethers were prepared by the action of 40% aqueous formaldehyde on the appropriate alcohols in presence of hydrogen chloride (cf. Henry, Bull. Acad. roy. Belg., 1893, [iii], **26**, 629; Favre, A., 1895, i, 14): *chloromethyl* n-*butyl ether*, b. p. 134°/760 mm.; *chloromethyl* iso*butyl ether*, b. p. 120—121°/760 mm.; and *benzyl chloromethyl ether*, b. p. 125°/40 mm. By condensing chloromethyl alkyl ethers with ethyl sodiomalonate, or with ethyl ethylsodiomalonate, in ethereal suspension, the following products were obtained: *ethyl methoxymethylethylmalonate*, b. p. 125—126°/18 mm.; *ethyl ethoxymethylethylmalonate*, b. p. 120—121°/13 mm.; *ethyl propoxymethylethylmalonate*, b. p. 135—140°/15 mm.; *ethyl* n-*butoxymethylethylmalonate*, b. p. 133°/5—6 mm.; *ethyl* iso*butoxymethylethylmalonate*, b. p. 135°/9—10 mm.; *ethyl benzyloxymethylethylmalonate*, b. p. 190—192°/10—11 mm.; *ethyl propoxymethylmalonate*, b. p. 107—108°/2—3 mm.; *ethyl diethoxymethylmalonate*, b. p. 123—125°/7—8 mm.; and *ethyl dipropoxymethylmalonate*, b. p. 124—125°/2—3 mm. The analogous preparation of ethyl dimethoxymethylmalonate was not successful (cf. Kleber, A., 1888, 1056; Simonsen, J.C.S., 1908, **93**, 1780). The above substituted ethyl malonates were condensed with carbamide by means of alcoholic sodium ethoxide, and the following substituted barbituric acids obtained: 5-*methoxymethyl*-5-*ethyl*-, m. p. 184°; 5-*ethoxymethyl*-5-*ethyl*-, m. p. 166°; 5-*propoxymethyl*-5-*ethyl*-, m. p. 174°; 5-n-*butoxymethyl*-5-*ethyl*-, m. p. 135°; 5-iso*butoxymethyl*-5-*ethyl*-, m. p. 177°; 5-*benzyloxymethyl*-5-*ethyl*-, m. p. 139—140°; 5 : 5-*diethoxymethyl*-, m. p. 201—203°; 5 : 5-*dipropoxymethyl*- m. p. 187°; and 5-*propoxymethyl-barbituric acid*, m. p. 147°. 5-*Ethoxymethyl*-5-*ethyl*-2-*thiobarbituric acid*, m. p. 147°, is also described. The latter, and its analogues, could not be desulphurised by the action of chloroacetic acid, without deep-seated decomposition being produced.

F. G. WILLSON.

Polarimetric study of inorganic and organic dimolybdomalates. Application of the law of Oudemans. E. DARMOIS and P. GABIANO (Compt. rend., 1926, **182**, 269—271).—By the neutralisation of the complex acid $2MoO_3,C_4H_6O_5$ with oxides, carbonates, or bases, the *lithium*, *sodium*, *potassium*, *ammonium*, *barium*, *calcium*, *methylamine*, *diethylamine*, *aniline*, and p-*toluidine* salts of dimolybdomalic acid have been obtained. These form efflorescent crystals of the general formula

$$4MoO_3,2C_4H_4O_5,M_2,xH_2O$$

and $4MoO_3,2C_4H_4O_5,M,xH_2O$ for uni- and bi-valent cations, respectively. The number of molecules of water of crystallisation varies, and the following values are found for x: lithium 12, ammonium 5, sodium 9, potassium 5, calcium 18, barium 12, aniline 1. Solutions of corresponding copper and nickel salts were obtained, but could not be crystallised. The molecular rotatory power of solutions for the green mercury ray diminishes with increasing dilution owing to decomposition of the complex. At a given molecular concentration, in agreement with Oudemans' law, $(M)_\nu$ is independent of the base and characterises the ion $[4MoO_3,2C_4H_6O_5]^{\cdots\cdot}$. The rotatory dispersion of all these salts is identical between 0·002 and 0·04*M*.

W. HUME-ROTHERY.

β-Sulphobutyric acid. H. J. BACKER and A. BLOEMAN (Rec. trav. chim., 1926, **45**, 100—109; cf. Haubner, A., 1892, 424; Beilstein and Wiegand, A., 1885, 740).—β-Sulphobutyric acid is best prepared by the method of Beilstein and Wiegand (*loc. cit.*), or by boiling ethyl β-bromobutyrate with an excess of a solution of ammonium sulphite for 1 hr. The acid is isolated as its barium salt ($+2H_2O$), becoming anhydrous at 110°, from which the free acid is obtained in a crystalline form, m. p. 72°. The following salts were prepared: normal *copper* ($4H_2O$), which forms an unstable complex *salt* ($+3C_5H_5N$); *copper hydrogen* ($+4H_2O$); *cobalt* ($+4H_2O$), which forms an unstable complex *salt* ($+3C_5H_5N$); *nickel* ($+4H_2O$) (complex *salt* with pyridine); *aniline* salt, m. p. 162° (decomp.); *benzidine hydrogen*; normal benzidine, decomp. 200°. By boiling crotonanilide with a solution of potassium hydrogen sulphite in 4% alcohol and subsequent treatment with barium hydroxide, *barium butyranilide-β-sulphonate* ($+H_2O$) is obtained, from which the free *acid*, m. p. 173—178°, is obtained [*copper*, *cobalt* ($+5H_2O$), and *nickel* ($+5H_2O$) salts are described]. The *aniline* salt is obtained when aniline β-sulphobutyrate is heated under reflux with excess of aniline for 3 hrs., and exists as an internal salt. With *o*-phenylenediamine, β-sulphobutyric acid yields *α-benzimidoazopropyl-β-sulphonic acid* [*barium* salt ($+H_2O$), *cobalt* ($+5H_2O$), *nickel* ($+5H_2O$) salts are described], which has also the composition of an internal salt, $CHMe(SO_3H)\cdot CH_2\ll^{N-}_{NH}>C_6H_4$.

J. W. BAKER.

Active components of *r*-β-sulphobutyric acid. H. J. BACKER and A. BLOEMAN (Rec. trav. chim., 1926, **45**, 110—123).—*r*-β-Sulphobutyric acid and its derivatives (cf. preceding abstract) have been resolved into their optically active isomerides by means of their alkaloidal salts, and the optical data for various wave-lengths are given. The following normal salts of *r*-β-sulphobutyric acid are described: *strychnine*, *brucine*, *cinchonine*, *quinine*, and the *hydrogen* salts of strychnine and brucine. d-β-*Sulphobutyric acid*, $M[\alpha]_D$ +3·6°, is obtained by fractional crystallisation of the brucine salt, and the following normal salts are described: *barium* ($+1H_2O$), $M[\alpha]_D$ +37°; *thallium*, *cobalt*, *nickel*, and the *hydrogen* salts of barium, thallium, and copper. l-β-*Sulphobutyric acid* may be obtained by fractional crystallisation of the quinine salt, or, better, by converting the mother-liquor from the first crop of the *d*-acid crystals into the barium salt, which then contains about 30% of the racemic salt. Since the solubilities of the *l*- and racemic salts are approximately equal, one

crystallisation yields the nearly pure l-*barium* salt. The normal *copper* salt is described. The *strychnine* and *brucine* salts of *r*-butyranilide-β-sulphonic acid are described, and the acid is resolved by means of the latter, yielding the l-*butyranilide-β-sulphonic acid*, m. p. 165—168°, $M[\alpha]_D$ −17° (the same acid is obtained by the action of aniline on the *l*-isomeride of the parent acid); the *barium*, *copper*, *cobalt*, and *nickel* salts are described. In absolute alcoholic solution the *l*-acid exhibits dextrorotation, probably since it exists as an internal salt which is ionised in water. α-Benzimidazopropyl-β-sulphonic acid does not form crystalline alkaloidal salts, but the active forms are obtained by the action of *o*-phenylenediamine on the active parent acid, barium *l*-α-*benzimidazopropyl*-β-*sulphonate* (*cobalt* salt) being obtained from the *d*-acid, whilst the *l*-acid yields *barium* d-α-*benzimidazopropyl*-β-*sulphonate*.

J. W. Baker.

Preparing saturated aldehydes from unsaturated aldehydes. Badische Anilin- u. Soda-Fabrik.—See B., 1926, 108.

"Crossed dismutation" between aldehyde and ketone. C. Neuberg and G. Gorr (Biochem. Z., 1926, **166**, 444—449).—Fractionation of the product of reaction of methyl *n*-propyl ketone and benzaldehyde in presence of aluminium ethoxide gives a small fraction which, on treatment with potassium hydroxide in an autoclave at 150°, yields methyl-*n*-propylcarbinol and benzoic acid.

P. W. Clutterbuck.

Conversion of methylglyoxal into pyruvic acid. C. Neuberg and G. Gorr (Biochem. Z., 1926, **166**, 442—443).—Methylglyoxal in dilute solution is readily converted by bromine water into pyruvic acid, which is isolated as the *p*-nitrophenylhydrazone (yield 74—77%). In the presence of sodium acetate (in amount equivalent to the hydrogen bromide produced) the yield is 90%. P. W. Clutterbuck.

Dehydration of α-glycols. Molecular transformations from ketones to ketones. A. Favorsky and A. Tschingaren (Compt. rend., 1926, **182**, 221—223).—When treated with chromic acid, α-phenyl-β-methylpropan-α-ol yields α-*phenyl*-β-*methylpropan*-α-*one*, b. p. 91·5—92·5°/10·5 mm., *semicarbazone*, m. p. 167—168°, which when heated with zinc chloride at 350—360° gives 38% of β-phenylbutan-γ-one, among the oxidation products of which is acetophenone. L. F. Hewitt.

Derivatives of dipropyl ketone. L. Mathus and F. Gibon (Bull. Soc. chim. Belg., 1925, **34**, 303—313).—Reduction of dipropyl ketone with alcohol and sodium yields dipropylcarbinol, which, on distillation with sulphuric acid below 100°, is dehydrated to Δ^{γ}-*heptene*, b. p. 95·8°/768 mm. Attempts to isolate the two expected geometrical isomerides were unsuccessful. By the action of the gaseous hydrogen halides on dipropylcarbinol, δ-*bromoheptane*, b. p. 159—160°, and δ-*chloroheptane*, b. p. 144—145°/758 mm., are formed. Addition of bromine to Δ^{γ}-heptene yields γδ-*dibromoheptane*, b. p. 98—99°/11 mm.; γδ-*dichloroheptane*, b. p. 179—181°, is similarly formed. Hypochlorous acid also readily forms a mixture of the two γδ-*heptenechlorohydrins*. These, on treatment with solid potassium hydroxide, yield the ethylene *oxide*, $\begin{matrix}\text{CHEt}\\\text{CHPr}\end{matrix}\!>\!\text{O}$, b. p. 131—132°. It was found impossible to hydrate the oxide to the corresponding glycol, nor could the latter be prepared by heating γδ-dibromoheptane with potassium acetate. The dichloroheptane, however, when heated with potassium acetate and glacial acetic acid, yielded a mixture of the two monoacetins,

CHEt(OAc)·CHPr·OH

and CHEt(OH)·CHPr·OAc, which, on hydrolysis with sodium hydroxide, produced *heptane*-γδ-*diol*, m. p. 98—99°, b. p. 212°. On boiling δ-bromoheptane under atmospheric pressure, partial dissociation into heptene and hydrogen bromide occurs, and, on cooling, these reunite to a mixture of β- and γ-bromoheptanes. A. Davidson.

Catalytic oxidation of alkylvinylcarbinols to alkyl vinyl ketones in presence of palladium-black. R. Delaby (Compt. rend., 1926, **182**, 140—142; cf. A., 1923, i, 84; 1925, i, 632).—The vapour of the alcohol mixed with oxygen is passed over palladium-black under reduced pressure, and the reaction products are condensed by means of solid carbon dioxide. In this way, a 20% yield of ethyl vinyl ketone is obtained from ethylvinylcarbinol, and propylvinylcarbinol gives *propyl vinyl ketone* (*picrate*, m. p. 81°); *diethylaminoethyl propyl ketone*, b. p. 92—95°/20 mm., is obtained by the interaction of diethylamine and propyl vinyl ketone. If the reaction is not conducted at reduced pressures, explosions result. The alcohols, unlike allyl alcohol, are not oxidised in presence of palladium-black in the liquid state. The method of preparation of the ketones is unsatisfactory on account of the difficulty of condensation of the products at the pressures employed, and on account of the formation of dehydration products of the alcohols.

Diethylamine picrate has m. p. 71·5°.

L. F. Hewitt.

Preparation of propylidene- and *iso*amylidene-acetone with the intermediate formation of the corresponding ketonic alcohols. Pastureau and Zamenhof (Compt. rend., 1926, **182**, 323—325; cf. Barbier and Bouveault, A., 1894, i, 224; 1896, i, 637; Grignard and Dubien, A., 1925, i, 111).—By the condensation of propaldehyde and of *iso*valeraldehyde with acetone in presence of sodium hydroxide, yields of 25% and 50%, respectively, of propylidene- and *iso*amylidene-acetone were obtained. By the isolation of the intermediate ketonic alcohols and dehydration of these by distillation with 2% of anhydrous oxalic acid, yields of 54% and 63%, respectively, of the unsaturated ketones were obtained. δ-*Hydroxyhexan*-β-*one* has b. p. 90°/25 mm., d_4^{15} 0·951, n_D^{18} 1·4368, and δ-*hydroxy*-β-*methylheptan*-ζ-*one*, b. p. 75°/7 mm., d_4^{20} 0·9247, n_D^{20} 1·4366. L. F. Hewitt.

Hydroxymethylene-ketones. E. Benary, H. Meyer, and K. Charisius (Ber., 1926, **59**, [*B*], 108—112).—The instability of hydroxymethylene-compounds of the type R·CO·CH:CH·OH is restricted

to the initial members in the aliphatic and aromatic series. Stable derivatives are formed if R is an ethyl or a higher group or a substituted phenyl group.

Ethyl β-hydroxyvinyl ketone, $C_2H_5{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, b. p. 145—148°, m. p. 73°, is prepared in 80% yield by the cautious addition of a mixture of methyl ethyl ketone and ethyl formate to sodium wire covered by anhydrous ether. It exists entirely in the enolic form. The corresponding *anilide*, m. p. 128°, and the *benzeneazo*-derivative,

$$COEt{\cdot}C(CHO){:}N{\cdot}NHPh,$$

m. p. 137—138°, are described. n-*Propyl β-hydroxyvinyl ketone* is a somewhat unstable liquid, b. p. 51°/16 mm. *Ethyl αα-diethyl-γ-hydroxymethyleneacetoacetate*, b. p. 121°/13 mm., and the corresponding *copper* salt, m. p. 76°, and *anilide*, m. p. 70°, are described. *p*-Tolyl methyl ketone and ethyl formate afford p-*tolyl β-hydroxyvinyl ketone*, m. p. 40—41° [*copper* salt, m. p. about 218° (decomp.); *anilide*, m. p. 164—165°]; the corresponding *benzeneazo*-derivative, $C_6H_4Me{\cdot}CO{\cdot}C(CHO){:}N{\cdot}NHPh$, m. p. 144°, yields a *phenylhydrazone*, m. p. 161—162°. The hydroxymethylene-ketone is transformed by warm phenylhydrazine into 1-*phenyl*-5-p-*tolylpyrazole*, m. p. 94°. p-*Methoxyphenyl β-hydroxyvinyl ketone*, m. p. 50—51°, similarly yields a *copper* salt, m. p. 192—194°, an *anilide*, m. p. 158° after softening, a *benzeneazo*-derivative, m. p. 136—137°, and its *phenylhydrazone*, m. p. 218—219°, and 1-*phenyl*-5-p-*methoxyphenylpyrazole*, m. p. 90—91°. 1-*Naphthyl β-hydroxyvinyl ketone* could not be distilled without decomposition; the *copper* salt, m. p. 165—168°, and *anilide*, m. p. 116—118°, are described. H. WREN.

Keto-enol isomerism of ethylenebisacetylacetone. G. T. MORGAN and C. J. A. TAYLOR (J.C.S., 1926, 43—49).—Sodium acetylacetone, when refluxed with excess of ethylene dibromide at 160° for 12 hrs., yields a mixture separable by fractional distillation into (1) keto-*ethylenebisacetylacetone*, b. p. 97—99°/20 mm. (*α-tetraoxime*, m. p. 165°); (2) enol-*ethylenebisacetylacetone*, m. p. 99° (*β-tetraoxime*, decomp. 220—222°); (3) dienol-*ethylenebisacetylacetone*, m. p. 140—143°; (4) a dehydration product, $C_{24}H_{30}O_5$, of ethylenebisacetylacetone. With ferric chloride, the keto-form (1) reacts only very slowly; the enol and dienol forms give an instantaneous violet coloration. The monoenol form is converted by formation and subsequent decomposition of its sodium salt into the keto-form, and by decomposition of its copper salt is partly converted into the much less stable dienol form. B. W. ANDERSON.

Compounds of the aldoses with carbamide and their application to the synthesis of glucosides containing nitrogen. B. HELFERICH and W. KOSCHE (Ber., 1926, 59, [*B*], 69—79).—The preparation of aldosecarbamides (cf. Schoorl, A., 1902, i, 83) by the interaction of aldoses with carbamide in the presence of hydrochloric acid is greatly simplified and rendered more widely applicable by the observation that the removal of unchanged aldoses by fermentation is unnecessary. Modified methods for the preparation of *d*-glucosecarbamide, *d*-glucosemethylcarbamide, m. p. 215° (decomp.), $[\alpha]_D^{18}$ −31·8° in water (cf. Schoorl, *loc. cit.*), and *d*-glucosethiocarbamide (cf. Fischer, A., 1914, i, 663) are described. l-*Arabinosecarbamide* (*monohydrate*), m. p. 193° (decomp.) after softening at 180°, $[\alpha]_D^{18}$ +51·5° in water, is obtained in 30% yield from arabinose and carbamide in aqueous solution containing hydrochloric acid, whereas, under closely similar conditions, xylose affords *di*-d-*xylosecarbamide* (*monohydrate*), decomp. 255° after darkening at 230°, $[\alpha]_D^{20}$ −20·0° in water. Acetylation of *d*-glucosecarbamide with acetic anhydride and zinc chloride yields pentaacetylglucosecarbamide, $[\alpha]_D^{20}$ −15·9° in pyridine (cf. Schoorl, *loc. cit.*), which is readily hydrolysed by alcoholic sodium ethoxide to the parent substance, whereas treatment with acetic anhydride and pyridine gives *tetra-acetylglucosecarbamide*, m. p. about 100° after softening at 85°, $[\alpha]_D^{20}$ −8·2°, in which the amino-group is unsubstituted; acetyl chloride and pyridine transform the tetra- into the penta-acetyl derivative. *Tetra-acetyl*-N-*benzoyl*-d-*glucosecarbamide*, m. p. 211—212° after softening at 195°, $[\alpha]_D^{19}$ −28·8° in pyridine, is described. The tetra-acetyl compound appears to be suitable for the preparation of glucosides containing nitrogen; thus with diethylmalonyl chloride and pyridine it affords (?) *tetra-acetylveronal*-d-*glucoside*, (R=OAc)

$$CH_2(R){\cdot}CH(R){\cdot}CH{\cdot}[CH(R)]_2{\cdot}CH{\cdot}N\begin{array}{l}\diagup CO{\cdot}CEt_2\\ \diagdown CO{-}NH\end{array}\!\!>CO,$$
$$\qquad\qquad\qquad

the completely methylated lactones derived from dextrose, galactose, mannose, arabinose, and xylose show that those lactones prepared from the normal forms of these sugars exhibit rapid changes in specific rotation when dissolved in water or aqueous alcohol, in contrast to very slow changes in those lactones prepared from the labile or γ-sugars. It has already been established that in the case of xylose and arabinose the normal sugars are amylene-oxidic and the γ-forms butylene-oxidic in structure, and with the polarimetric data and application of Hudson's rule it is now shown that galactose and dextrose in their normal forms are amylene-oxidic and in their unstable forms are butylene-oxidic. This is confirmed by independent means. With lævulose, the labile sugar is the amylene-oxide form and the normal sugar the butylene-oxide. The revised structural formula of dextrose renders necessary the revision of the constitutional formulæ of di- and tri-saccharides.

B. W. ANDERSON.

Oxidation of dextrose by air in calcium hydroxide solution. M. H. POWER and F. W. UPSON (J. Amer. Chem. Soc., 1926, **48**, 195—202).—Dextrose (100 g.) was dissolved in a suspension of calcium oxide (75 g.) in water (4 litres), and a current of air, free from carbon dioxide, was drawn through the mixture at 25—28° for 236 hrs., at the end of which period 95% of the sugar had disappeared. The products of the oxidation consisted of carbon dioxide (4·87 g.), formic acid (22·8 g.), and non-volatile acids (80·7 g.). From the latter, the following derivatives were isolated: *d*-arabonphenylhydrazide (14·7 g.); brucine *d*-crythronate (6·0 g.); alcohol-soluble brucine salts (19·8 g.) from which 0·29 g. of quinine *l*-glycerate was obtained; hydrated calcium glycollate (6·37 g.) and dried calcium glycollate (1·3 g.); oxalic acid (4·1 g.) and unidentified hydroxy-acids. A comparative oxidation of lævulose under the same conditions gave 4·28% of carbon dioxide and 9·1% of oxalic acid.

F. G. WILLSON.

Acetone sugars. VII. Constitution of di-acetonegalactose [galactose di*iso*propylidene ether]. K. FREUDENBERG and K. SMEYKAL (Ber., 1926, **59**, [*B*], 100—107; cf. A., 1925, i, 367).—Galactose di*iso*propylidene ether contains a free hydroxy-group and is converted by the successive action of sodium in presence of dry ether and methyl iodide into di*iso*propylidenemethylgalactose, b. p. 109—115°/0·5 mm., $[\alpha]_{578}^{20}$ −66·6° in substance (cf. Freudenberg and Hixon, A., 1923, i, 1180), which is hydrolysed to *galactose ζ-methyl ether*, m. p. (indef.) 128°, $[\alpha]_{578}^{17}$ +114° to +77° in aqueous solution (*phenylhydrazone*, decomp. 182—183°, $[\alpha]_{578}^{17}$ +14·5° in pyridine; *phenylosazone*, m. p. 204—205°, $[\alpha]_{578}^{17}$ +135° in pyridine). The methyl ether is completely stable towards nitric acid under conditions which with galactose or galactonic acid lead to the production of mucic acid. It appears therefore that the methoxy-group is attached to the ζ-carbon atom, and this is completely established by the oxidation of the ether by silver oxide to methoxyacetic acid (identified as the silver salt) and ω-*methoxyacetoxyacetoveratrone*, $CH_2(OMe)\cdot CO_2\cdot CH_2\cdot CO\cdot C_6H_3(OMe)_2$, m. p. 70°. Galactose ζ-methyl ether is converted by yellow mercuric oxide in the presence of water and calcium carbonate into *ζ-methylgalactonic acid*, m. p. 156°, $[\alpha]_{578}^{17}$ −5·54° to −40·2° (*ammonium* salt, m. p. 185°, [α] ca. +30° in water; *phenylhydrazine* salt, m. p. 158—159°, $[\alpha]_{578}^{17}$ +4·7° in aqueous solution). It follows therefore that the ζ-hydroxy-group in galactose di*iso*propylidene ether is unsubstituted. Assuming that one *iso*propylidene residue is present in the αβ-position, the remaining residue must be in the γδ- or γε-position, according as the ether has the butylene- or amylene-oxide structure. The second alternative is preferred, since acetone is known to form five-membered more readily than six-membered rings and, further, the unique position of the ζ-hydroxy-group is thereby explained. It appears also that the amylene-oxide ring exists pre-formed in galactose, thus confirming the work of Haworth, Ruell, and Westgarth (A., 1925, i, 117) and Pryde, Hirst, and Humphreys (*ibid.*, 365). Di*iso*propylidenemethyl-galactose is derived from the α-form of the sugar and is produced from either the α- or the β-variety.

The authors consider that the *iso*propylidene-derivatives of the sugar in general contain the same arrangement of the bridge as exists in the parent sugar. Dextrose must therefore contain the butylene-oxide ring, whereas the amylene-oxide ring is present in lævulose and probably also in xylose and arabinose (cf. Hirst and Purves, J.C.S., 1923, **123**, 1352; Hirst and Robertson, A., 1925, i, 364); mannose and rhamnose appear to belong to the butylene-oxide type.

p-Toluenesulphonyldi*iso*propylidenegalactose is converted by alcoholic dimethylamine at 100° into *di*iso*propylidenegalactosyl-ζ-dimethylamine*, b. p. 110—115°/1—2 mm., $[\alpha]_{578}^{18}$ −85·7° in substance (*methiodide*, $[\alpha]_{578}^{18}$ −32° in water). It is hydrolysed by aqueous sulphuric acid to *galactosyl-ζ-trimethylammonium iodide*, $C_9H_{20}O_5NI,H_2O$, decomp. 140° after softening at 90°, $[\alpha]_{578}^{12}$ +65·3° to +51·8° in water.

A modified method for the preparation of di*iso*-propylideneglucose is described in detail.

H. WREN.

Specific action of α-glucosidase from yeast. B. HELFERICH, W. KLEIN, and W. SCHÄFER (Ber., 1926, **59**, [*B*], 79—85).—The hydrolytic action of α-glucosidase from yeast is inhibited by the introduction of a chloro-, bromo-, or methoxy-group in the ζ-position in α-methylglucoside or by conversion of the compound into the anhydro-glucoside. α-Methyl-*d-iso*rhamnoside is little affected by α-glucosidase. The action of the latter substance is more sensitive to alteration in the substrate than is that of β-glucosidase from emulsin (cf. Fischer and Zach, A., 1912, i, 239; 1913, i, 165).

βγε-Triacetyl-ζ-triphenylmethyl-α-methylglucoside (cf. Helferich and Becker, A., 1925, i, 10) is obtained in 60% yield by the action of triphenylmethyl chloride on α-methylglucoside in warm pyridine followed by addition of acetic anhydride to the cooled solution. It is converted by phosphorus pentachloride into *βγε-triacetyl-α-methylglucoside-ζ-chlorohydrin*, m. p. 98—99° after softening at 95°, $[\alpha]_D^{18}$ +163·8° in pyridine, which is most readily isolated by removal of phosphoryl chloride, hydrolysis with alcoholic

ammonia, filtration from triphenylcarbinol, evaporation of the filtrate to dryness, and extraction of the residue with ethyl acetate, which dissolves the sugar derivative and acetamide; the latter substance is eliminated by sublimation under diminished pressure, after which the residue is reacetylated by acetic anhydride and pyridine. The triacetate is hydrolysed by cold, aqueous barium hydroxide to *α-methylglucoside-ζ-chlorohydrin*,

$$CH_2Cl\cdot CH(OH)\cdot CH\cdot[CH\cdot OH]_2\cdot CH\cdot OMe,$$
$$\text{└——O——┘}$$

m. p. 110—112° after softening at 102°, $[\alpha]_D^{21}$ +139·72° in aqueous solution. *βγε-Triacetyl-α-methylglucoside-ζ-bromohydrin*, m. p. 117°, $[\alpha]_D^{19}$ +125·8°, prepared similarly to the corresponding chloro-compound, is hydrolysed by methyl-alcoholic ammonia to *α-methylglucoside-ζ-bromohydrin*, m. p. 129—130° after softening at 126°, $[\alpha]_D^{18}$ +107·4° in aqueous solution. *Anhydro-α-methylglucoside*,

$$\text{┌———O———┐}$$
$$CH_2\cdot CH(OH)\cdot CH\cdot CH\cdot CH(OH)\cdot CH\cdot OMe,$$
$$\text{└———O———┘}$$

prepared from triacetyl-α-methylglucosidebromohydrin, has m. p. 89—95°, $[\alpha]_D^{22}$ +40·3° in water. *Triacetyl-α-methyl*-d-iso*rhamnoside*, m. p. 75°, $[\alpha]_D^{20}$ +159·2° in chloroform, is obtained by the action of zinc dust and 50% acetic acid in the presence of a little platinic chloride on triacetyl-α-methylglucosidebromohydrin; it is hydrolysed by methyl-alcoholic ammonia to *α-methyl*-d-iso*rhamnoside*, b. p. 162—163°/1 mm., m. p. 98—99°. α-Methylglucoside ζ-methyl ether (cf. A., 1925, i, 10) has b. p. 195—200°/1 mm., $[\alpha]_D^{19}$ +127·9° in aqueous solution.

H. WREN.

Salicin. I. Exceptional rotations of the halogenotetra-acetyl derivatives of salicin. Synthesis of salicin. A. KUNZ (J. Amer. Chem. Soc., 1926, **48**, 262—268).—Tetra-acetylsalicin bromide (cf. Zemplén, A., 1922, i, 563, 564; Zemplén and Braun, A., 1925, i, 1081), when treated with silver carbonate in aqueous acetone, affords *tetra-acetylsalicin*, m. p. 120°, $[\alpha]_D^{25}$ −14·1° in chloroform, which can be acetylated to the penta-acetate with acetic anhydride and pyridine, or converted into the chloride by the action of phosphorus pentachloride in chloroform. Tetra-acetylsalicin iodide is obtained analogously from the penta-acetate. Reduction of tetra-acetylsalicin chloride, bromide, or iodide, with zinc dust and 50% acetic acid, affords *tetra-acetyl-β-o-tolylglucoside*, m. p. 141°, $[\alpha]_D^{25}$ −25·4° in chloroform, which, on de-acetylation as above, yields β-o-tolylglucoside (cf. Ryan, J.C.S., 1899, **75**, 1056), or when treated with bromine in chloroform in sunlight below 0°, yields tetra-acetylsalicin bromide, from which penta-acetylsalicin was obtained by treatment with silver carbonate, followed by acetylation.

F. G. WILLSON.

Synthetic glucosides of pyrimidine derivatives. I. Synthesis of methyl*iso*cytosine-*d*-glucoside. A. HAHN, H. FASOLD, and L. SCHÄFER (Z. Biol., 1926, **84**, 35—40).—*Methyl*iso*cytosinetetra-acetyl*-d-*glucoside*, $C_5H_6ON_3\cdot C_6H_7O_5(Ac)_4$, m. p. 142—145°, $[\alpha]_D^{21}$ −19·1°, obtained by the action of acetobromoglucose on the *silver* salt of methyl*iso*cytosine, $C_5H_6ON_3Ag$, in boiling xylene solution, is isolated as the *picrate*, $C_{25}H_{28}O_{17}N_6$, decomp. 170—180° after softening at 150°, from which the free tetra-acetylglucoside is obtained by treatment with aqueous ammonia. *Methyl*iso*cytosine-*d*-glucoside*, $C_5H_6ON_3\cdot C_6H_7O(OH)_4$, a β-glucoside, m. p. 190° (decomp.), $[\alpha]_D^{24}$ −66·91°, is obtained from the tetra-acetyl derivative by methyl-alcoholic ammonia, and does not form a picrate; treatment with an aqueous or alcoholic solution of picric acid yields the picrate of methyl*iso*cytosine. Neither methyl*iso*cytosine-*d*-glucoside nor its tetra-acetyl derivative reduces Fehling's solution.

J. S. H. DAVIES.

Relationship between optical rotatory power and structure in chemistry of the polysaccharides. H. PRINGSHEIM and J. LEIBOWITZ (Ber., 1925, **58**, [*B*], 2808—2814).—Assuming the truth of the principle of optical superposition, the methods elaborated by Hudson for the calculation of the optical activity of sugars have been extended to polysaccharides. Calculation shows that the difference between the molecular rotation of amylotriose and amylobiose is equal to that between amylobiose and dextrose; this relationship is approximately observed experimentally, although the polysaccharides are equilibrium mixtures of α- and β-forms instead of individuals, as required by theory. For the corresponding acetates better agreement is found, since in this case homogeneous α- or β-varieties may be obtained by suitable choice of acetylating agent. On the assumption that trihexosan stands to dihexosan in the same relationship as amylotriose to amylobiose, the differences in molecular rotation must be the same for each pair of polysaccharides; this is the case with the compounds themselves and their acetates. The stereochemical calculations indicate the correctness of the symmetrical constitutions of di- and tri-hexosan (cf. Pringsheim, A., 1924, i, 1170).

It is remarkable that the members of each of the two polyamylose series have almost the same specific rotations: α-series, 136—139°; β-series 152—157°. Support is thus given to the hypothesis that the polymerisation of di- and tri-amylose to the more complex polyamyloses occurs exclusively by means of intermolecular forces without displacement of intramolecular main valencies. Similarly, the fundamental units of inulin, irisin, lichenin, and salep mannan have the same optical activity as the polysaccharides, their polymerides, or associates. The optical behaviour appears therefore to be a function of the constitution of the fundamental molecule and almost independent of the state of polymerisation or association. If this is the case, trihexosan and dihexosan cannot be the fundamental units of amylopectin and amylose, respectively.

Little is known of the constitution of the polyamyloses obtained by fermentative degradation of starch. Application of Hudson's rules to the formula proposed for diamylose by Karrer (A., 1922, i, 435) shows that the calculated and observed optical activities cannot be brought into line either on the assumption that it is a maltose anhydride with two maltose unions or that it contains a gentiobiose linking. Similarly, the fundamental unit of cellulose

should be completely or nearly optically inactive; these conditions are not fulfilled by Karrer's "cellosan" formulæ (*loc. cit.*), which demands $[\alpha]_D$ +115° for a cellobiose and a maltose linking, or $[\alpha]_D$ −11° for a cellobiose and gentiobiose union, or by Pringsheim's cellobiose anhydride formula, for which, on the assumption of a symmetrical configuration, the specific rotation +15° is calculated; if configurative asymmetry (presence of α- and β-glucosidic linking) be assumed, the necessary data for the calculation are not available. H. WREN.

Relations between rotatory power and structure in the sugar group. C. S. HUDSON, H. PRINGSHEIM, and J. LEIBOWITZ (J. Amer. Chem. Soc., 1926, **48**, 288—291).—See preceding abstract.

Amyloseoctadextrin. P. KLASON and K. SJÖBERG (Ber., 1926, **59**, [*B*], 40—45; cf. Brown and Morris, J.C.S., 1889, **55**, 449). Starch is allowed to remain in contact with 11% hydrochloric acid at the atmospheric temperature during at least three months; the acid is removed and the residue is washed with water and finally neutralised cautiously by alkali hydroxide. It is dissolved in boiling water, freed from amylose by means of charcoal, and the solution is fractionally precipitated with methyl alcohol until a portion, $[\alpha]_D$ +196°, is obtained. This portion is further purified by agitation with cold water, and finally crystallised from water. Determinations of *M* indicate the formula $(C_{12}H_{20}O_{10})_8,H_2O$ for this amylodextrin, which it is proposed to designate "amyloseoctadextrin." It appears to form *hydrates* with 24, 16, 10, and $6H_2O$. It behaves towards iodine in exactly the same manner as Lintner's erythrodextrin II; the latter substance, therefore, at any rate contains amylodextrin, and it is proposed to delete the term "erythrodextrin" from the literature in favour of the older nomenclature. Amyloseoctadextrin contains 0·017% P_2O_5, but it is not established whether this is united organically to the carbohydrate. It has $[\alpha]_D$ +195·6°, in agreement with Lintner's observation; the data of Brown and Morris appear low. Its reducing power is R=10·6. Amylodextrin is saccharified rather more rapidly than soluble starch by malt amylase, but reaction becomes greatly retarded after 75% of it has been transformed into maltose. Amylodextrin, soluble starch, and maltose are hydrolysed at equal rates by sulphuric acid (5%). The "residual substance," obtained by enzymic fission of amylodextrin, is identical with that derived from amylose (cf. Sjöberg, A., 1924, i, 1169), and probably identical with the dihexosan of Pringsheim and Wolfsohn (*ibid.*, i, 714). The relationship of amylodextrin to amylose is thus established. Two classes of amylodextrins therefore exist, the amylosedextrins giving a dihexosan when saccharified with malt amylase, and the amylopectindextrins yielding a trihexosan under similar conditions. H. WREN.

Complex stannous iodides. T. KARANTASSIS (Bull. Soc. chim. 1926, [iv], **39**, 43—44; cf. A., 1925, ii, 1182).—*Tetramethylammonium stannous iodide*, $SnI_3{\cdot}NMe_4$, is prepared by dissolving molecular proportions of stannous and tetramethylammonium iodides in the presence of excess of hydriodic acid. The solution is warmed and hydrochloric acid is added together with tin-foil to prevent oxidation, and the resulting solution allowed to crystallise. The corresponding *stannous aniline iodide*, $SnI_3{\cdot}NH_3Ph$, and *stannous pyridine iodide*, $SnI_3{\cdot}NH{\cdot}C_5H_5$, are similarly prepared, whilst for *tetramethylarsonium iodide*, $SnI_3{\cdot}As(CH_3)_4$, the preparation is similar except that the tin-foil is not added.

W. HUME-ROTHERY.

Mechanism of the synthesis of α-amino-acids by means of Strecker's reaction. I. Kinetic study of the disappearance of hydrocyanic acid. C. SANNIÉ (Bull. Soc. chim., 1925, [iv], **37**, 1557—1576).—Mutually inconsistent results have been obtained in studying the action of hydrocyanic acid on aldehyde-ammonia in presence of hydrochloric acid (Strecker, Annalen, 1850, **75**, 27; 1854, **91**, 349; H. Strecker, *ibid.*, 1864, **130**, 217; Urech, A., 1874, 147; Erlenmayer and Passavant, A., 1880, 313; Tiemann, A., 1882, 55, 57; Eschweiler, A., 1894, i, 267; Delépine, A., 1904, i, 20). The author, regarding the reaction from the kinetic point of view, has studied the disappearance of the hydrocyanic acid and finds that application of the law of mass action does not permit the velocity constant to be calculated. Disappearance of the hydrocyanic acid takes place according to the formula $(x+kt^2)(x-a)+ax=0$, where a is the initial concentration of hydrocyanic acid and x the amount transformed in time t. This gives $k=1/t\,.\,[x/(a-x)]\,.\,x/t$ as the value of the velocity constant. Disappearance of the cyanogen ion is thus of the nature of an irreversible bimolecular reaction, with a perturbation factor which is proportional to x and inversely proportional to t.

H. J. EVANS.

Compounds of formaldehyde with glycine. H. KRAUSE (Z. physiol. Chem., 1925, **150**, 306—308).—A discussion of the results of Bergmann and Ensslin (A., 1925, i, 1046) and those of the author (A., 1918, i, 156, 337). H. I. COOMBS.

Butyl esters of the simpler amino-acids. I. W. T. J. MORGAN (J.C.S., 1926, 79—84).—The butyl esters of monoamino-acids, being more stable and less volatile than the corresponding ethyl esters, should provide more suitable means for the determination of these acids. From n-*butyl glycine hydrochloride*, m. p. 69—71°, n-*butyl glycine*, b. p. 81—81·5°/18 mm., d^{16} 0·9703 (*picrate*, m. p. 113°; *benzoquinone* derivative, m. p. 179—180°), and n-*butyl carbamidoacetate*, m. p. 119°, are obtained, and from iso*butyl glycine hydrochloride*, m. p. 84—88°, iso*butyl glycine*, b. p. 79·5—80·5°/18 mm., d^{20} 0·9609 (*picrate*, m. p. 82—87°; *benzoquinone* derivative, m. p. 171—172°), are prepared. The following were also prepared: n-*butyl* dl-*alanine*, b. p. 81·5—82°/16 mm., d^{19} 0·9342 (*picrate*, m. p. 124°; *hydrochloride*, m. p. 58—61°); iso*butyl* dl-*alanine*, b. p. 77—78°/19 mm., d^{18} 0·9330 (*picrate*, m. p. 132—133°; *hydrochloride*, m. p. 60—63°), n-*butyl* dl-*valine*, b. p. 98—98·5°/17 mm., d^{14} 0·9266 (*picrate*, m. p. 91—92°; *hydrochloride*, m. p. 59—60°), n-*butyl* dl-*leucine*, b. p. 113·5°/18 mm., $d^{15·5}$ 0·8733 (*picrate*, m. p. 139°; *hydrochloride*,

m. p. 110—111°), and iso*butyl* dl-*leucine*, b. p. 110°/19 mm., $d^{18\cdot4}$ 0·9066 (*picrate*, m. p. 135—136°; *hydrochloride*, m. p. 97—99°). B. W. ANDERSON.

Heat of reaction in the formation of calcium cyanamide [from calcium carbide]. H. H. FRANCE and F. HOCHWALD.—See B., 1926, 88.

Mixed aquo-ammonocarbonic acids. I. Ammonolysis to ammonocarbonic acid. J. S. BLAIR (J. Amer. Chem. Soc., 1926, **48**, 87—95).—Mixed aquo-ammonocarbonic acids are derivatives of both water and ammonia in the sense in which carbonic acid is a derivative of water. They comprise such substances as carbamide and biuret, and may be regarded as being formed by loss of water, ammonia, or both, from one of three hypothetical mixed aquo-ammono-orthocarbonic acids, $C(OH)_{1,\,2,\,3}(NH_2)_{3,\,2,\,1}$. As a class they may be ammonolysed to guanidine by heating the solutions in liquid ammonia at 300° in sealed tubes. The reaction is incomplete, and is inhibited by the presence of traces of water. The nature of the equilibrium has been approximately determined in the case of carbamide.

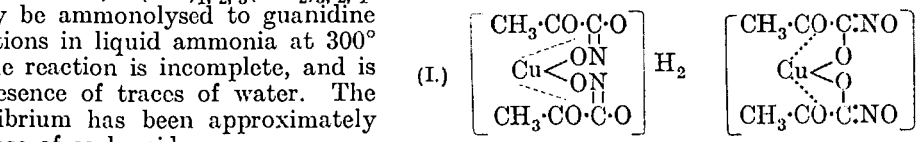
R. CUTHILL.

Mixed aquo-ammonocarbonic acids. II. Salt formation in liquid ammonia solution. J. S. BLAIR (J. Amer. Chem. Soc., 1926, **48**, 96—103; cf. preceding abstract).—The following salts of the mixed aquo-ammonocarbonic acids have been prepared by the interaction of potassamide and the acid in liquid ammonia solution: monopotassium carbamide, dipotassium carbamide, *monopotassium biuret*, $C_2H_4O_2N_3K$; *tripotassium biuret*, $C_2H_2O_2N_3K_3$; *monopotassium carbonyldicarbamide*, $C_3H_5O_3N_4K$, and *dipotassium carbonyldicarbamide*, $C_3H_4O_3N_4K_2$. *Monopotassium ethyl allophanate*, $C_4H_7O_3N_2K$, has been obtained in a similar manner from ethyl allophanate, and monopotassium carbamate and *dipotassium carbamate*, CHO_2NK_2, from ammonium carbamate.

R. CUTHILL.

Carbamide and guanidine derivatives of aliphatic sulphonic acids. III. R. ANDREASCH (Monatsh., 1925, **46**, 23—30; cf. A., 1924, i, 1290).—Condensation of α-bromopropionyl bromide with guanidine hydrochloride at 105—106° affords *α-bromopropionylguanidine* (*bromoplatinate*), which, when treated with potassium sulphite, yields *α-sulphopropionylguanidine*, m. p. 306° (decomp.) after softening at 295°. *α-Bromobutyrylguanidine* (*hydrobromide*; *hydrobromide-chloroplatinate*), *α-sulphobutyrylguanidine*, m. p. 314° (decomp.) after softening and turning brown at 300°, *α-bromoisobutyrylguanidine* (*bromoplatinate*), and *α-sulphoisobutyrylguanidine*, m. p. 168°, are obtained similarly. Treatment of α-bromopropionamide with boiling aqueous ammonium sulphite affords the *ammonium* salt of *α-sulphopropionamide*. The *potassium* (+H_2O) and *ammonium* salts of *α-sulphobutyramide*, and the *ammonium* salt of *α-sulphoisobutyramide*, obtained analogously, are described. Bromodiethylacetamide ("neuronal") does not react analogously with sulphites, but yields only α-ethylcrotonamide. α-Bromobutyryl- and α-bromo*iso*butyryl-carbamide (cf. Eeckhout, Arch. exp. Path. Pharm., 1907, **57**, 347) could not be obtained by the action of carbamide on the corresponding bromoacyl bromides. 5-Bromo-5-nitro-1 : 3-dimethylbarbituric acid (bromodimethyldilituric acid) yields, when treated with potassium sulphite, the potassium salt of dimethyldilituric acid. The sodium salt of bromodimethyldilituric acid exists in two hydrated forms, containing 1 mol. and 4 mols. of water, respectively (cf. Andreasch, A., 1895, i, 336; Techow, *ibid.*, i, 83; Biltz and Sedlatscheck, A., 1924, i, 429). F. G. WILLSON.

α-Ketoformhydroxamic acids and their derivatives. XI. C. GASTALDI and R. STRATTA (Gazzetta, 1925, **55**, 835—843).—Pyruvylhydroxamic acid (A., 1923, i, 1236) forms double sodium cupric and potassium cupric salts, which, according to Werner's theory, are salts of a dibasic acid, (I) or (II).



The *sodium cupric* salt (+4·5H_2O) explodes at about 230° and the *potassium cupric* salt (+2·5H_2O) at about 200°; the *barium cupric* salt (+4·5H_2O) loses ammonia at 160° and explodes slightly at 210°. Pyruvylhydroxamic acid forms a *dimeride*, m. p. 137° (decomp.). A new method of preparing pyruvylhydroxamic acid is described and conductivity data are given for the acid, its sodium and potassium cupric salts, its oxime, its benzoyl derivative, and the α- and β-oximes of the latter. T. H. POPE.

Supposed nitroprusside of bivalent iron. L. CAMBI (Atti R. Accad. Lincei, 1926, [vi], **3**, 8—13).—The existence of sodium hyponitritoferropentacyanide, reported by Ungarelli (A., 1925, i, 526) as a result of the action of sodium hyponitrite on Hofmann's sodium aquoferropentacyanide, is not confirmed. The above reagents retain their individual properties when mixed in solution, although the decomposition of the hyponitrite is accelerated by the presence of the complex salt. The compound obtained by Ungarelli was apparently sodium ferrocyanide, formed by the decomposition of the aquoferropentacyanide, or perhaps, in part, present as an impurity. The ferropentacyanide group has no tendency to react with the hyponitrite ion, although it will react with a compound containing the unsaturated nitroso-group. The author has prepared a number of *compounds* of this type, *e.g.*,

$Na_3[Fe(CN)_5ONPh]$,

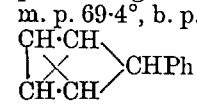
from sodium ferropentacyanide and nitrosobenzene.

F. G. TRYHORN.

Catalysis and the deformation of molecules. N. D. ZELINSKI [with I. N. TITZ] (Ber., 1925, **58**, [*B*], 2755—2763).—In part, a theoretical discussion of the mechanism of catalysis. The author's observations on catalytic hydrogenation and dehydrogenation lead him to the conclusion that the formation of intermediate products is not necessarily an essential feature of catalytic action, but that the process is due to deformation of the molecule; somewhat similar views have been expressed by Mendeléev,

Raschig (A., 1907, ii, 455, 863), and Bodenstein (A., 1924, ii, 745). In hydrogenation and dehydrogenation, the main factor appears to be the degree of dispersion of the catalyst and its increased surface tension, and not the intermediate production of compounds of metal and hydrogen. The surface energy of the catalyst causes changes in the vibrations of the molecules and atoms, thus deforming the molecules coming into contact with it and facilitating the establishment of new equilibria. The surface energy of the catalyst causes deep-seated changes in the chemical nature of substances coming into contact with it.

The form of the molecule has a profound influence on catalytic processes. Only *cyclo*hexane and its derivatives suffer catalytic dehydrogenation; other polymethylene rings do not exhibit this phenomenon. The contact isomerisation of α-pinene to *i*-pinene (A., 1911, i, 997) and the irreversible transformation of pinene into dihydropinene and cymene (A., 1925, i, 821) are further examples of the profound influence of the form of molecules. Examination of the behaviour of polycyclic compounds towards dehydrogenation has given somewhat unexpected results. *cyclo*Hexyl*cyclo*pentane behaves abnormally, since dehydrogenation affects both nuclei, so that the expected phenyl*cyclo*pentane is not produced, its place being taken by a saturated *hydrocarbon*, $C_{11}H_{10}$, m. p. 69·4°, b. p. 248—249°, for which the constitution



CHPh is provisionally assumed. Phenyl-*cyclo*pentane, on the other hand, could not be dehydrogenated in the presence of palladised or platinised asbestos or of platinised charcoal. Dehydrogenation of the *cyclo*pentamethylene ring depends therefore on its combination with the *cyclo*hexyl group. The latter radical readily loses hydrogen by the catalysis, and forces the pentamethylene ring to do the same, thus affording an instance of "conjugated dehydrogenation." The transformation of 1-*cyclo*hexyl-3-methyl*cyclo*pentane into diphenyl is still more surprising, and appears to be an example of the profound deformation of a molecule by purely catalytic action without assistance of any chemical reagents.

The following new compounds are incidentally described: cyclo*hexyl*cyclo*pentanol*, b. p. 115—118°/10 mm., from *cyclo*pentanone and magnesium *cyclo*hexyl bromide; cyclo*hexyl*cyclo*pentane*, b. p. 225—227°, d_4^{21} 0·8813, n_D^{21} 1·4767; *phenyl*cyclo*pentanol*, b. p. 132—133°/18 mm., d_4^{19} 1·0609, n_D^{19} 1·5472, from *cyclo*pentanone and magnesium phenyl bromide; *phenyl*-cyclo*pentane*, b. p. 215—217°, d_4^{19} 0·9503, n_D^{19} 1·5305; 1-cyclo*hexyl*-3-*methyl*cyclo*pentan*-1-*ol*, b. p. about 125°/15 mm.; 1-cyclo*hexyl*-3-*methyl*cyclo*pentane*, b. p. 231—233°, d_4^{17} 0·8902, n_D^{17} 1·4787. H. WREN.

Displacement of atoms and groups in the benzene nucleus. M. P. DE LANGE (Rec. trav. chim., 1926, **45**, 19—60).—A detailed summary of published data concerning the replacement of atoms and groups (other than hydrogen) in the benzene nucleus by other groups, has been made, in order to elucidate the conditions under which such replacements occur; and further experimental work has been carried out on the replacement of the groups $-CO_2H$, COH, and $-AsO_3H_2$ by $-NO_2$ when one or two methoxy-groups are present. The data (for which the original paper must be consulted) are summarised in four sections: (1) replacement of groups in the presence of –OH and –OR; (2) replacements in the presence of $-NH_2$ or –NHR; (3) replacements in the presence of $-CH_3$ group; (4) replacement of groups by hydrogen. The differences between direct substitution, in which the entering group attacks the nucleus at the position of substitution, and indirect substitution, in which it first enters the side-chain and subsequently migrates into the nucleus, are stressed. The latter occurs with much greater ease and leads exclusively to *o*-*p*-substitution, and, in the presence of one or more of the groups OH, OR, NH_2, NHR, or Me, especially in the *m*-position to each other, the groups CO_2H, SO_3H, I, Br, Cl can be replaced in the benzene ring in such an order that the first mentioned can always be replaced by one following in the series given. When *p*-methoxybenzoic acid is nitrated with a mixture of sulphuric and fuming nitric acids, 2 : 4-dinitro- and 2 : 4 : 6-trinitro-anisole and dinitroanisic acid are produced (the carboxyl group being partly replaced); whilst with nitric acid in acetic anhydride at low temperatures, mononitroanisic acid is the sole product. Nitration of anisaldehyde with fuming nitric acid at −10° yields pure 3-nitroanisaldehyde, m. p. 86° (*azine*, m. p. 241°; *semicarbazone*, m. p. 250°; *phenylhydrazone*, m. p. 131°; p-*nitrophenylhydrazone*, m. p. 228°), whilst in acetic anhydride *nitroanisaldehyde diacetate*, m. p. 92°, is obtained, from which a quantitative yield of the nitroanisaldehyde is obtained on hydrolysis. Nitration with a mixture of nitric and sulphuric acids above 0° (cf. Einhorn and Grabfeld, A., 1888, 477; Wörner, A., 1896, i, 225) yields a mixture of 3 : 5-dinitro-4-methoxybenzaldehyde and 2 : 4 : 6-trinitroanisole, which has m. p. 73°, unchanged by recrystallisation from light petroleum, this explaining the incorrect data for the m. p. of mono- and di-nitroanisaldehyde given by the earlier workers. If the mixture is dissolved in benzene, the addition of light petroleum then precipitates 3 : 5-dinitro-4-methoxybenzaldehyde (*semicarbazone*, m. p. 188°; p-*nitrophenylhydrazone*, m. p. 275°). On treatment with an alcoholic solution of ammonia or methylamine, 3 : 5-dinitro-4-methoxybenzaldehyde yields, respectively, 3 : 5-*dinitro*-4-*aminobenzaldehyde*, m. p. 171°, and 3 : 5-*dinitro*-4-*methylaminobenzaldehyde*, m. p. 120°. Nitration of 3 : 4-dimethoxybenzaldehyde (veratraldehyde), or any of its three isomeric mononitro-derivatives, with a mixture of nitric and sulphuric acids yields only trinitroveratrole, the presence of the two methoxy-groups facilitating the replacement of the aldehyde group by the nitro-group. The following derivatives of 6-nitroveratraldehyde are described: *azine*, decomp. 263°; *semicarbazone*, m. p. 246°; *phenylhydrazone*, m. p. 218° (decomp.); p-*nitrophenylhydrazone*, m. p. 261°. *p*-Methoxy- and *p*-ethoxy-phenylarsinic acids are obtained in good yield from *p*-anisidine and *p*-phenetidine, respectively, by diazotisation and treatment with sodium arsenite in the presence of cuprous

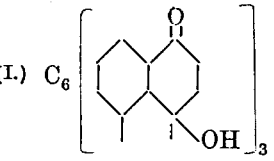
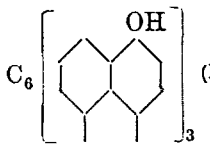
oxide as a catalyst (cf. Bart, A., 1913, i, 115). Both arsinic acids are nitrated by a mixture of nitric and sulphuric acids without loss of the arsinic acid residue, to yield, respectively, 3 : 5-*dinitro*-4-*methoxy*- and 3 : 5-*dinitro*-4-*ethoxy*-*phenylarsinic acids*, exploding at 265° and 275°, respectively. Treatment with alcoholic ammonia converts these acids into 3 : 5-dinitro-5-aminophenylarsinic acid, m. p. 285—295° (cf. Benda, A., 1912, i, 328), whilst with methylamine is obtained 3 : 5-dinitro-4-methylaminophenylarsinic acid (cf. Boehringer, D.R.-P. 285604), which with fuming nitric acid yields 3 : 5-dinitro-4-nitromethylaminophenylarsinic acid, exploding at 205° (cf. D.R.-P. 285572). Nitration of 3 : 4-dimethoxyphenylarsinic acid (cf. Fargher, J.C.S., 1920, **117**, 869) yields *dinitro*-3 : 4-*dimethoxyphenylarsinic acid*, decomp. 215°. Thus the CO_2H group appears to be easily removed from the benzene nucleus, the COH group less readily, whilst the AsO_3H_2 group is securely attached, and can be replaced by a nitro-group with great difficulty or not at all. In the nitration of *m*-xylene-4-sulphonic acid, the sulphonic acid group is removed with great difficulty, a very small amount of trinitro-*m*-xylene being produced; whilst mesitylenesulphonic acid on nitration yields a mixture of dinitromesitylenesulphonic acid, together with a large amount of trinitromesitylene, the presence of three methyl groups in the *m*-position causing the sulphonic group to be more easily replaced by the nitro-group.

J. W. Baker.

Preparation of 1-halogeno-2-nitronaphthalenes and 2-nitronaphthalene. H. H. Hodgson and E. Kilner (J.C.S., 1926, 7—9).—Slow decomposition in the cold of diazotised 2-nitro-1-naphthylamine in presence of cuprous chloride and hydrochloric acid gives a good yield of 1-*chloro*-2-*nitronaphthalene*, m. p. 76°. Similarly, 1-*bromo*-2-*nitronaphthalene*, m. p. 97°, and 1-*iodo*-2-*nitronaphthalene*, m. p. 111°, are obtained, but in poorer yields. Under suitable conditions, a 30% yield of 2-nitronaphthalene, m. p. 79°, may be obtained from 2-nitro-1-naphthylamine. B. W. Anderson.

Decacyclene. II. Decacyclenetrisulphonic acid and its derivatives. K. Dziewoński and J. Pochwalski (Bull. Inter. Acad. Polonaise, 1925, **A**, 165—178; cf. A., 1924, i, 1056).—Sulphonation of decacyclene (trinaphthylenebenzene) with cold 100% sulphuric acid, the mixture being finally heated at 100° to complete the reaction, furnishes *decacyclenetrisulphonic acid*, $C_6(C_{10}H_5{\cdot}SO_3H)_3$ (*sodium*, *barium*, and *calcium* salts described), yielding yellow solutions with a green fluorescence which dye wool and silk a golden-yellow. The acid and its salts have markedly colloidal properties. By the action of concentrated hydrochloric acid at 150°, the sulphonic acid groups are removed and the parent hydrocarbon is regenerated. The first products of the action of phosphorus pentachloride on the salts are readily decomposed by water, but at 150° there results a mixture of *trichlorodecacyclene*, $C_{36}H_{15}Cl_3$, and *tetrachlorodecacyclene*, $C_{36}H_{14}Cl_4$, neither of which melts at 350°.

The products of alkali fusion of the trisulphonic acid are brown or black, giving fluorescent solutions. The first product, at 140—200°, is *hydroxydecacyclenedisulphonic acid* (*sodium* salt), from which *hydroxydecacyclene*, $C_{36}H_{17}{\cdot}OH$, m. p. 367°, is obtained by the action of concentrated hydrochloric acid at 150°. *Dihydroxydecacyclenesulphonic acid* (*sodium* and *barium* salts) is also produced, together with the disulphonic acid, and is converted by hydrochloric acid into *dihydroxydecacyclene*, sparingly soluble and of very high m. p. Fusion of the trisulphonic acid with alkali at 260—280° and oxidation of the product by a current of air furnishes *trinaphthaquinolbenzene* (I), as a brown, amorphous powder, reduced by zinc dust

(I.)  (II.) 

in alkaline or acetic acid solution to *trihydroxydecacyclene* (II), isolated as its *tripropyl ether*, or its *triacetyl* derivative, m. p. above 350°. The substance may be used as a vat dye. Oxidation with chromic acid converts it into truxenequinonetricarboxylic acid (A., 1923, i, 777), from which fact the three hydroxyl groups are proved to be in the α-position in three separate naphthalene nuclei.

G. M. Bennett.

***N*-Methylsulphites of secondary aromatic-aliphatic amines.** Farbw. vorm. Meister, Lucius, u. Brüning.—See B., 1926, 141.

Acetyldiphenylamine from keten. C. D. Hurd (J. Amer. Chem. Soc., 1926, **48**, 291).—Acetyldiphenylamine is formed, but not precipitated, when keten is passed through an ethereal solution of diphenylamine, best yields being obtained at low temperatures (cf. van Alphen, A., 1925, i, 80).

F. G. Willson.

Mechanism of the formation of triphenylguanidine and phenylthiocarbimide from thiocarbanilide. W. J. S. Naunton (J.S.C.I., 1926, **45**, 34—35T).—It is preferable to formulate the mechanism of the formation of triphenylguanidine and phenylthiocarbimide from thiocarbanilide by the action of hydrochloric acid as being due to the breaking down of a hypothetical compound formed by the addition of carbodiphenylimide to the mercapto-form of thiocarbanilide. In an analogous way the breaking down of a hypothetical thiosulphocarbanilide, NHPh·C(:NPh)·S·S·S·C(:NPh)·NHPh, would explain the presence of anilinobenzthiazole, which is invariably formed in the preparation of mercaptobenzthiazole by heating thiocarbanilide with sulphur.

Beckmann rearrangement involving optically active radicals. L. W. Jones and E. S. Wallis (J. Amer. Chem. Soc., 1926, **48**, 169—181).—In the preparation of benzylmethylacetic acid (cf. Conrad, A., 1878, 732; Conrad and Bischoff, Annalen, 1880, **204**, 177) better yields are obtained when methylation of the ethyl acetoacetate precedes benzylation. Hydrolysis of ethyl benzylmethylacetoacetate is best carried out in 50% alcohol with considerable excess

of potassium hydroxide (cf. Kipping and Hunter, J.C.S., 1903, **83**, 1005). d-*Methyl benzylmethylacetate* has $[\alpha]^{20}$ +26·75°. It condenses with alcoholic hydroxylamine in presence of sodium ethoxide with formation of d-*benzylmethylacethydroxamic acid*, m. p. 121·5°, $[\alpha]_D^{20}$ +63·2°. The corresponding racemic acid has m. p. 124·4° (*benzoyl* derivative, m. p. 119—119·5°). The *benzoyl* derivative of the *d*-acid, m. p. 116°, $[\alpha]_D^{20}$ +54·5°, yields a crystalline *potassium* salt when treated with alcoholic potassium ethoxide at −12°. This is precipitated by the addition of ether previously cooled to −10°, and can be collected and dried in a vacuum desiccator, but when subsequently brought into contact with air it rearranges explosively and spontaneously, with formation of s-*di*-α-*benzylethylcarbamide*, m. p. 199°, which is also obtained similarly from the above racemic acid. d-*Benzylmethylacetazide*, obtained by the action of the corresponding chloride (cf. Pickard and Yates, J.C.S., 1909, **95**, 1019) on sodium azide in ether at 5°, decomposes slowly at 10°, gives a rotation of +30·77° in a 50 mm. tube at 5°, and is decomposed by water with formation of the above carbamide. When its solution in benzene is kept at 35°, rearrangement takes place, with formation of d-α-*benzylethylcarbimide*, b. p. 82°/5 mm., $[\alpha]_D^{20}$ +52·5° in benzene, the (unimolecular) velocity constant of the rearrangement being 0·01178 at 35°. The racemic carbimide, obtained similarly, has b. p. 78°/3 mm. When treated with ammonia in benzene, the above *d*-carbimide affords d-α-*benzylethylcarbamide*,

$$CH_2Ph\cdot CHMe\cdot NH\cdot CO\cdot NH_2,$$

m. p. 136°, $[\alpha]_D^{20}$ +10·7° in acetone. The corresponding racemic carbamide has m. p. 149°. Hydrolysis of the *d*-carbimide with concentrated hydrochloric acid yields d-α-*benzylethylamine hydrochloride*, hygroscopic, m. p. 147°, $[\alpha]_D^{20}$ +16·6° in water.

F. G. Willson.

Rearrangement of hydroxamic acids isomeric with triphenylacethydroxamic acid. L. W. Jones and F. B. Root (J. Amer. Chem. Soc., 1926, **48**, 181—195; cf. A., 1922, i, 248).—*p*-Benzhydrylbenzoyl chloride, $CHPh_2\cdot C_6H_4\cdot COCl$ (cf. Staudinger and Clar, A., 1911, i, 638), condenses with hydroxylamine in ether with formation of p-*benzhydrylbenzhydroxamic acid*, m. p. 156—157°, the *benzoyl* derivative of which is insoluble in warm aqueous alkalis, but yields the *potassium* salt, decomp. 91°, and *sodium* salt, decomp. 109°, when treated with the corresponding alcoholic ethoxides, and the *silver* salt, decomp. 190°, when treated with alcoholic silver nitrate. When boiled with water, the potassium salt affords carbon dioxide and s-*di*-p-*benzhydrylphenylcarbamide*, m. p. 262—263°, whilst alcohol at 100° affords chiefly p-*benzhydrylphenylurethane*, m. p. 103°. *Acetyl*-p-*benzhydrylbenzhydroxamic acid*,

$$CHPh_2\cdot C_6H_4\cdot CO\cdot NH\cdot OAc,$$

m. p. 157—158° (*potassium* salt, decomp. 130°; *sodium* salt, decomp. 140°; *silver* salt, decomp. 200° after darkening at 150°) is described. p-*Benzhydrylbenz*-p-*toluidide*, m. p. 164°, and p-*benzhydrylbenzamide*, m. p. 149°, were prepared. The latter affords the above urethane when treated with alcoholic sodium ethoxide and bromine, and this, when treated with phosphorus pentachloride in chloroform, yields p-*benzhydrylphenylcarbimide*, which, when treated with *p*-aminotriphenylmethane (cf. Baeyer and Löhr, A., 1890, i, 1141), affords the above carbamide, m. p. 262°. The *hydroxylamine* salt, m. p. 146—148° (decomp.), of *o*-benzhydrylbenzoic acid (cf. Bäyer, A., 1880, 650) decomposes when heated, with formation of the free acid and hydroxylamine (cf. Jones and Oesper, A., 1910, i, 13). The action of thionyl chloride on *o*-benzhydrylbenzoic acid affords 9-chloro-9-phenylanthrone (cf. Haller and Guyot, A., 1899, i, 221), whilst the action of phosphoryl chloride on *sodium* o-*benzhydrylbenzoate* yields a trace of the acid chloride, phenylanthrone (cf. Lossen, A., 1875, 1769), and a *compound*, m. p. 276°, possibly the anhydride. o-*Benzhydrylbenzoyl chloride*, m. p. 85°, can be obtained by the action of thionyl chloride on the acid in carbon disulphide and chloroform. Condensation with ethereal hydroxylamine affords o-*benzhydrylbenzhydroxamic acid*, m. p. 177—178° (decomp.), which decomposes when heated with formation of s-*di*-o-*benzhydrylphenylcarbamide*, m. p. 196°. o-*Benzhydrylbenzamide*, m. p. 129—130°, and the corresponding *anilide*, m. p. 152—153°, are described. When oxidised with chromic acid in acetic acid, the former yields diphenylphthalide. *Benzoyl*-o-*benzhydrylbenzhydroxamic acid*, m. p. 118—120° (*potassium* salt, darkens at about 200°; *silver* salt, darkens above 210°), yields the above carbamide, m. p. 196°, when boiled with aqueous *N*-potassium hydroxide. m-*Benzhydrylbenzoic acid*, m. p. 179°, prepared by the Sandmeyer reaction from *m*-aminotriphenylmethane, is described.

The relative resistance to rearrangement shown by the above compounds, as compared with the case of rearrangement of the isomeric triphenylacethydroxamic acid, supports the conclusion that the ease of rearrangement of such derivatives has some connexion with the tendency of the group, attached to the carbohydroxamic group, to exist as a free radical, and is not dependent on its mol. wt.

F. G. Willson.

Acenaphthene series. IV. Aminoacenaphthenesulphonic acids. G. T. Morgan and V. E. Yarsley (J.S.C.I., 1925, **44**, 513—515T).—Acenaphthene-4-sulphonic acid has been nitrated to a nitroacenaphthene-4-sulphonic acid, probably containing the nitro-group in position 3, for on reduction with iron and acidified water an aminoacenaphthenesulphonic acid is obtained, from which a non-coupling sultone is produced by decomposing its diazonium sulphonate. Reduction with hyposulphite is accompanied by sulphonation, leading to 3-*aminoacenaphthene*-2 : 4-*disulphonic acid*, which also furnishes a sultone. By the reduction of 3-nitroacenaphthene with sodium hydrogen sulphite, 3-aminoacenaphthene is obtained, with a small proportion of 3-aminoacenaphthene-2-sulphonic acid.

Geometrical stereoisomerism in the *cyclo*hexane series. II. 2 : 5-Dimethyl*cyclo*hexanols and 2 : 5-dimethyl*cyclo*hexanone. M. Godchot and P. Bedos (Bull. Soc. chim., 1925, [iv], **37**, 1637—1651; cf. A., 1925, i, 258, 537).—The action of hypochlorous acid on 1-methyl-Δ^3-*cyclo*hexene yields the

two isomeric 2-chloro-5-methyl*cyclo*hexanols, which by the action of magnesium methyl iodide form the two isomeric 2 : 5-dimethyl*cyclo*hexanols, distinguished by means of their allophanates, m. p. 157—158° and 125°. All these four substances are converted by chromic acid oxidation into the same 2 : 5-*dimethyl*cyclo*hexanone*, b. p. 171—173°, *semicarbazone*, m. p. 122°, and are therefore considered to differ from the stereochemical point of view only by reason of the orientation of the hydroxyl group. The *cis*-configuration, with respect to the 2-methyl and the hydroxyl groups, is assigned to the compound yielding the allophanate of m. p. 157—158°, on account of its formation from the oxide of 1-methyl-Δ^3-*cyclo*hexene. The orientation of the second methyl group is unknown, but since that of the two methyl groups is similar in the two 2 : 5-dimethyl*cyclo*hexanols, whilst that of the hydroxyl group varies, the *trans*-structure is assigned to the compound yielding an allophanate of m. p. 125°. On similar grounds the conclusion is reached that the 2-chloro-5-methyl-*cyclo*hexanol of b. p. 103—105°/14 mm. has the *cis*-structure, the isomeride of b. p. 95—97°/14 mm. being the *trans*-compound. H. J. EVANS.

Δ^2-*cyclo*Hexenol and Δ^2-*cyclo*hexenone. A. KÖTZ and K. RICHTER (J. pr. Chem., 1925, [ii], **111**, 373—400).—When Δ^2-*cyclo*hexenol is treated with benzoyl chloride in pyridine solution, Δ^2-cyclo*hexenyl benzoate*, b. p. 160—165°/15 mm., is obtained, and this gives a good yield of *cyclo*hexanyl benzoate on reduction with palladium-black. Similarly, Δ^2-cyclo*hexenyl acetate*, b. p. 62°/12 mm., is readily reduced to *cyclo*hexanyl acetate. An *isomeride*, m. p. 108°, of *cyclo*hexan-1 : 2 : 3-triol (*tribenzoate*, m. p. 165°) is formed by the action of dilute acetic acid on *cyclo*hexenol-2 : 3-oxide. Δ^2-*cyclo*Hexenol, when treated with hypochlorous acid, yields two forms of 2-*chloro*cyclo*hexan*-1 : 3-*diol*, needles, m. p. 90°, and thick prisms, m. p. 135° (*diacetate*, b. p. 140—145°/12—15 mm., d_{15}^{20} 1·1989). When crude 2-chloro*cyclo*hexane-1 : 3-diol is heated either with acetyl chloride in benzene solution or with 30% sulphuric acid, 2-*chloro*-Δ^2-cyclo*hexenone*, m. p. 70°, is formed.

Convenient methods are described for the preparation from glycerol α-monochlorohydrin of glycide and αβ-propylene glycol, which latter yields propaldehyde on dehydration. The analogy between these open-chain compounds and the *cyclo*hexane analogues is brought out by extending these same methods to the preparation from 2-chloro*cyclo*hexane-1 : 3-diol of *cyclo*hexenol-2 : 3-oxide (not isolated) and Δ^2-*cyclo*hexenone.

When treated with hypochlorous acid, Δ^2-*cyclo*hexenone yields 2-*chloro*cyclo*hexan*-3-*ol*-1-*one*, m. p. 54—55°, which readily loses water to form 2-chloro-Δ^2-*cyclo*hexenone. Methods are described for the preparation of *cyclo*hexanone from Δ^2-*cyclo*hexenone and of the latter from Δ^2-*cyclo*hexenol. R. W. WEST.

Reaction between methyl alcohol and phenol at high temperature under pressure. V. IPATIEV, J. ORLOV, and G. RAZOUBAIEV (Bull. Soc. chim., 1925, [iv], **37**, 1576—1577).—When phenol is heated with methyl alcohol for 24 hrs. at 440° under 200 atm. pressure, *o*-cresol is formed, together with small quantities of benzene, its homologues, and anisole; *m*- and *p*-cresols are not obtained. A similar reaction occurs using ethyl alcohol, but the yield of ethylphenol is less. H. J. EVANS.

Reaction between triacetin and phenol. Preparation of triacetin. S. KAWAI (Bull. Inst. Phys. Chem. Res., 1926, **5**, 43—46).—A mixture of sodium phenoxide, prepared from 28·2 g. of phenol, 6·9 g. of sodium, and 21·8 g. of triacetin, is heated at 140—150° for 2 hrs.; the cooled product is extracted with ether or benzene and distilled at 178—197°/13 mm. It is then treated with large amounts of water; from the oily layer separates 2·9 g. of glycerol αα′-diphenyl ether, m. p. 81—82°. Triacetin is prepared by the following method in 84% of the theoretical yield. A mixture of 70 g. of anhydrous glycerol and 525 g. of acetic anhydride is shaken until a homogeneous mixture is obtained. When the rise of temperature of the mixture ceases, it is boiled under reflux for 2 hrs. and distilled. A further distillation is sufficient for purification; it boils at 258—259°/756 mm. K. KASHIMA.

Nitration of *m*-bromophenol. H. H. HODGSON and F. H. MOORE (J.C.S., 1926, 155—161).—Nitroderivatives of *m*-bromophenol are prepared in a similar way to those of *m*-chlorophenol (A., 1925, i, 1144). Mononitration yields 24% of 3-bromo-6-nitrophenol (Auwers and Dienes, Chem. Zentr., 1924, II, 2268), m. p. 42° (*methyl ether*, m. p. 85·5°; *benzoate*, m. p. 104°; scarlet *sodium* salt), and 50% of 3-*bromo*-4-*nitrophenol* (*methyl ether*, m. p. 45°; *benzoate*, m. p. 102°; amber *sodium* salt). 3-Chloro-6-nitrophenol gives a *methyl ether*, m. p. 72°, a *benzoate*, m. p. 91°, and a scarlet *sodium* salt, and 3-chloro-4-nitrophenol a *methyl ether*, m. p. 56·5°, a *benzoate*, m. p. 96°, and an orange *sodium* salt. *m*-Bromophenol gives, on sulphonation, nitration, and hydrolysis, 3-*bromo*-2-*nitrophenol*, which exists in two forms, (*a*) colourless, hydrated, m. p. 33°, (*b*) yellow, anhydrous, m. p. 65—67° (red *sodium* salt; *methyl ether*, m. p. 73°; *benzoate*, m. p. 133°). The corresponding forms of 3-chloro-2-nitrophenol are (*a*) colourless, $+H_2O$, m. p. 37·5—38°, (*b*) yellow, anhydrous, m. p. 45—47°. Dinitration in glacial acetic acid yields 3-bromo-4 : 6-dinitrophenol, m. p. 92° (Körner, A., 1876, i, 231), the silver salt of which exists in three forms: yellow, amorphous; yellow, crystalline; and red, crystalline. 3-*Bromo*-2 : 6-*dinitrophenol*, m. p. 131° (red *silver* salt, soluble in ammonia), and 3-*bromo*-2 : 4-*dinitrophenol* (yellow *silver* salt, insoluble in ammonia), can be separated by conversion into the silver salts. Evidence for their constitution is furnished by the formation from both of 2 : 4-dinitro-*m*-phenylenediamine, m. p. 258°, and 2 : 4-dinitroresorcinol, m. p. 146°. 3-Bromo-2 : 4 : 6-trinitrophenol has m. p. 149° (cf. Tijmstra, A., 1902, i, 717). 3-*Bromo*-2 : 5 : 6-*trinitrophenol* has m. p. 146°. *Potassium* 3-*bromo*-2 : 5 : 6-*trinitrophenol*-4-*sulphonate* explodes on heating. H. E. F. NOTTON.

Bromophenols. XIII. Exchangeability of halogen atoms and nitro-groups in some halogenonitrophenol ethers. M. KOHN and M. HELLER (Monatsh., 1925, **46**, 91—100).—3 : 5-Dibromoanisole,

obtained by methylation of the corresponding dibromophenol, has b. p. 257—261° (cf. Blau, A., 1887, 242; Blanksma, A., 1907, i, 126). When treated with cold, fuming nitric acid, it yields a dinitro-derivative, probably 3 : 5-*dibromo*-2 : 4-*dinitroanisole*, m. p. 175°, which can be demethylated only by the action of concentrated sulphuric acid at 180—190°, when 3 : 5-*dibromo*-2 : 4-*dinitrophenol*, m. p. 146—147°, is obtained. The above dibromodinitroanisole reacts with aniline, with formation of 2 : 4-*dinitro*-3 : 5-*dianilinoanisole*, red, m. p. 177—178°. 2 : 4 : 6-Trichloroanisole, b. p. 238—240°, is readily obtained by treating the corresponding phenol with methyl sulphate in alkaline solution (cf. Hugounenq, A., 1890, 240). It yields 2 : 4 : 6-trichloro-3 : 5-dinitroanisole (cf. Hugounenq, *loc. cit.*) when treated with cold nitric and sulphuric acid, and this, when treated with concentrated sulphuric acid at 185°, affords 2 : 4 : 6-*trichloro*-3 : 5-*dinitrophenol*, m. p. 165—167° (*potassium* salt, golden-yellow; *pyridine* salt, m. p. 139—148°). When 2 : 6-dibromo-3 : 5-dinitroquinol dimethyl ether (cf. Kohn and Guttmann, A., 1925, i, 1263) is treated with hydrobromic acid in boiling glacial acetic acid, and the product methylated with methyl sulphate in alkaline solution, 2 : 3 : 5 : 6-tetrabromoquinol dimethyl ether, m. p. 192—194°, is obtained (cf. Kohn and Grün, *ibid.*, 1265). By the same method, 2 : 6-dichloro-3 : 5-dinitroquinol dimethyl ether is converted into 2 : 6-*dichloro*-3 : 5-*dibromoquinol dimethyl ether*, m. p. 170—172°. The latter can also be obtained by brominating 2 : 6-dichloroquinol dimethyl ether, which has b. p. 258—259°/756 mm. It is suggested that the replacement of the nitro-group by bromine is preceded by the addition of hydrobromic acid to the nitro-group, the resulting —NO(OH)Br group then losing nitrous acid.

F. G. Willson.

Bromophenols. XIV. Halogenophenols. M. Kohn and A. Rosenfeld (Monatsh., 1925, **46**, 101—117).—By the continued action of bromine (2 mols.) in aqueous potassium bromide on a cold, aqueous suspension of *p*-chlorophenol, 4-*chloro*-2 : 6-*dibromophenol*, m. p. 90°, is obtained, and this, on methylation, affords the corresponding 4-*chloro*-2 : 6-*dibromoanisole*, m. p. 74°, b. p. 265—270°. Cold, fuming nitric acid converts the latter into 4-*chloro*-2 : 6-*dibromo*-3-*nitroanisole*, m. p. 58°, whilst in presence of sulphuric acid the nitration proceeds with formation of 4-*chloro*-2 : 6-*dibromo*-3 : 5-*dinitroanisole*, m. p. 146°, which yields, when boiled with hydrobromic and acetic acids, the corresponding *chlorodibromodinitrophenol*, m. p. 191°. The action of excess of bromine in the cold, under the above conditions, converts *p*-chlorophenol into 4-*chloro*-2 : 4 : 6-*tribromo*-1-*keto*-$\Delta^{2:5}$-cyclo*hexadiene*, dark yellow, decomp. when heated, which yields, on reduction with aqueous sulphurous acid, the above 4-chloro-2 : 6-dibromophenol, whilst the controlled action of warm, concentrated sulphuric acid affords 4-*chloro*-2 : 3 : 6-*tribromophenol*, m. p. 104°. The last is oxidised by cold, fuming nitric acid to tribromobenzoquinone, whilst the *methyl ether*, m. p. 94°, is converted by this reagent into 4-*chloro*-2 : 3 : 6-*tribromo*-5-*nitroanisole*, m. p. 120—121°, from which the corresponding 4-chloro-2 : 3 : 6-tribromo-5-nitrophenol, m. p. 141—142° (*potassium* salt, yellow; benzoyl derivative, m. p. 154°), is obtained by demethylation. Treatment of *p*-chlorophenol in alkaline solution with iodine in aqueous potassium iodide affords 4-*chloro*-2 : 6-*diiodophenol*, m. p. 109°, the *methyl ether* of which has m. p. 79°, and forms monoclinic crystals, $a : b : c = 0{\cdot}9237 : 1 : 0{\cdot}5539$, $\beta = 96° 11' 20''$, angle of extinction 27°. Tri-iodophenol has m. p. 160°. Tri-iodoanisole forms monoclinic crystals with some of the edges characteristically rounded. Treatment of 3 : 5-dibromophenol in alkaline solution with iodine in aqueous potassium iodide affords 3 : 5-*dibromo*-2 : 4 : 6-*tri-iodophenol*, m. p. 199° (decomp.) after evolution of iodine from 180° [*methyl ether*, m. p. 202—205° (decomp.)], which, when treated with cold, fuming nitric acid, yields 3 : 5-*dibromo*-2 : 6-*di-iodobenzoquinone*, m. p. 260° (decomp.) (cf. Torrey and Hunter, A., 1912, i, 475). The action of alkaline potassium persulphate on 4-chloro-2 : 6-di-iodophenol and on 3 : 5-dibromo-2 : 4 : 6-tri-iodophenol, affords greyish-violet, amorphous *substances*.

F. G. Willson.

Bromophenols. XV. Pseudophenols. M. Kohn and A. Rosenfeld (Monatsh., 1925, **46**, 119—130).—3 : 5-Dibromo-2-hydroxybenzyl bromide (cf. Auwers, A., 1906, i, 258) forms monoclinic crystals, $a : b : c = 0{\cdot}79994 : 1 : 0{\cdot}56812$, $\beta = 96° 58' 52''$, d 2·5066. When treated with ethereal hydrazine hydrate, it yields *di*-(3 : 5-*dibromo*-2-*hydroxybenzyl*)*hydrazine*, m. p. 176°, whilst phenylhydrazine affords similarly *α-phenyl-α*-(3 : 5-*dibromo*-2-*hydroxybenzyl*)*hydrazine*, m. p. 159°. When treated with potassium nitrite in acetic acid, the dibromohydroxybenzyl bromide affords a mixture of 5-*bromo*-3-*nitro*-2-*hydroxybenzyl acetate*, yellow, m. p. 134·5°, and 3-bromo-5-nitro-2-hydroxybenzyl acetate, m. p. 132°. The action of nitrite and acetic acid on 3 : 5-dibromo-2-hydroxybenzylaniline (cf. Auwers and Büttner, A., 1899, i, 36), with simultaneous replacement of bromine by a nitro-group, gives a *nitrosoamine*, m. p. 139—140°. 3 : 5-Dibromo-4-hydroxybenzyl bromide condenses similarly with phenylhydrazine, with formation of as-*phenyl*-3 : 5-*dibromo*-4-*hydroxybenzylhydrazine*, m. p. 141°, and with nitrite and acetic acid, with formation of a corresponding bromonitrohydroxybenzyl acetate, m. p. 112—114° (cf. Auwers, *loc. cit.*) (*potassium* salt, red), for which crystallographic data are given.

F. G. Willson.

Molecular compounds of the phenols. VII. Behaviour of hydrogenated cresols and related compounds. G. Weissenberger, F. Schuster, and K. Wojnoff (Monatsh., 1925, **46**, 1—8; cf. A., 1925, ii, 766).—The vapour pressures of mixtures of *o*-, *m*-, and *p*-cresols with toluene show positive deviations from those calculated from the van 't Hoff relation, indicating the formation of normal binary mixtures. With methyl alcohol, the corresponding deviations are negative, decreasing in the order *o*-, *m*-, *p*-. Ethyl acetate also gives negative deviations, but the deviation is greatest with *m*-cresol. Chloroform gives positive deviations, greatest with *m*-cresol, carbon disulphide behaving similarly, but showing the greatest deviation with *p*-cresol. The

three hexahydrocresols give positive deviations both with chloroform and with ethyl acetate, the last result corresponding with the smaller residual valency present in the fully saturated compounds as compared with the cresols. Viscosity and surface-tension measurements for the above mixtures are recorded.

F. G. WILLSON.

Molecular compounds of the phenols. VIII. Localisation of the residual valency. G. WEISSENBERGER, F. SCHUSTER, and R. HENKE (Monatsh., 1925, **46**, 47—56).—Comparison of the deviations of the vapour pressures of mixtures of phenol, *o*-, *m*-, and *p*-cresol, and pyrogallol, respectively, and methyl alcohol, ethyl alcohol, and acetone, with those calculated, shows that pyrogallol exhibits a considerably greater tendency to form molecular compounds than the monohydric phenols, indicating that the residual valency, as far as these solvents are concerned, is centred in the phenolic hydrogen. As the deviations in the case of pyrogallol are about six times those of the monohydric phenols, whilst the molecular compound of pyrogallol with acetone contains 1 mol. of this compound to 3 mols. of acetone (cf. Schmidlin and Lang, A., 1910, i, 836), it is concluded that the residual valency of each phenolic hydrogen atom is intensified by that of its neighbours. With mixtures of the cresols and pyrogallol with ethyl acetate, the deviations are approximately equal in all four cases, a result ascribed to steric hindrance (cf. Baeyer and Villiger, A., 1902, i, 355). Mixtures of the hexahydrocresols with methyl alcohol show positive vapour-pressure deviations, indicating absence of molecular compounds, this being ascribed to the extinguishing of the residual valency of the phenolic hydrogen by saturation of that of the nucleus. Mixtures of benzaldehyde and methyl alcohol, and of *cyclo*hexanone and ethyl acetate show positive deviations, molecular compounds not being formed. Viscosity and surface-tension measurements for the above mixtures are recorded.

F. G. WILLSON.

***s*- and *as*-Hemellitenol.** K. VON AUWERS and F. WEENERT (Ber., 1925, **58**, [*B*], 2815—2818).—Reduction of 4-hydroxy-2 : 3-dimethylbenzaldehyde by Clemmensen's method leads to the production of 2 : 3 : 4-trimethylphenol, m. p. 67—68° immediately after distillation or m. p. 81° after preservation or crystallisation. The substance is identical with the supposed 3 : 4 : 5-trimethylphenol obtained by Jacobson by sulphonation of hemellitene and fusion of the sulphonate with potassium hydroxide; the *acetate*, b. p. 239—241°, and *phenylurethane*, m. p. 126·5—127·5°, are described. The *benzeneazo*-compound has m. p. 110—111°. For purposes of comparison 4-hydroxy-2 : 6-dimethylbenzaldehyde has been similarly converted into 2 : 4 : 6-trimethylphenol (cf. von Auwers and Saurwein, A., 1922, i, 1031); the corresponding *acetate*, m. p. 59—60°, and *phenylurethane*, m. p. 148—149°, are described.

H. WREN.

Compounds containing an atom of quinquevalent boron and their optical activity. J. BÖESEKEN (Rec. trav. chim., 1926, **45**, 151—152).—Supplementary to a previous paper (Böeseken and Mijs, A., 1925, i, 911) acknowledging the work of Hermans and giving a brief historical review of the stereochemistry of boron.

J. W. BAKER.

Nitration of creosol [3-methoxy-*p*-cresol], acetylcreosol, and homoveratrole. Substitution in complex benzene derivatives. M. OBERLIN (Arch. Pharm., 1925, **263**, 641—668).—When 3-methoxy-*p*-cresol (creosol) is nitrated it yields 5-*nitro*-3-*methoxy*-p-*cresol*, m. p. 81—82°. This nitration is effected by the action of a cold ethereal solution of nitric acid (*d* 1·52) : it cannot be carried out by treating the phenol, in aqueous-alcoholic solution, with sodium nitrite and sulphuric acid, for the *product* so obtained, m. p. 130—131°, contains no nitrogen. When the above nitro-compound is methylated (with methyl sulphate), it yields 5-nitrohomoveratrole, m. p. 56—58° (cf. Cousin, Ann. Chim., 1898, [vii], **13**, 539). On further nitration, by dissolving in warm nitric acid (*d* 1·40), 5-nitrohomoveratrole is converted into 5 : 6-dinitrohomoveratrole, m. p. 119—120° (Robinson, J.C.S., 1916, **109**, 1090). 5-Nitro-3-methoxy-*p*-cresol, when treated with hot acetic anhydride and a little sulphuric acid, affords the corresponding *acetoxy*-compound, m. p. 89—90°, which also is further nitrated, but less readily than the methoxy-derivative, 5 : 6-*dinitro*-4-*acetoxy*-m-*tolyl methyl ether*, m. p. 151—152°, being so produced. This compound undergoes hydrolysis when dissolved in cold (or gently warmed) sulphuric acid, and so affords 5 : 6-*dinitro*-3-*methoxy*-p-*cresol*, m. p. 163—164°, from which, again, 5 : 6-dinitrohomoveratrole is readily obtained. This compound is also produced by direct nitration (using nitric acid of *d* 1·47) of homoveratrole, and that it is truly an *o*-dinitro-compound is shown by its yielding on reduction a *diamine*, which interacts with phenanthraquinone to give 7 : 8-*dimethoxy*-5-*methyl*-2 : 3-*phenanthrenoquinoxaline*, m. p. 181—182°, and with oxalic acid to give 2 : 3-*dihydroxy*-7 : 8-*dimethoxy*-5-*methylquinoxaline*, m. p. above 300°. Whilst 3-methoxy-*p*-cresol is nitrated in the 5-position, its acetyl derivative, on the other hand, resembles homoveratrole (Cousin, *loc. cit.*) in yielding the 6-nitro-derivative (cf. Cardwell and Robinson, J.C.S., 1915, **107**, 259). When this compound is nitrated further, or when 4-acetoxy-*m*-tolyl methyl ether is directly treated with nitric acid (*d* 1·52) at 20°, but then in smaller yield because of oxidation, 2 : 6-*dinitro*-4-*acetoxy*-m-*tolyl methyl ether*, m. p. 101—102°, is produced. The position of one nitro-group (6) in this product being known, that of the other is determined by the following facts. The compound is hydrolysed readily to 2 : 6-*dinitro*-3-*methoxy*-p-*cresol*, m. p. 107—108° (*benzoyl* derivative, m. p. 111—112°), which, on methylation, affords 2 : 6-*dinitrohomoveratrole*, m. p. 90—91°. This is reduced to a *diamine* which yields no quinoxaline derivatives and is therefore not an *ortho*-diamine; further, on partial reduction with ammonium hydrosulphide, it is reduced to 2-*nitro*-6-*aminohomoveratrole*, m. p. 104—105° (*benzoyl* derivative, m. p. 170—171°), together with a *by-product*, m. p. 196—197°. The amino-group here is readily displaced when the corresponding diazonium sulphate is heated with alcohol and copper powder, and 2-*nitrohomoveratrole*

(an oil, b. p. 108—110°/0·5 mm.; 115—117°/1 mm.) is so produced. This nitrohomoveratrole is oxidised by a hot, dilute solution of potassium permanganate to 2-nitroveratric acid (m. p. 200—202°), identical with an authentic specimen prepared from 2-nitroveratraldehyde. It was found impossible to obtain the desired nitrohomoveratrole direct from this aldehyde *via* either its *hydrazone*, m. p. 111—112°, or its *semicarbazone*, m. p. 245°. When 2-nitrohomoveratrole is nitrated further, the 2 : 6-dinitro-derivative is produced.

2 : 6-Dinitro-3-methoxy-*p*-cresol undergoes further nitration when treated with potassium nitrate and sulphuric acid, and yields 2 : 5 : 6-*trinitro*-3-*methoxy*-p-*cresol*, m. p. 83—84° (*acetyl* derivative, m. p. 109—110°). By the usual treatment with methyl sulphate this is converted into 2 : 5 : 6-*trinitrohomoveratrole*, m. p. 100—101°. There being no doubt that this compound has the given constitution, Robinson's product (m. p. 73—74°, *loc. cit.*) must be an isomeride, and her explanation of its formation is unsound.

The three 6-mononitro-compounds referred to above all dissolve in concentrated sulphuric acid to red solutions, differing thus from their isomerides and congeners. The same property is shown by similarly constituted compounds, *e.g.*, 6-nitrohomopiperol, and it appears to be a general rule that the 6-nitro-derivatives of 3 : 4-dialkoxy-(methylenedioxy- or -4-acyloxy-)compounds show this behaviour.

In the light of the above results the general problem of substitution in this series is reviewed, with copious citation from the literature, the recent work of Perkin and Robinson being given particular attention. Jones and Robinson's rule (J.C.S., 1917, **111**, 903) is amplified by the following statements: (i) benzene derivatives of the type 1-alkyl-3-alkoxy-4-alkoxy- or -acyloxy-benzene (methylenedioxy- behaves as di-alkoxy-) are always substituted first in the 6-position; (ii) if the group in position 1 is unsaturated, *e.g.*, aldehydic, 6-substitution still preponderates; (iii) if the group in position 4 is hydroxyl, it exerts its normal influence, and substitution takes place in position 5, *i.e.*, *ortho* to the hydroxy-group. Contrary to the implication of Bain, Perkin, and Robinson (*ibid.*, 1914, **105**, 2396, 2403), 2-nitropiperonal has not yet been prepared. W. A. SILVESTER.

Mono- and di-methoxypicric acids and their chlorides. H. H. SCHLUBACH and F. MERGENTHALER (Ber., 1925, **58**, [*B*], 2732—2736).—The free phenyl radical is known to be capable of only a very transitory existence (cf. Wieland, Popper, and Seefried, A., 1922, i, 772; Schlubach and Goes, *ibid.*, 1204). In the hope of increasing its stability to such an extent as to render possible its isolation, the influence of substituents has been examined. The analogy between the effect of the introduction of phenyl groups in methyl chloride and that of nitro-groups in chlorobenzene suggests a close analogy between 1 : 3 : 5-trinitrobenzene and triphenylmethane. Examination of *M* of hexanitrodiphenyl in boiling nitrobenzene gives, however, no indication of the dissociation of the compound into free radicals. The further introduction of methoxy-groups into picryl chloride has therefore been examined, but their effect appears to be stabilising, since the electrical conductivity of the methoxypicric acids and their chlorides is less than that of picric acid and picryl chloride, respectively.

Tetranitrophenol, m. p. 139°, is converted by methyl-alcoholic sodium methoxide at the atmospheric temperature into 2 : 4 : 6-*trinitro*-3-*methoxyphenol*, m. p. 87·5°. Attempts to replace the hydroxy-group by chlorine by means of phosphorus pentachloride were unsuccessful. 1-*Chloro*-2 : 4 : 6-*trinitro*-3-*methoxybenzene*, m. p. 86°, was therefore prepared by treating *m*-chloroanisole with nitric acid (*d* 1·51) and concentrated sulphuric acid. 1 : 3 : 5-Trinitrobenzene is converted by sodium methoxide into 3 : 5-dinitroanisole, which is readily demethylated by aluminium chloride to 3 : 5-dinitrophenol, m. p. 123—124°. A solution of this substance in concentrated sulphuric acid is slowly added to a mixture of nitric acid (*d* 1·51) and concentrated sulphuric acid at −15°, whereby 2 : 3 : 4 : 5 : 6-pentanitrophenol is obtained in 52% yield; it is converted by sodium methoxide into 2 : 4 : 6-trinitro-3 : 5-dimethoxyphenol, m. p. 76·5° (yield 70%). The direct conversion of the latter phenol into the corresponding chloride could not be accomplished. Trichlorodinitrobenzene was therefore converted by methyl-alcoholic sodium methoxide into 1-*chloro*-2 : 4-*dinitro*-3 : 5-*dimethoxybenzene*, m. p. 220°, which was further nitrated to 1-*chloro*-2 : 4 : 6-*trinitro*-3 : 5-*dimethoxybenzene*, m. p. 88·5°. H. WREN.

Bromophenols. XII. Bromo- and bromonitro-ethers of pyrogallol. M. KOHN and S. GRÜN (Monatsh., 1925, **46**, 75—90; cf. A., 1925, i, 1265).—In the preparation of pyrogallol trimethyl ether by the action of methyl sulphate in alkaline solution, the addition of a small proportion of sodium hyposulphite prevents excessive atmospheric oxidation, thereby improving the quality of the crude product. Whilst the action of 1 mol. of bromine in carbon tetrachloride solution on 1 mol. of pyrogallol trimethyl ether does not lead to a single substance, 4-*bromopyrogallol trimethyl ether*, b. p. 260—266°, can be obtained from the trimethyl ether by application of Rosenmund's method (cf. A., 1923, i, 1095). This is converted, by the action of cold, fuming nitric acid, into 4-*bromo*-5 : 6-*dinitropyrogallol trimethyl ether*, pale yellow, m. p. 134—135°. Bromination of pyrogallol trimethyl ether, or of the above 4-bromo-derivative, in carbon tetrachloride, affords 4 : 6-*dibromopyrogallol trimethyl ether*, b. p. 294—296°/748 mm., and this, when treated with nitric acid in acetic acid solution, yields 5-*nitro*-4 : 6-*dibromopyrogallol trimethyl ether*, m. p. 110°, monoclinic prisms, $a : b : c = 1·81668 : 1 : 1·12290$, $\beta = 90°\ 10'\ 47''$. When treated with hydrobromic acid in glacial acetic acid, it is converted into tribromopyrogallol (cf. Hlasiwetz, Annalen, 1867, **142**, 249). Treatment of 5-nitropyrogallol trimethyl ether (cf. Will, A., 1888, 457) with hydrobromic acid in acetic acid affords 5-nitropyrogallol (cf. Barth, Monatsh., 1880, **1**, 882). 5-Nitropyrogallol forms monoclinic needles or prisms, showing very high double refraction ($\beta - \alpha = 0·245$ for sodium light) (cf. von Lang, Chem. Kryst., **4**, 81; Sitzungsber. Akad. Wiss. Wien, 1880,

II, **82**, 1038). Pyrogallol 1 : 3-dimethyl ether is converted by the action of bromine into 4 : 5 : 6-*tribromopyrogallol* 1 : 3-*dimethyl ether*, m. p. 134° (*benzoyl* derivative, m. p. 130—131°; *sodium* and *potassium* salts). This forms monoclinic, doubly refracting prisms, for which detailed crystallographic data are appended. Methylation with methyl sulphate affords the corresponding trimethyl ether. 4 : 5-*Dibromopyrogallol* 1 : 3-*dimethyl ether*, m. p. 75—76° (*benzoyl* derivative, m. p. 122—123°), is obtained by the action of bromine in carbon tetrachloride on pyrogallol 1 : 3-dimethyl ether. It yields 4 : 5-*dibromopyrogallol trimethyl ether*, b. p. 308—313°/748 mm., on methylation, and the latter, on treatment with nitric acid in acetic acid, affords 6-*nitro*-4 : 5-*dibromopyrogallol trimethyl ether*, m. p. 84—86°.

F. G. Willson.

Condensation of phenol ethers with carbinols. T. Széki (Acta R. Univ. Hungar. Francisco-Josephinæ, 1925, **2**, 5—10; cf. A., 1924, i, 165).—Benzhydrol and various other aromatic carbinols condense readily with di- and tri-methoxybenzenes in glacial acetic acid solution under the influence of hydrogen chloride. From benzhydrol and the three isomeric dimethoxybenzenes 2 : 4-, 3 : 4-, and 2 : 5-dimethoxytriphenylmethanes are obtained, whilst phenyl-*o*-tolylcarbinol yields 2 : 4-*dimethoxydiphenyl*-o-*tolylmethane*, $CHPh(C_7H_8)\cdot C_6H_3(OMe)_2$, m. p. 115°, 3 : 4-*dimethoxydiphenyl*-o-*tolylmethane*, m. p. 84°, and with 1 : 2 : 4-trimethoxybenzene 2 : 4 : 5-*trimethoxydiphenyl*-o-*tolylmethane*, m. p. 100°. *m*-Dimethoxybenzene with phenyl-α-naphthylcarbinol yields 2 : 4-*dimethoxydiphenyl*-α-*naphthylmethane*, m. p. 132°, and with 2 : 4 : 5-trimethoxyphenyl-α-naphthylcarbinol, 2 : 4 : 5 : 2′ : 4′-*pentamethoxydiphenyl*-α-*naphthylmethane*, m. p. 120°. 1 : 2 : 4-Trimethoxybenzene also gave rise to the following: β-2 : 4 : 5-*trimethoxyphenyl*-β-1-*naphthylpropane*, $CMe_2[C_6H_2(OMe)_3]\cdot C_{10}H_7$, m. p. 118°, from dimethyl-α-naphthylcarbinol; *benzoyl*-2 : 4 : 5-*trimethoxydiphenylmethane*, $CHPhBz\cdot C_6H_2(OMe)_3$, m. p. 147·5°, from benzoin; *benzoyl*-2 : 4 : 5-*trimethoxytriphenylmethane*, $CPh_2Bz\cdot C_6H_2(OMe)_3$, m. p. 163°, from phenylbenzoin; αα-*diphenyl*-α-2 : 4 : 5-*trimethoxyphenylethane*, $CPh_2Me\cdot C_6H_2(OMe)_3$, m. p. 121°, from diphenylmethylcarbinol; αβ-*diphenyl*-α-2 : 4 : 5-*trimethoxyphenylethane*, $CH_2Ph\cdot CHPh\cdot C_6H_2(OMe)_3$, m. p. 82°, from phenylbenzylcarbinol, and αβ-*diphenyl*-β-2 : 4 : 5-*trimethoxyphenylpropane*, $CPhMe[C_6H_2(OMe)_3]\cdot CH_2Ph$, m. p. 111°, from phenylbenzylmethylcarbinol.

G. M. Bennett.

Syntheses in the *p*-cymene series from *iso*propyl alcohol. III. Syntheses by means of magnesium cuminyl chloride. L. Bert (Bull. Soc. chim., 1925, [iv], **37**, 1577—1591; cf. Blanc, A., 1923, i, 549).—*p*-Cuminol is most advantageously prepared by the action of oxygen on magnesium cuminyl chloride and treating the product with dilute hydrochloric acid. p-iso*Propylphenylacetaldehyde* was prepared by condensing ethyl orthoformate with magnesium cuminyl chloride and subsequent treatment with hydrochloric acid. It has b. p. 243°, 120°/15 mm., *semicarbazone*, m. p. 181°. The following *p*-cuminyl esters were prepared: *formate*, b. p. 120°/12 mm.; *acetate*, b. p. 136°/16·5 mm., d_4^{25} 0·995, n_D^{25} 1·497; *propionate*, b. p. 142·5—143·5°/15 mm., $d_4^{19\cdot5}$ 0·985, $n_D^{19\cdot5}$ 1·500; *butyrate*, b. p. 143—144°/15 mm., d_4^{7} 0·982, n_D^{7} 1·504; iso*butyrate*, b. p. 146°/17 mm., d_4^{8} 0·983, n_D^{8} 1·506; *valerate*, b. p. 168°/22 mm., d_4^{20} 0·959, n_D^{20} 1·490; *benzoate*, b. p. 220°/20·5 mm., d_4^{19} 1·076, n_D^{19} 1·555; *phenylacetate*, b. p. 222°/18·5 mm., $d_4^{19\cdot5}$ 1·044, $n_D^{19\cdot5}$ 1·544; and the following esters of *p*-cumylacetic acid: *propyl*, b. p. 159°/29 mm., d_4^{16} 0·971, n_D^{16} 1·495; iso*propyl*, b. p. 147°/18 mm., d_4^{20} 0·961, n_D^{20} 1·487; *butyl*, b. p. 180°/24 mm., d_4^{16} 0·965, n_D^{16} 1·492; iso*butyl*, b. p. 161°/17 mm., d_4^{19} 0·962, n_D^{18} 1·488; iso*amyl*, b. p. 180°/19 mm., d_4^{25} 0·9555, n_D^{25} 1·489; iso*octyl*, b. p. 199°/17 mm., d_4^{21} 0·929, n_D^{21} 1·481; *benzyl*, b. p. 217°/15·5 mm., $d_4^{25\cdot5}$ 1·055, $n_D^{25\cdot5}$ 1·550; *cuminyl*, b. p. 244°/18·5 mm., d_4^{21} 1·011, n_D^{21} 1·534. Esters of cuminyl alcohol and of cumylacetic acid exhibit high exaltation of molecular refraction, although less than that of esters of *p*-cuminic acid. The m. p. of dicuminyl is 58°.

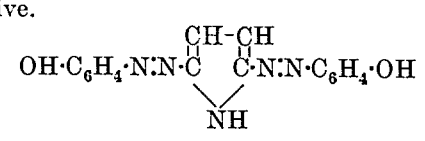
H. J. Evans.

Tautomeric forms of hydroxyphenylazocarboxylamide. A. Pieroni [with G. Buzzi] (Gazzetta, 1925, **55**, 793—804; cf. A., 1924, i, 772, 774).—The author has prepared isomerides which he regards as the tautomeric compounds *p*-hydroxyphenylazocarboxylamide, $OH\cdot C_6H_4\cdot N{:}N\cdot CO\cdot NH_2$ (I), and *p*-benzoquinonesemicarbazone, $O{:}C_6H_4{:}N\cdot NH\cdot CO\cdot NH_2$ (II),

Compound (I), obtained from *p*-aminophenol through the diazonium chloride and diazonium cyanide, forms red needles, m. p. 172° (gas), and, like its isomeride, is converted by hydrogen peroxide in glacial acetic acid solution into p-*hydroxyphenylazoxycarboxylamide*, $OH\cdot C_6H_4\cdot NO{:}N\cdot CO\cdot NH_2$, m. p. 153° (decomp.).

Compound (II) (cf. Thiele and Barlow, A., 1899, i, 47), prepared by the action of semicarbazide on benzoquinone, forms yellow crystals which become red at 120° and has m. p. 172° (decomp.). It forms a *potassium* derivative, which, when treated with carbon dioxide, gives the original compound and not isomeride (I), and probably has the formula $O{:}C_6H_4{:}N\cdot NK\cdot CO\cdot NH_2$. When gently heated with water, compound (II) is converted into (I).

In general, *p*-hydroxyphenylazoxycarboxylamide behaves like other azoxyamides. Alkali decomposes it thus: $OH\cdot C_6H_4\cdot NO{:}N\cdot CO\cdot NH_2 \longrightarrow OH\cdot C_6H_4\cdot NO{:}NH + CO_2 + NH_3$. With pyrrole in an alkaline medium it forms the *bisazo*-derivative (III), and with bromine in acetic acid solution it yields 3 : 5-*dibromo*-p-*hydroxyphenylazoxycarboxylamide*, m. p. 212°, which in an alkaline medium reacts with β-naphthol to form 3 : 5-*dibromo*-p-*hydroxybenzeneazo*-β-*naphthol*, m. p. 232°, and with pyrrole to form the *bisazo*-derivative.



(III.)

Both the above bisazopyrrole derivatives dissolve in dilute alkali solution to give intensely blue liquids, which, when treated with an acid, even with carbonic

acid in the case of the non-brominated compound, become orange-yellow and deposit the deep red bisphenolazopyrroles. The sensitiveness of compound III as an indicator approaches that of litmus, the bromo-derivative being slightly more acidic.

T. H. POPE.

Comparative study of azo dyes made with H-acid and acetyl-H-acid. W. W. LEWERS and A. LOWRY.—See B., 1926, 85.

Azo colouring matters. BRITISH DYESTUFFS CORP., LTD., J. BADDILEY, J. HILL, and A. RILEY.—See B., 1926, 85.

Ring systems containing a *para*-bridge. G. HELLER (J. pr. Chem., 1925, [ii], **111**, 368—372).—When *benzoyl*-p-*benzamidobenzoylhydrazine*, m. p. 262° (decomp.), is heated with acetic anhydride, acetylation and ring formation take place with formation of a *substance*, $C_{23}H_{19}O_4N_3$, m. p. 226°. *p*-Aminobenzoylhydrazine evolves ammonia at 280° with formation of a *substance*, $(C_7H_6ON_2)_x$, m. p. 312° (*acetyl* derivative, m. p. 340°). It is thought that this substance, which separates from water as $C_7H_6ON_2,0{\cdot}5H_2O$, contains a *para*-bridge and probably has the constitution of p-*benzo*iso*pyrazolone*, $C_6H_4<^{NH}_{CO}>NH$ (cf. Thode, A., 1904, i, 347). *Ethyl* p-*hydrazinobenzoate*, m. p. 118° (*acetyl* derivative, m. p. 148—149°), is described. R. W. WEST.

Naphthenic acids. M. NAPHTALI (Chem. Umschau, 1926, **23**, 1—4).—I.—Oxidation with hydrogen peroxide (Dakin's synthesis). Crude naphthenic acid (*d* 0·9716, acid number 267, unsaponifiable matter 6·14%) was freed from unsaponifiable matter, converted into the ammonium salt, and oxidised with 30% hydrogen peroxide. The oily oxidation products (acid number 61·3) contained a small quantity of a "ketone," a brown, viscous mass. The acid number after removing the "ketone" was raised to 61·73, and after removing "hydroxy-acids," obtained by boiling with 0·5*N*-alcoholic potassium hydroxide, the acid number was 67·67. This depression of the acid number to about one-fourth of the expected value was not due to lactone or ketone formation, condensation, or polymerisation, for the oxidised naphthenic acid yielded a copper salt containing 12% of copper, whilst copper naphthenate $(C_{12}H_{21}O_2)_2Cu$, corresponding with the acid number 283, requires 13·4% Cu, whereas the copper salt of a monobasic polynaphthenic acid, corresponding with the acid number 67, requires 3·67% Cu, and that of a dibasic polynaphthenic acid requires 7·33% Cu. The naphthenic acid regenerated from the copper salt had an acid number of 66·65.

II.—Oxidation with permanganate or nitric acid (Tütünnikow's reaction). In spite of statements to the contrary, it is held that the Tütünnikow reaction (the formation of a green solution of copper naphthenate in light petroleum or benzene), for which directions are given, can in general be used for detecting naphthenic acids in presence of fatty acids, provided that the latter have been previously removed by oxidation with potassium permanganate. Linoleic acid, however, is not oxidised by permanganate, yet gives the green light petroleum reaction, thus vitiating the utility of the test. It can, however, be oxidised by careful treatment with nitric acid (*d* 1·35—1·4), after which the general test can be applied. J. S. H. DAVIES.

Organic peroxides. IX. Hydrolysis (and aminolysis) of diacyl peroxides. Iodometric determination of benzoyl peroxide. H. GELISSEN and P. H. HERMANS (Ber., 1926, **59**, [*B*], 63—68; cf. this vol., 63, and previous abstracts).—Benzoyl peroxide is only very slowly hydrolysed when dissolved in aqueous acetone at 13°; in solution, however, it reacts instantaneously with potassium iodide with quantitative liberation of iodine. In aqueous suspension, slow liberation of iodine occurs by the dissolved portion of peroxide; the reaction is restricted by acetic and, notably, by hydrochloric acids. Addition of a solution of benzoyl peroxide in acetone to neutral potassium bromide solution causes immediate separation of bromine, which is set free slowly if the solution is acidified with hydrochloric acid. Similar results are obtained in aqueous alcoholic solution. In anhydrous acetone, benzoyl peroxide and sodium iodide immediately liberate iodine. The reaction is not regarded as an instance of true oxidation (accompanied by liberation of oxygen), since rupture occurs between the two halves of the molecule; when diacyl peroxides behave as oxidising agents the action is preceded by hydrolysis, in which rupture occurs between the carbonyl group and the oxygen bridge, with production of a per-acid (cf. Freer and Novy, A., 1902, i, 368; Clover and Richmond, A., 1903, i, 396).

Wieland's conception of the dialkyl and diacyl peroxides as dehydrogenating agents (A., 1921, i, 890) is based on the behaviour of benzoyl peroxide towards quinol in the presence of ether and hydrogen activators, but his conclusions appear valid only if complete absence of moisture can be assured, and are not in harmony with the observation that hydrogen bromide and iodide do not react with diacyl peroxides more readily than the corresponding salts.

Hydrolysis of dibenzoyl peroxide is very markedly accelerated by the presence of alkali alkoxide or hydroxide. Similarly, ammonia causes rapid conversion of benzoyl peroxide in the presence of acetone or acetone and water into benzamide and perbenzoic acid; the latter compound subsequently oxidises any excess of ammonia to nitrogen without apparent production of hydroxylamine.

Benzoyl peroxide is rapidly and accurately determined by dissolving the sample (0·2 g.) in pure acetone (10 c.c.), adding 3 c.c. of a concentrated aqueous potassium iodide solution (which may be faintly acidified), diluting with water, and immediately titrating the liberated iodine. H. WREN.

Preparation of benzoyl hydroperoxide (perbenzoic acid). J. LEVY and R. LAGRAVE (Bull. Soc. chim., 1925, [iv], **37**, 1597—1600).—Pure benzoyl peroxide, 20 g., is dissolved in 300 c.c. of dry toluene and the solution cooled below −5°. To this is added a solution of 4 g. of sodium in 85 c.c. of absolute alcohol cooled to 0°. The whole is shaken vigorously and treated with ice-water until further addition

ceases to clarify the mixture. The toluene is decanted and the aqueous solution extracted with ether to remove ethyl benzoate; the residue is cooled and treated with dilute sulphuric acid, which precipitates the perbenzoic acid as an oil. This is dissolved in chloroform and the resulting solution stored for use. Ethereal solutions are as stable as those in chloroform, but are much less active as oxidising agents.

H. J. EVANS.

Alkamine esters of *N*-substituted *p*-aminobenzoic acids. FARBW. VORM. MEISTER, LUCIUS, U. BRÜNING.—See B., 1926, 107.

Photochemistry of some derivatives of cinnamic acid. H. STOBBE (Ber., 1925, **58**, [*B*], 2859—2863).—Methyl *trans*-cinnamate, m. p. 33·4°, is converted to a small extent by protracted exposure to sunlight into methyl α-truxillate and Liebermann's poly-ester, the former of which is derived from the solid cinnamic ester, whereas the latter is produced from the portions melted by the heat of the sun. *trans*-Cinnamamide is converted during 5 months of summer sunshine into α-truxilldiamide to the extent of 75%; a similar result is obtained when a suspension of the amide in hydrochloric acid is used. *trans*-Cinnamanilide remains unchanged after 6 months' exposure in the solid state or suspended in hydrochloric acid. *allo*Cinnamic anhydride is converted into a mixture of 80% *trans*- and 20% *allo*-anhydride without production of β-truxinic anhydride, whereas *trans*-cinnamic anhydride remains unchanged apart from slight resinification. Cinnamaldehyde (cf. Ciamician and Silber, A., 1911, i, 647) yields after 8 months' exposure to sunlight a mixture of 60% unchanged aldehyde, 33% cinnamic acid, and 7% polycinnamaldehyde; the last substance appears to be a tetrameride, which is readily depolymerised to unimolecular cinnamaldehyde by dry distillation. It reduces permanganate in acetic acid solution, but does not yield an oxime or react with ammoniacal silver solution or Schiff's reagent. It appears to stand to cinnamaldehyde in the same relationship as paracetaldehyde to acetaldehyde, and to contain the fourth cinnamaldehyde molecule united in such a manner that the aldehydic group is involved. α-Bromocinnamic acid remains unchanged to the extent of 91% after 7 months' exposure to sunlight or 375 hrs.' to the light of the mercury vapour lamp; the residue is converted by autoxidation into oxalic acid, benzoic acid, and free bromine. Resinification does not occur; traces of a polymeride could not be detected.

H. WREN.

Reactions of ethyl aminocinnamates with bromine. H. W. UNDERWOOD and E. L. KOCHMANN (J. Amer. Chem. Soc., 1926, **48**, 254—257).—Treatment of ethyl *o*-aminocinnamate with 4 mols. of bromine in chloroform affords a *perbromide*, $C_{11}H_{11}O_2NBr_7$, dark red, which is converted on recrystallisation from acetic acid and alcohol into *ethyl* α : β : 3 : 5-*tetrabromo*-2-*aminohydrocinnamate* [*ethyl* αβ-*dibromo*-β-(3 : 5-*dibromo*-2-*aminophenyl*)*propionate*], light yellow, m. p. 251—253°, the latter being the product obtained similarly when the bromine applied is limited to 1 mol. Ethyl *m*-aminocinnamate and 4 mols. of bromine afford similarly *ethyl* αβ-*dibromo*-β-(2 : 4 : 6-*tribromo*-3-*aminophenyl*)*propionate*, m. p. 145°, whilst the application of 2 mols. of bromine yields *ethyl* 2 : 4 : 6-*tribromo*-3-*aminocinnamate*, m. p. 110°, from which the corresponding *tribromoaminocinnamic acid* is obtained on hydrolysis with alcoholic potassium hydroxide. Ethyl *p*-aminocinnamate and 8 mols. of bromine yield a *substance*, $C_{11}H_{12}O_2NBr_5$, which, when recrystallised from acetic acid, is converted into an *ethyl* (?)-*bromo*-β-(3 : 5-*dibromo*-4-*aminophenyl*)*propionate*, m. p. 112·5°, and this, when treated with alcoholic potassium hydroxide, affords an acid *solid*, $C_9H_7O_2NBr_2$, decomp. at m. p. Limitation of the bromine in the last bromination to 2 mols. affords tarry products.

F. G. WILLSON.

Reactions of nitroso-derivatives with unsaturated compounds. III. Dinitrones corresponding with α-diketonic acids. L. ALESSANDRI (Gazzetta, 1925, **55**, 729—744; cf. A., 1924, i, 968).—Phenylpropiolic acid (1 mol.) and nitrosobenzene (slightly more than 2 mols.) are dissolved in ether and kept in the dark. After 10 months the mixture yields crystals, m. p. 170° (decomp.), but the amount is insufficient for further investigation. Unaltered phenylpropiolic acid and azoxybenzene are also isolated. When ethyl phenylpropiolate (1 mol.) and nitrosobenzene (2 mols.) dissolved in chloroform are kept in the dark for 22 days, a dimorphous *dinitrone*, $C_{23}H_{20}O_4N_2$, is isolated; from hot, strong alcohol it separates in orange-yellow prisms, m. p. 143—144°, whilst from cold, dilute alcohol it is obtained in paler silky needles, m. p. 145—146°. Hydroxylamine hydrochloride converts the former product into oximinophenyl*iso*oxazolone. Ethyl *p*-nitrosobenzoate (2 mols.) and ethyl phenylpropiolate (1 mol.) dissolved in acetic acid give, after 15 days in the dark, crystals of a *dinitrone*, $C_{29}H_{28}O_8N_2$, m. p. 188°, which decompose in sunlight. When the same experiment is carried out in chloroform, a small quantity of the same product is obtained, accompanied by *pp'*-dicarbethoxyazoxybenzene. Ethyl phenylpropiolate (1 mol.) and *p*-nitrosodimethylaniline (2 mols.) dissolved in chloroform and left in the dark at the ordinary temperature for 1 month yielded: (*a*) a *dinitrone*, m. p. 164° (decomp.), (*b*) *pp'*-tetramethyldiaminoazoxybenzene, (*c*) unaltered nitrosodimethylaniline. The product (*a*) crystallised from alcohol has m. p. 134—135° (slight decomp. at 139°); it appears to be stable to light. Its molecular formula is $C_{27}H_{30}O_4N_4,C_2H_5\cdot OH$, and it probably has the constitution:

$NMe_2\cdot C_6H_4\cdot NO{:}CPh\cdot C(CO_2Et)(OEt)\cdot N(OH)\cdot C_6H_4\cdot NMe_2$.

W. E. ELLIS.

Nitration of β-naphthoic acid and some new amino- and nitro-naphthoic acids. H. A. HARRISON and F. A. ROYLE (J.C.S., 1926, 84—89).—Repetition of the work of Ekstrand (A., 1891, i, 932) shows that at least 95% of the nitration product of β-naphthoic acid is a mixture of the 5- and 8-nitro-derivatives. A trace of 1-nitro-β-naphthoic acid is also formed. The α : 6-, α : 7-, β : 6-, β : 7-, and β : 8-aminonaphthoic acids can all be prepared from the corresponding hydroxynaphthoic acids by heating with ammonia and sulphur dioxide, but the α : 2-

and β : 2-acids yield only α- and β-naphthylamine, respectively.

6-*Amino*-1-*naphthoic acid* is light brown, m. p. 203°; *hydrochloride*; *acetyl* derivative, m. p. 170—172°. 7-*Amino*-1-*naphthoic acid*, light brown, m. p. 223—224°; *hydrochloride*, warty clusters; *acetyl* derivative, m. p. 229—230°. 6-*Amino*-2-*naphthoic acid*, pale yellow, m. p. 225° (cf. Dziewoński, Schoenówna, and Waldmann, A., 1925, i, 1056); *hydrochloride*; *acetyl* derivative, m. p. 230—232°. 7-*Amino*-2-*naphthoic acid*, pale yellow, has m. p. 245°; *acetyl* derivative, m. p. 200—201° (decomp.). The fluorescence of these compounds in various solvents is described. They are all convertible by the method of Veselý (A., 1922, i, 690) into the corresponding nitro-derivatives, of which the following are new: 6-*nitro*-2-*naphthoic acid*, m. p. 310° (*ethyl* ester, m. p. 177°) 7-*nitro*-2-*naphthoic acid*, m. p. 262° (*ethyl* ester, m. p. 131°; cf. Ekstrand, *loc. cit.*). H. E. F. Notton.

Reactions of lactones with aromatic hydrocarbons and aluminium chloride. E. J. King (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 29—30).—Although phthalide might be expected to give diphenylmethane-*o*-carboxylic acid or *o*-benzoylbenzyl alcohol, actually only the former is formed. Diphenylphthalide does not react. Phthalide with naphthalene in benzene solution reacts only with the benzene. In carbon disulphide solution, naphthalene with phthalide or phenylphthalide gives only β-naphthyl derivatives. Coumarin reacts with benzene and aluminium chloride to give a small amount of a *product*, m. p. 82°, which reacts with bromine in the cold to give a *product*, m. p. 112°, indicating that the first compound is unsaturated. J. S. Carter.

α- and β-Naphthoxypropionic acids, their mononitro-derivatives and optical isomerides. E. Fourneau and Balaceano (Bull. Soc. chim., 1925, [iv], **37**, 1602—1628; cf. Fourneau and Sandulesco, A., 1923, i, 35, 572).—Direct nitration of α- and β-naphthoxypropionic acids yields only one mononitro-derivative of each, the 4-derivative from the α-, and the 1-derivative from the β-acid. Condensation of ethyl α-bromopropionate with the sodium salts of mononitronaphthols occurs only in the case of the β-compounds. Resolution of the naphthoxypropionic acids into their optically active components was effected by means of their cinchonine salts; the optical isomerides of the nitro-acids were prepared by nitration of the respective unsubstituted acids. Optical isomerides of the ethyl ester, amides, and anilides of the acids were prepared from the corresponding acid chlorides.

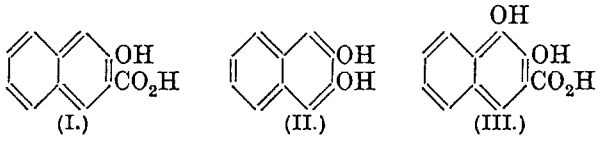
Nitration of active β-naphthoxypropionic acid is accompanied by change of sign and increase of rotatory power; this change does not occur in the case of the α-acid. All the derivatives of active α-naphthoxypropionic acid exhibit the same sign of optical rotation as the acid, but the chlorides and amides of the two β-acids are of opposite sign to the acid from which they are prepared. The esters are of the same sign as the parent acids. Derivatives of the nitro-α-acids are prepared without change of sign; in the case of the nitro-β-acids the chloride is of the same sign as the acid, but gives rise to an amide of opposite sign. The authors point out the frequency with which the value 46·66° occurs in their measurements of optical activity.

The following are described: d- and l-α-*naphthoxypropionamide*, m. p. 192°, racemic mixture, m. p. 152°; d- and l-α-*naphthoxypropionanilide*, m. p. 205°, racemic mixture, m. p. 173°; d- and l-β-*naphthoxypropionic acid*, m. p. 117°, racemic mixture, m. p. 108°, l-*chloride*, d- and l-*ethyl* esters, m. p. 43—44°, racemic mixture, m. p. 52—53°, d- and *l-amides*, m. p. 197°, racemic mixture, m. p. 169°; d- and l-4-*nitro*-α-*naphthoxypropionic acid*, m. p. 141—142°, racemic mixture, m. p. 174°, d-*chloride*, *methyl* ester, m. p. 98°, d- and l-*ethyl* esters, m. p. 55°, racemic mixture, m. p. 60°, d- and l-*amides*, m. p. 225°, racemic mixture, m. p. 201—202°, d- and l-*anilides*, m. p. 215°, racemic mixture, m. p. 186°, 4-*amino*-α-*naphthoxypropionic acid*, m. p. 248—250° (decomp.); d- and l-1-*nitro*-β-*naphthoxypropionic acid*, m. p. 179°, racemic mixture, m. p. 193°, d- and l-*ethyl* esters, m. p. 102°, racemic mixture, m. p. 83°, *methyl* ester, m. p. 74°, d- and l-*amides*, m. p. 190°, racemic mixture, m. p. 157°, d- and l-*anilides*, m. p. 205°, racemic mixture, m. p. 171°. H. J. Evans.

Chemistry and pharmacology of a new benzyl compound (betilon). U. Hintzelmann, G. Joachimoglu, and H. Ohle (Biochem. Z., 1925, **164**, 126—134).—"Betilon," $CHPh(O{\cdot}SO_3Na){\cdot}CO_2{\cdot}CH_2Ph$, may be crystallised by precipitation of its solution in 95% alcohol with ether or of its acetone solution with benzene. It contains 1 mol. of water of crystallisation which is removable on keeping in a vacuum over calcium chloride, but which is readily reabsorbed on keeping in moist air, m. p. 106°; *barium* salt ($+6H_2O$) melts at 90° in its own water of crystallisation; *brucine* salt, m. p. 212° (decomp.); *strychnine* salt, m. p. 212—214° (decomp.). "Betilon" gives with dilute acids mandelic and sulphuric acids and benzyl alcohol, whilst with 0·02*N*-sodium hydroxide it is converted in ½ hr. completely into benzyl alcohol and sodium mandelic sulphate. The pharmacological properties of "betilon" are investigated.

P. W. Clutterbuck.

[Constitution of naphthalene and its derivatives.] K. Fries (Ber., 1925, **58**, [*B*], 2845—2851).—The constitution (I) has been assigned to 2-hydroxy-3-naphthoic acid by Lesser, Kranepuhl, and Gad (A., 1925, i, 1424) on account of its colour



and tendency to pass into ββ-quinonoid derivatives, whereas 2 : 3-dihydroxynaphthalene, which cannot be converted into 2 : 3-naphthaquinone, is formulated according to (II). 2-Hydroxy-3-naphthoic acid is, however, readily converted into 3-amino-β-naphthol identical with the product derived from 2 : 3-dihydroxynaphthalene; also, there does not appear to be in the literature any indication of the occurrence of ββ-derivatives of naphthalene in isomeric forms. Further, if the structure (I) be

assumed, 2-hydroxy-3-naphthoic acid must behave towards substituents in the same manner as 2-hydroxy-1-naphthoic and 1-hydroxy-2-naphthoic acids; this is not the case, since with 2-hydroxy-3-naphthoic acid substitution occurs readily and initially in position 1, the compound behaving like a true derivative of β-naphthol in which the presence of the group $-\overset{1}{C}H{:}\overset{2}{C}(OH)-$ is undoubted by Lesser, Kranepuhl, and Gad. In analogy with (I) the structure (III) must be assigned to the coloured 1 : 2-dihydroxy-3-naphthoic acid, which, however, is very readily oxidised to 1 : 2-naphthaquinone-3-carboxylic acid. All attempts to explain the colour of these hydroxy-acids and their derivatives by isomerisation to 2 : 3-quinonoid compounds appear inadmissible, since they do not take account of the extreme difficulty of producing 2 : 3-dihydronaphthalene or its derivatives; in spite of many efforts, an individual of this class has never been isolated.

[With F. HASS.]—Attempts to convert 2-hydroxy-3-naphthamide into 3-amino-β-naphthol by Hofmann's method are unsuccessful, since bromination occurs in the nucleus with production of 1-bromo-2-hydroxy-3-naphthamide (cf. Lesser, Kranepuhl, and Gad, *loc. cit.*). 2-Hydroxy-3-naphthoyl chloride, m. p. 99° (corresponding amide, m. p. 217°), is conveniently prepared by the gradual addition of potassium 2-hydroxy-3-naphthoate to a mixture of benzene and thionyl chloride. If 2-hydroxy-3-naphthoic acid is warmed with an excess of thionyl chloride, 1-*chloro*-2-*hydroxy*-3-*naphthoyl chloride*, m. p. 128°, is produced; *methyl* 1-*chloro*-2-*hydroxy*-3-*naphthoate*, m. p. 116°, and 1-*chloro*-2-*hydroxy*-3-*naphthamide*, m. p. 225°, are described. 2-Hydroxy-3-naphthoic acid and ethyl chloroformate afford the corresponding *ethylcarbonato*-derivative, m. p. 141°, from which the *chloride*, m. p. 65°, *methyl* ester, m. p. 60°, and *amide* are derived; the last compound passes when heated above 100° or boiled with glacial acetic acid into 2 : 4-*diketo*-3 : 4-*dihydro*lin-1 : 3-*naphthoxazine*,

$$C_{10}H_6\!<\!\begin{matrix}O-CO\\ CO\cdot NH\end{matrix}\!>$$

m. p. 300°. 2-Hydroxy-3-naphthhydrazide is converted by nitrous acid into 2-*hydroxy*-3-*naphthazide*, m. p. 133° (decomp.), which when heated in dry benzene affords 2-*hydroxy*-3-*naphthylcarbimide*, m. p. 205°, and is transformed by boiling methyl alcohol into *methyl* 2-*hydroxy*-3-*naphthylcarbamate*, m. p. 201°; the carbimide and carbamate when acted on by potassium hydroxide and concentrated hydrochloric acid, respectively, pass into 3-amino-β-naphthol, m. p. 235°, identical with the product described in the literature. 1 : 6-*Dibromo*-2-*hydroxy*-3-*naphthoic acid*, m. p. 246° (decomp.), is prepared by bromination of 1-bromo-2-hydroxy-3-naphthoic acid in warm, glacial acetic acid; the *sodium* salt is described. Further bromination in acetic acid in the presence of sodium acetate gives a keto-bromide; otherwise, 1 : 6 : 8-*tribromo*-3-*naphthoic acid*, m. p. 320°, is produced. H. WREN.

Photosyntheses. I. αββ-Triphenyl-β-hydroxypropionic acid. R. DE FAZI (Atti R. Accad. Lincei, 1925, [vi], **2**, 266—269; cf. Paternò, A., 1911, i, 65).—The photo-reactions of benzophenone with butyric acid and phenylacetic acid, respectively, both produce carbon dioxide and are therefore believed to be analogous. In the latter case, by opening the reaction tube, removing the crystalline deposit of αββ-triphenyl-β-hydroxypropionic acid and benzophenone, and restarting the action, successive deposits of this mixture are obtained; the reaction is balanced. Its course is believed to be: (i) $Ph_2CO+CH_2Ph\cdot CO_2H = CPh_2(OH)\cdot CHPh\cdot CO_2H$; (ii) $2CH_2Ph\cdot CO_2H = CH_2Ph\cdot CO_2\cdot CH_2Ph + CO_2 + H_2$; (iii) $2Ph_2CO + H_2 = CPh_2(OH)\cdot CPh_2\cdot OH$. The isolation of only a small quantity of benzyl phenylacetate is explained by its reacting on its own account with benzophenone (cf. Paternò and Forlì-Forti, A., 1911, i, 66).

W. E. ELLIS.

Possible enhanced activity of newly-formed molecules. F. R. GOSS and C. K. INGOLD (J.C.S., 1925, **127**, 2776—2781).—Several instances are discussed of substances which, although they appear to be the obvious intermediates in a reaction, nevertheless fail to react in the expected manner when tested under the conditions of the reaction in question. These facts tend to support the suggestion in the title of the paper.

The formation of ethyl *cyclo*butane-1 : 4-dicarboxylate (10%) in the action of sodium ethoxide on ethyl α-chloropropionate might involve as intermediates either ethyl acrylate or ethyl γ-chloro-α-methylglutarate,

$$CHMe(CO_2Et)\cdot CH_2\cdot CHCl\cdot CO_2Et,$$

yet under similar treatment ethyl acrylate yields ethyl β-ethoxypropionate and ethyl α-methyleneglutarate (9 : 1), whilst the chloromethylglutaric ester yields a mixture of its lactonic ester, ethyl α-methylglutaconate, *trans-cyclo*propanedicarboxylic acid, and *α'-ethoxy-α-methylglutaric acid*, a liquid (*ethyl* ester, b. p. 126—129°/12—14 mm.), but in neither case is any of the *cyclo*butanedicarboxylic acid produced. Although the unsaturated linking is not normally semi-polar, it is suggested that this may be so in the newly-formed molecule of acrylic ester.

The conversion of α-campholenic acid (b. p. 139°/1 mm.) by heating with silver oxide and water into camphor must apparently involve either *cis*- or *trans*-α-campholanic acids (b. p. 140°/1 mm. and 141°/1 mm., respectively), and yet neither of these acids yields any trace of camphor under the same conditions.

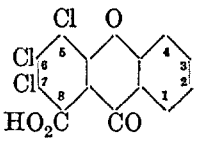
Hydrolysis of 3-methoxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid, $\begin{matrix}CH(CO_2Et)\\ CH(CO_2Et)\end{matrix}\!>\!CMe\cdot OMe$, must apparently give as first product acetosuccinic acid. Actually when 20% hydrochloric acid or 64% potassium hydroxide solutions are used no succinic acid but only lævulic acid is isolated, although the former was to be expected with alkaline hydrolysis. On the other hand, the action of concentrated alkali on 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylic acid yields only succinic and acetic acids, although the same intermediate must be assumed.

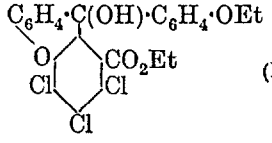
Lastly, the case of Balbiano's acid is cited, since the hydroxytrimethyl*cyclo*propanedicarboxylic acid, which has the correct structure and configuration of an intermediate in the conversion of camphoric into

Balbiano's acid, is nevertheless not convertible into the latter acid. G. M. BENNETT.

Preparation of pyrocatechol-*o*-carboxylic acid. Condensation of pyrocatechol with glycerol. S. KAWAI (Bull. Inst. Phys. Chem. Res., 1926, **5**, 47—49).—A mixture of pyrocatechol, potassium hydrogen carbonate, and glycerol is kept for 1 day and heated in a current of carbon dioxide for 16 hrs. over a phenol bath. 1 : 2-Dihydroxybenzene-3 : 6-dicarboxylic acid, pyrocatechol-*o*-carboxylic acid, and pyrocatechyl glyceryl ether were isolated from the reaction product. Under the same conditions, no reaction occurred between pyrogallol and glycerol or between mannitol and pyrocatechol. K. KASHIMA.

o-Hydroxybenzoyl-o-tetrachlorobenzoic acid, *iso*phenoltetrachlorophthalein, and some of their derivatives. W. R. ORNDORFF and T. PARSONS (J. Amer. Chem. Soc., 1926, **48**, 283—288; cf. A., 1925, i, 35).—o-2′-*Hydroxybenzoyltetrachlorobenzoic acid*, m. p. 210° (*diacetate*, m. p. 168°), is obtained by condensing tetrachlorophthalic anhydride with phenol in tetrachloroethane in presence of aluminium chloride (cf. Ullmann and Schmidt, A., 1920, i, 53). When heated with 30% aqueous sodium hydroxide, both the above yield 5 : 6 : 7-*trichloroxanthone*-8-*carboxylic acid* (I), m. p. 262—265° (decomp.) (*barium* and

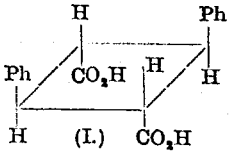
(I.) 



(II.)

sodium salts). When heated with phenol and stannic chloride at 95—100°, *o*-2′-hydroxybenzoyltetrachlorobenzoic acid gives iso*phenoltetrachlorophthalein*, m. p. 293° [*diacetate*, m. p. 189°; *dibenzoate*, m. p. 245°; *dimethyl ether*, m. p. 183° (cf. Orndorff and Black, A., 1909, i, 389)], which is an indicator giving a reddish-violet end-point at p_H 9·2. Tetrachlorofluoran, m. p. 298° (decomp.) (cf. Orndorff and Black, *loc. cit.*), is obtained as a by-product. The compound obtained by the action of ethyl iodide on tetrachlorofluoran in presence of alcoholic potassium hydroxide (*loc. cit.*) has probably the constitution (II). Phenoltetrachlorophthalein has m. p. 307°. F. G. WILLSON.

Configuration and degradation of ε-truxillic acid. X. R. STOERMER, J. NEUMAERKER, and R. SCHMIDT (Ber., 1925, **58**, [*B*], 2707—2718; cf. Stoermer and Bachér, A., 1922, i, 830; 1924, i, 400).—A detailed account is given of the reasons for revising the configuration assigned previously to ε-truxillic acid and regarding it as a *cis*-compound (I) despite its inability to yield a unimolecular anhydride.



ε-Truxillic acid is converted by piperidine at 160° into a mixture of ε-*truxilldipiperidide*, m. p. 189°, and ε-*truxillpiperidic acid*, $C_{23}H_{25}O_3N$, m. p. 220° (*methyl* ester, m. p. 91°; *ethyl* ester, m. p. 110°). Short treatment of the dipiperidide with alcoholic alkali hydroxide produces ε-truxillpiperidic acid, identical with that obtained directly; the production of an isomeric acid could not be detected. Tertiary diols are readily formed by the action of magnesium aryl bromides on truxillic esters. For purposes of comparison, α-*tetraphenyltruxilldiol*, m. p. 262°, and γ-*tetraphenyltruxilldiol*, m. p. 219°, have been prepared. ε-*Tetraphenyltruxilldiol*,

$$OH{\cdot}CPh_2{\cdot}C_4H_4Ph_2{\cdot}CPh_2{\cdot}OH,$$

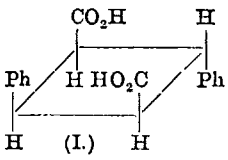
m. p. 219°, gives a *benzoyl* derivative, m. p. 169°. ε-*Tetraethyltruxillidiol*, m. p. 201°, is transformed by phosphoric oxide into an oily product containing unsaturated components with a small amount of a crystalline substance, m. p. 146—147°. Whereas the α-diol, in conformity with its *trans*-configuration, fails to yield an anhydride, dehydration of the γ-diol is readily effected by phosphoric oxide in the presence of benzene, whereby the γ-*diol anhydride*, m. p. 208°, is obtained. Similarly, the ε-diol is transformed by short treatment with zinc chloride into the corresponding *anhydride*, $Ph_2C_4H_4<\begin{matrix}CPh_2\\CPh_2\end{matrix}>O$, m. p. 170°, which is reconverted by alcoholic potassium hydroxide into the ε-diol, or, preferably, by hydrogen bromide into the corresponding *dibromide*, m. p. 126°, which is also obtained from the diol and phosphorus tribromide. The *dichloride*, m. p. 175—176°, is transformed by boiling glacial acetic acid into the ε-diol. The *cis*-nature of the ε-acid is thus established. The following analogous derivatives are described: ε-*tetra*-p-*tolyltruxilldiol*, m. p. 232°, and the corresponding *anhydride*, m. p. 195°, *dichloride*, m. p. 155°, and *dibromide*, m. p. 112°; ε-*tetra*-o-*tolyltruxilldiol*, m. p. 219°, and the *anhydride*, m. p. 146°; ε-*tetra*-p-*anisyltruxilldiol*, m. p. 224°, and the *anhydride*, m. p. 84°; ε-*tetra*-p-*phenetyltruxilldiol*, m. p. 174°, and the *anhydride*, m. p. 92°.

Ammonium ε-*truxillate*, decomp. 186°, is converted at 200—205° into ε-*truxillimide*, m. p. 198°, ε-truxilldiamide, ε-*truxillamic acid*, m. p. 213°, and ε-truxillic acid. The imide is more conveniently prepared by the action of zinc chloride dissolved in boiling glacial acetic acid on the diamide; it is converted by aqueous ammonia into the corresponding -amic acid and diamide, by ethereal ammonia into the diamide; with aniline at 170—180° it affords ε-*truxillamide-anilide*, m. p. 222°. Ethylation of the imide could not be effected through the *sodium* or *potassium* (m. p. 224°) salts. ε-*Truxillethylimide*, m. p. 144°, is, however, obtained by the action of ethyl bromide, ignited potassium carbonate, potassium iodide, and copper powder on a solution of the imide in boiling alcohol; phenylation could not be effected under similar conditions. *Methyl* ε-*truxillamate*, m. p. 145°, and *ethyl* ε-*truxillamate*, m. p. 140—141°, are described. ε-Truxillanilic acid (cf. Stoermer and Emmel, A., 1920, i, 438), m. p. 239°, is conveniently prepared by heating ε-truxillic acid with the theoretically requisite quantity of aniline at 210—220°; the *sodium* and *calcium* salts and the *methyl* ester, m. p. 157°, are described. The acid is converted by acetic anhydride and sodium acetate at 145—150° into ε-*truxillanil*, m. p. 252° (yield 25%). ε-Truxillamic acid is converted at 220—225° into a mixture of ε-truxillic acid and ε-truxilldiamide. The anilic acid undergoes a similar change in the presence of boiling acetic anhydride (in the absence of sodium

acetate, *vide supra*), whilst the amideanilide under like conditions is transformed into diamide and dianilide.

Attempts have been made in the case of the ε-acid to decarboxylate a truxillic acid to a diphenyl-*cyclo*butanemonocarboxylic acid. ε-Truxillamic acid is transformed by sodium hypochlorite into 3-*amino*-2 : 4-*diphenyl*cyclo*butane*-1-*carboxylic acid*, m. p. 188° (decomp.); the corresponding *methyl* ester and the *hydrochloride*, m. p. 244° (decomp.), are described. The methyl ester is transformed by nitrous acid into methyl 3-hydroxy-2 : 4-diphenyl*cyclo*butane-1-carboxylate, which could not be caused to crystallise, and appears to be mixed with considerable amounts of unsaturated *cyclo*butene compounds; it is hydrolysed to 3-*hydroxy*-2 : 4-*diphenylbutane*-1-*carboxylic acid*, anhydrous, m. p. 166—167° (decomp.), and *dihydrate*. Treatment of the ester with phosphorus pentachloride in the presence of ether followed by acting on the chloro-ester with hydriodic acid, zinc dust, and red phosphorus, gives a halogen-free product from which 2 : 4-*diphenyl*cyclo*butane*-1-*carboxylic acid*, m. p. (indef.) 172°, is obtained in small amount after hydrolysis; the product is, however, accompanied by so much *cyclo*butene compound that its individuality is not regarded as placed beyond doubt. Attempts to convert the amino-acid into the halogen-free acid by bromine and nitric oxide yielded a product, m. p. 171—174°, which appears identical with that just described. H. WREN.

γ-Truxillic acid. XI. R. STOERMER and F. FRETWURST (Ber., 1925, **58**, [*B*], 2718—2725).—Further evidence is adduced in favour of the configuration (I), assigned to γ-truxillic acid by Stoermer and Carl (A., 1923, i, 930).



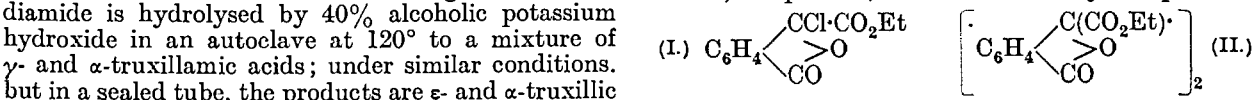
γ-Truxillic anhydride is converted by hot, concentrated aqueous ammonia into *γ-truxillamic acid*, m. p. 240° (slight decomp.), the *calcium* salt of which is described. The acid is converted by boiling 15% hydrochloric acid, or, preferably, by nitrous acid in acetic acid solution, into γ-truxillic acid. Alcoholic potassium hydroxide (20%) hydrolyses the acid mainly to α-truxillic acid, whereas γ-truxillic acid remains unchanged under these conditions. γ-Truxillamic acid is converted by prolonged boiling with a large excess of 10% potassium hydroxide solution into a mixture of little α-truxillic acid, and α- and γ-truxillamic acids, in which the second acid predominates greatly. α-Truxillamic acid under analogous conditions yields a similar mixture, whereas α-truxillic acid remains unchanged. α-Truxilldiamide is hydrolysed by 40% alcoholic potassium hydroxide in an autoclave at 120° to a mixture of γ- and α-truxillamic acids; under similar conditions, but in a sealed tube, the products are ε- and α-truxillic acids. ε-Truxillic acid is obtained in addition to unchanged α-acid from the latter acid and alcoholic potassium hydroxide at 200°. *Methyl γ-truxillamate*, m. p. 154°, and ethyl γ-truxillamate, m. p. (indef.) 135—138°, are described; the latter ester does not appear to be mixed with an isomeride.

γ-Truxillamic acid is very readily resolved into its optical antipodes by morphine in alcoholic solution, from which morphine *l*-γ-truxillamate separates. l-*γ-Truxillamic acid*, m. p. 258—259° (slight decomp.), $[\alpha]_D^{20}$ −11·05° in glacial acetic acid (*methyl* ester, m. p. 153—154°, $[\alpha]_D^{20}$ +8·55° in acetone), and d-*γ-truxillamic acid*, m. p. 258—259° (*ethyl* ester, m. p. 168—169°, $[\alpha]_D^{20}$ −12·78° in acetone), are described.

γ-Truxillimide, m. p. 208°, is most conveniently prepared by heating ammonium γ-truxillamate in an open tube at 245—250° until ammonia ceases to be evolved; α- and γ-truxillamic acids are simultaneously formed in minor amount. Similar products are obtained if the experiment is performed in a sealed tube at 180—200°, but the γ-diamide is also formed in small amount. γ-Truxillimide is not conveniently obtained by acting on γ-truxillamic acid with acetic anhydride, since, even in the presence of anhydrous sodium acetate, *γ-truxillacetamic acid*, m. p. 185°, is formed in considerable quantity; it is hydrolysed by 10% alcoholic potassium hydroxide to γ-truxillamic acid, by 15% hydrochloric acid to γ-truxillic acid. γ-Truxillimide is hydrolysed by sodium carbonate solution or by cold alcoholic potassium hydroxide to γ-truxillamic acid. The *potassium* and *sodium* salts of γ-truxillimide are described. *γ-Truxillanil*, m. p. 194°, is prepared by the action of bromobenzene, copper powder, and potassium iodide on the imide dissolved in boiling benzene. *γ-Truxillethylimide*, m. p. 142°, is similarly obtained. It is hydrolysed to *γ-truxillethylamic acid*, m. p. 217°, which is readily prepared from the γ-anhydride and ethylamine in alcoholic solution; it is reconverted by acetic anhydride and sodium acetate at 160° into γ-truxillethylimide. The action of nitrous acid on γ-truxillethylamic acid in glacial acetic acid affords the corresponding *nitroso*-derivative, m. p. 172—173° (decomp.), which is converted by warm sodium carbonate solution into γ-truxillic acid. γ-Truxillanilic acid similarly yields a *nitroso*-derivative, decomp. 129—130°, which is converted by hydrochloric acid into γ-truxillanilic acid, by potassium hydroxide into γ-truxillic acid. H. WREN.

β-Hydroxy-β-*o*-carboxyphenylpropionic anhydride and β-hydroxy-β-4-hydroxy-*o*-carboxyphenylpropionic acid. CHEM. FABR. WEILER-TER MEER.—See B., 1926, 8.

Esters of bisphthalidecarboxylic acids. A. CORNILLOT (Compt. rend., 1926, **182**, 142—143).—Zinc methyl iodide reacts with ethyl α-chlorophthalide-α-carboxylate (I) (cf. this vol., 168) at 35°, giving two optically inactive stereoisomeric *ethyl bisphthalide-α-carboxylates* (II), the externally compensated isomeride, m. p. 188°, and the internally compensated



one, m. p. 159°, in the proportion of one of the former to two of the latter. Zinc ethyl iodide reacts with the ethyl ester more sluggishly, whilst the methyl ester does not react with either of the organo-zinc compounds. The bisphthalidecarboxylates are readily hydrolysed by alkalis, giving a mixture of phthalonic and phthalide-α-carboxylic acids, separ-

able easily by means of their semicarbazones. The same isomeric bisphthalidecarboxylates are formed on treating the α-chlorophthalide ester with reduced silver in contact with ethyl alcohol. L. F. HEWITT.

Action of ultra-violet rays on aldehydes. Hexahydrobenzaldehyde, phenylacetaldehyde, and hydrocinnamaldehyde. A. FRANKE and F. SIGMUND (Monatsh., 1925, **46**, 61—74).—Hexahydrobenzaldehyde is conveniently prepared by distilling calcium hexahydrobenzoate with calcium formate. Optimum conditions are detailed for this reaction, as well as for the hydrogenation of ethyl benzoate. On exposure to ultra-violet rays, hexahydrobenzaldehyde yields carbon monoxide, *cyclo*hexane, and the dimeride (cf. Wallach and Isaac, A., 1906, i, 563).

Condensation of hexahydrobenzaldehyde with formaldehyde in presence of potassium hydroxide affords 1 : 1-*dimethylol*cyclo*hexane*, m. p. 95°, b. p. 143—144°/10 mm. Phenylacetaldehyde, b. p. 204—208° (cf. Stobbe and Lippold, A., 1915, i, 261), does not evolve carbon monoxide under the influence of ultra-violet rays, but is partly converted into a yellow *oil*, b. p. 220—305°, and a brownish-red, viscous residue. Hydrocinnamaldehyde is also practically unaffected by ultra-violet light. It condenses with formaldehyde in presence of potassium hydroxide with formation of *αγ-dihydroxy-β-benzyl-β-methylolpropane*, m. p. 76°, b. p. 185—203°/4—5 mm. (cf. Hosäus, A., 1893, i, 617; Koch and Zerner, A., 1901, i, 633). F. G. WILLSON.

Catalytic reactions. I. Oxidation of anethole. R. HORIUCHI and S. UYEDA (J. Chem. Soc. Japan, 1924, **45**, 203—209).—The authors have used nitrates of mercury, lead, iron, and copper in the oxidation of anethole to anisaldehyde (Labbé, A., 1900, i, 177). When 1 part of anethole is heated on a sand-bath with 2 parts of glacial acetic acid, 3·5 parts of nitric acid (*d* 1·107), and 0·1 part of nitrate of mercury or lead, a fairly violent reaction occurs at 88° without evolution of nitrogen peroxide; the yield of anisaldehyde is 35—40%, anisic acid 3—5%, and recovered anethole 19—25%, the remainder being resinous substance. The salts of iron and copper have no catalytic action. In these reactions, the decomposition of nitric acid is concluded to be $2HNO_3=H_2O+2N+5O$ through the reactions: $2HNO_3=H_2O+2NO_2+O$; $HgNO_3+2NO_2=Hg(NO_3)_2+NO$; $Hg(NO_3)_2=HgNO_3+NO_2+O$; $NO_2=N+2O$, and $NO=N+O$. In the case of lead nitrate, the presence of an unstable $Pb(NO_3)_4$ is assumed, which may be produced when nitrogen peroxide is passed into nitric acid containing suspended lead peroxide and is soluble in water. The decomposition of nitric acid is therefore the same as in the case of mercurous nitrate: $2HNO_3=H_2O+2N+5O$ through $4HNO_3=2H_2O+4NO_2+2O$, $Pb(NO_3)_2+4NO_2=Pb(NO_3)_4+2NO$, $Pb(NO_3)_4=Pb(NO_3)_2+2NO_2+2O$, $2NO=N_2+2O$, and $2NO_2=N_2+4O$. K. KASHIMA.

Chloro-derivatives of *m*-hydroxybenzaldehyde. H. H. HODGSON and H. G. BEARD (J.C.S., 1926, 147—155; cf. Friedländer, A., 1915, i, 593; Krause, A., 1899, i, 281).—The preparation of chloro-derivatives of *m*-hydroxybenzaldehyde follows similar lines to that of the corresponding bromo-derivatives (A., 1925, i, 674), but chlorination takes place most readily in the 2-position. The 2-monochloro-, the 2 : 6-dichloro-, and the 2 : 4 : 6-trichloro-derivatives can be obtained by regulated chlorination. Monochlorination of *m*-hydroxybenzaldehyde in various solvents yields almost completely 2-*chloro*-3-*hydroxybenzaldehyde*, m. p. 139·5°, identical with the product obtained in the usual way from 2-nitro-3-hydroxybenzaldehyde (*acetyl* derivative, m. p. 62°; *benzoyl* derivative, m. p. 88°; *oxime*, m. p. 149°; orange-red p-*nitrophenylhydrazone*, m. p. 244—245°; pale yellow *semicarbazone*, m. p. 236—237°). 2-*Chloro*-3-*methoxybenzoic acid* has m. p. 160°. 4-*Chloro*-3-*hydroxybenzaldehyde*, from 4-nitro-3-hydroxybenzaldehyde, has m. p. 121° (*oxime*, hydrated, decomp. 106—110°, anhydrous, m. p. 126°; violet-red p-*nitrophenylhydrazone*, m. p. 226—227°; pale yellow *semicarbazone*, m. p. 238—239°). 4-*Chloro*-3-*methoxybenzoic acid* has m. p. 215—216°. 2-Chlorobenzaldehyde gives on nitration 2-chloro-5-nitrobenzaldehyde, m. p. 78—79° (cf. Erdmann, A., 1893, i, 160). 2-Chloro-5-nitrobenzaldoxime gives on reduction 2-*chloro*-5-*aminobenzaldoxime*, m. p. 159—160°, which by hydrolysis, diazotisation, and decomposition of the diazo-compound gives 6-*chloro*-3-*hydroxybenzaldehyde*, m. p. 111° (*oxime*, hydrated, also anhydrous, m. p. 146—147°; red p-*nitrophenylhydrazone*, m. p. 250—251°; pale yellow *semicarbazone*, m. p. 236°), identical with the product obtained in small yield from 6-nitro-3-hydroxybenzaldehyde, and from the monochlorination of *m*-hydroxybenzaldehyde. 2 : 6-*Dichloro*-3-*hydroxybenzaldehyde*, obtained by direct chlorination of *m*-hydroxybenzaldehyde or of the 2- or 6-chloro-derivatives, has m. p. 140° (*oxime*, m. p. 174—175°, orange-red p-*nitrophenylhydrazone*, m. p. 205—206°). *m*-Hydroxybenzaldehyde also yielded a little 4 : 6-dichloro-3-hydroxybenzaldehyde (Friedländer, *loc. cit.*), whilst 6-chloro-3-hydroxybenzaldehyde gave, principally, a mixture of dichloro-derivatives, m. p. 120°, which defied resolution. 4-Chloro-3-hydroxybenzaldehyde is quantitatively chlorinated to 2 : 4-*dichloro*-3-*hydroxybenzaldehyde*, m. p. 141° [*oxime*, m. p. 188°; orange-red p-*nitrophenylhydrazone*, m. p. 277—278° (decomp.)]. 2 : 4 : 6-Trichloro-3-hydroxybenzaldehyde (cf. Krause, *loc. cit.*) separates with acetic acid of crystallisation, which is lost on exposure to the air, m. p. 114° [yellow *sodium* salt; *oxime*, m. p. 174°; yellow-orange p-*nitrophenylhydrazone*, m. p. 272—273° (decomp.)]. An improved method of preparing the methyl ethers is described. 6-Nitro-3-methoxybenzoic acid has m. p. 255° (Rieche, A., 1889, 1169, gives 132—133°) (*silver* salt). Nitration of *m*-methoxybenzaldehyde yields the 2- and 6-nitro-derivatives only. 2-*Chloro*-3-*methoxybenzaldehyde* has m. p. 56° (*oxime*, m. p. 130·5°; p-*nitrophenylhydrazone*, m. p. 226—227°; p-*bromophenylhydrazone*, m. p. 155—156°). 4-*Chloro*-3-*methoxybenzaldehyde* has m. p. 52° (*oxime*, m. p. 98—99°; p-*nitrophenylhydrazone*, m. p. 251°; p-*bromophenylhydrazone*, m. p. 134°). 6-*Chloro*-3-*methoxybenzaldehyde* has m. p. 62° (*oxime*, m. p. 101·5°; p-*nitrophenylhydrazone*, m. p. 229°; p-*bromophenylhydrazone*, m. p. 100°). 6-Chloro-3-methoxybenzoic

acid has m. p. 170—171° (cf. Peratoner, A., 1898, i, 641). 2 : 6-*Dichloro*-3-*methoxybenzaldehyde* has m. p. 102° (p-*nitrophenylhydrazone*, m. p. 214—215°); 2 : 6-*dichloro*-3-*methoxybenzoic acid*, m. p. 149·5°; 2 : 4-*dichloro*-3-*methoxybenzaldehyde*, m. p. 82° (p-*nitrophenylhydrazone*, m. p. 258—260°); 2 : 4-*dichloro*-3-*methoxybenzoic acid*, m. p. 163°. 2 : 4 : 6-*Trichloro*-3-*methoxybenzaldehyde* has m. p. 76°, and 2 : 4 : 6-trichloro-3-methoxybenzoic acid, m. p. 109° (Zincke, A., 1891, i, 708, gives m. p. 90°). H. E. F. Notton.

Refractometric investigation of hexahydromethylacetophenones [hexahydrotolyl methyl ketones]. S. van Woerden (Rec. trav. chim., 1926, **45**, 124—150).—The view, more particularly that of Auwers, that the molecular refraction and dispersion of a compound may be determined by the summation of additive atomic refractions, is attacked by the author, who supports the alternative view of Eykman that the value of atomic refractions is dependent on the constitution of the molecule, true comparison being made only between compounds which, with close agreement, show only one definite constitutional difference. This view is supported by a re-examination of the data obtained by Auwers (A., 1912, ii, 1013) for compounds of the type PhRC:O, in which R is an alkyl group of increasing mol. wt., it being shown that as the alkyl group becomes larger the exaltation diminishes regularly, except for a slight increase from ethyl to *iso*propyl; whilst a determination of the value of $[R_L]_\alpha$ for each CH_2 group gives values which are below the normal value between the first and second, and second and third terms, above the normal value between the third and fourth, and fourth and fifth, and normal for higher members of the series. The explanation of Auwers (A., 1915, ii, 297) of the observation that in the methylacetophenones (and analogously constituted benzene derivatives) position isomerides have divergent refractometric values, which is based entirely on the conjugated system of double linkings, cannot be correct, since the occurrence of double linkings in the ring is not a necessary condition for the production of differences in molecular refraction and dispersion amongst position isomerides of exocyclic ketones. This is supported by the investigations of Eykman on the dimethyl*cyclo*hexanes (A., 1912, ii, 311) and the investigations of the author on hexahydroacetophenone and its three isomeric methyl derivatives. Detailed refractometric and density data are tabulated, which show that the values for CH_2 are greatest in the *p*-position and smallest in the *o*-position, whilst in the *m*-position they approximate closely to those in the *p*-position. The ketones were prepared in accordance with the general scheme: $C_6H_{10}R{\cdot}OH \longrightarrow C_6H_{10}R{\cdot}Cl \longrightarrow C_6H_{10}R{\cdot}MgCl \longrightarrow C_6H_{10}RMe{\cdot}CH{\cdot}OH \longrightarrow C_6H_{10}R{\cdot}CO{\cdot}Me$ (R=H or Me). 3-*Methyl*cyclo*hexylmethylcarbinol*, b. p. 89·5—94°/13 mm., has not been previously prepared, and the following data for *o*-methylhexahydroacetophenone have not been previously recorded: $d^{30\cdot4}$ 0·8972, n_α 1·44419, n_D 1·44646, n_β 1·45225, n_γ 1·45708; $d^{43\cdot85}$ 0·8866, n_α 1·43872, n_D 1·44103, n_β 1·44674, n_γ 1·45145. Acetophenone which has been subjected to a rigorous purification is reduced by hydrogen and platinum, yielding ethyl*cyclo*hexane and *cyclo*hexylmethylcarbinol. J. W. Baker.

Preparation of 1-hydrindone. C. Courtoy and J. Krolikowski (Compt. rend., 1926, **182**, 320—323; cf. Gabriel and Haussmann, A., 1889, 1172; Weissgerber, A., 1911, i, 623).—1-Chloroindane is oxidised in 90—95% yield to 1-hydrindone when treated with chromic acid at 55—57°. Crude indene may be advantageously employed for the preparation of 1-chloroindane. L. F. Hewitt.

Behaviour of certain hydrindones towards phenylhydrazine. H. Leuchs and G. Kowalski (Ber., 1925, **58**, [*B*], 2822—2827; cf. A., 1913, i, 855; 1925, i, 1281).—2-Benzyl-1-hydrindone is converted by an excess of phenylhydrazine into the compound $C_{28}H_{25}N_3$. The behaviour of other hydrindones with this reagent has been examined. 1-Hydrindone yields only the corresponding phenylhydrazone, m. p. 134—135° (in an evacuated tube); the varying m. p. recorded in the literature are due to introduction of impurity during recrystallisation and catalytically enhanced decomposition when heated in open tubes, and not to the production of structural or geometrical isomerides. Transformation could not be effected with sulphur dioxide or hydrogen sulphide. *o*-Benzyleneindole, $C_{15}H_{17}N$, m. p. 254—255° in an evacuated tube, in contrast to the substance $C_{22}H_{17}N$ (from the compound $C_{28}H_{25}N_3$; cf. A., 1925, i, 1281), does not add hydrogen chloride or phenylhydrazine at 150°; protracted treatment with acetic anhydride affords a *monoacetyl* derivative, $C_{17}H_{13}ON$, m. p. 140°. 1-Hydrindoneoxime is converted by acetyl chloride into the corresponding acetate; isomerisation does not take place. 2-*Ethyl*-1-*hydrindone*, b. p. 144°/18 mm., is prepared in 65—75% yield by the action of aluminium chloride on β-phenyl-α-ethylpropionyl chloride in the presence of light petroleum; a crystalline *trihydrate* is described. It yields a *semicarbazone*, m. p. 200—203° (slight decomp.), a non-crystalline *phenylhydrazone*, a p-*bromophenylhydrazone*, m. p. 82°, and 2-*bromo*-2-*ethyl*-1-*hydrindone*, m. p. 45—46°. The oxime could not be obtained. With an excess of phenylhydrazine it does not yield a compound analogous with the substance $C_{28}H_{25}N_3$.

Bis-α-hydrindone-2 : 2′-spiran is converted by phenylhydrazine at 130° into a mixture of the known bis-α-hydrindone-2 : 2′-spiranbisphenylhydrazone, m. p. 200—201° (decomp.) (cf. A., 1912, i, 179), and an isomeric *bisphenylhydrazone*, m. p. 222°; in addition, the *phenylhydrazide* of 2-*o*-carboxybenzyl-1-hydrindone, m. p. about 238° (decomp.), is produced. 2-*o*-Carboxybenzyl-1-hydrindone and an excess of phenylhydrazine at 130° yield the phenylhydrazide and the bisphenylhydrazone, m. p. 222°, in about equal proportions.

In an addendum, the author points out that the previous description of ethyl 1-hydrindone-2-glyoxylate (cf. Leuchs and Kowalski, this vol., i, 66) and several of its derivatives by Ruhemann had been inadvertently overlooked. H. Wren.

Formation of 2-phenyl-3-arylindones from benzylidenephthalide, their hydrolysis to a new acid, and the preparation of a stereoisomeric benzylidenephthalide. R. WEISS and R. SAUERMANN (Ber., 1925, **58**, [*B*], 2736—2740).—Benzylidenephthalide dissolved in benzene is converted by an ethereal solution of the appropriate Grignard reagent into 2 : 3-diphenylindone, m. p. 153—155°, 2-*phenyl*-3-*o*-*tolylindone*, m. p. 123—125°, and 2-*phenyl*-3-*α*-*naphthylindone*, m. p. 183—185°; attempts to isolate the intermediately formed *o*-aryldeoxybenzoins were unsuccessful.

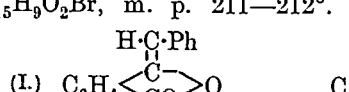
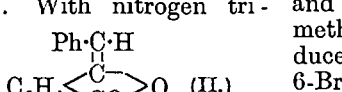
Benzylidenephthalide is converted by ammonia in boiling aqueous alcoholic solution into allo*deoxybenzoin-o-carboxylic acid*, m. p. 165°; the acid is isomeric with that obtained by the action of alcoholic potassium hydroxide on benzylidenephthalide. The possible formulæ of these acids are

$$CH_2Ph\cdot CO\cdot C_6H_4\cdot CO_2H$$

and the two *cis–trans*-isomeric enolic forms,

$$CHPh{:}C(OH)\cdot C_6H_4\cdot CO_2H,$$

but it is not yet possible to assign definite constitutions to the individuals. *allo*Deoxybenzoin-*o*-carboxylic acid is converted by acidification of its solutions in alkali hydroxide, or, preferably, by treatment of a suspension of it in alcohol with hydrogen chloride, into allo*benzylidenephthalide*, m. p. 185—187°, isomeric with benzylidenephthalide; its formation suggests that it is produced from an enolic form of deoxybenzoin-*o*-carboxylic acid. It is not hydrolysed by alkali hydroxide and does not react with magnesium phenyl bromide or magnesium benzyl chloride. Towards bromine, it behaves analogously to benzylidenephthalide, yielding allo*bromobenzylidenephthalide*, $C_{15}H_9O_2Br$, m. p. 211—212°. With nitrogen tri-

(I.)  (II.) 

oxide, it yields the *compound*, $C_{15}H_{10}O_3N_2$, m. p. 206—210°. Benzylidene- and *allo*benzylidenephthalides are probably *cis–trans*-isomerides (I) and (II). H. WREN.

Reaction of acetyl derivatives of organic acids with benzene and aluminium chloride. J. CRYER (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 29).—The mixed anhydride of benzoic and acetic acids gives an almost quantitative yield of benzophenone, but very little acetophenone. Acetylsalicylic acid, phenyl acetate, and ethyl acetate each react to give acetophenone. J. S. CARTER.

Preparation of 5(?)-nitro-3-amino-6-hydroxyacetophenone. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 85.

Acetylnaphthols [hydroxynaphthyl methyl ketones]. II. K. FRIES and K. SCHIMMELSCHMIDT (Ber., 1925, **58**, [*B*], 2835—2845; cf. Fries, A., 1921, i, 423).—The uncertainty with regard to the constitution of the compound obtained by Witt and Braun (A., 1915, i, 414) by the action of acetyl chloride and aluminium chloride on nerolin and regarded by them as 2-hydroxy-3-naphthyl methyl ketone has been removed by synthesis of the latter. The synthetic product and its methyl ether differ completely from the compounds obtained by Witt and Braun, which must therefore be regarded as 2-hydroxy-α-naphthyl methyl ketone (cf. Fries, *loc. cit.*).

2-Methoxy-α-naphthyl methyl ketone, m. p. 58°, is conveniently obtained by the action of acetyl chloride and aluminium chloride on β-naphthyl methyl ether; the *benzylidene* derivative, m. p. 139°, is described. 2-Hydroxy-α-naphthyl methyl ketone affords a *hydrazone*, m. p. 130°, which is converted by concentrated sulphuric acid into 3-*methyl*-4 : 5-*benzoindazole*, m. p. 216°, identical with the compound described as 3-methyl-ββ-naphthindazole by Witt and Braun. Methyl 2-methoxy-3-naphthoate, b. p. 191°/15 mm., m. p. 49°, is hydrolysed to the corresponding colourless acid, which, when slowly distilled under atmospheric pressure, becomes isomerised to methyl 2-hydroxy-3-naphthoate, m. p. 72°. Potassium 2-methoxy-3-naphthoate is transformed by thionyl chloride in the presence of benzene into 2-*methoxy*-3-*naphthoyl chloride*, b. p. 200°/17 mm., m. p. 57°, which, with zinc methyl iodide dissolved in toluene, affords 2-*methoxy*-3-*naphthyl methyl ketone*, b. p. 210—212°/20 mm., m. p. 48° (*benzylidene* derivative, m. p. 121°). Demethylation of 2-methoxy-3-naphthyl methyl ketone by aluminium chloride in the presence of benzene affords 2-*hydroxy*-3-*naphthyl methyl ketone*, m. p. 112°; the corresponding *sodium* salt, *acetyl* derivative, m. p. 101°, and *hydrazone*, m. p. 144°, are described.

6-Bromo-2-methoxynaphthalene is conveniently prepared by bromination of β-naphthol to 1 : 6-dibromo-β-naphthol, reduction of the latter with tin and hydrochloric acid in the presence of alcohol, and methylation of the 6-bromo-β-naphthol thus produced with methyl sulphate and potassium hydroxide. 6-Bromo-2-methoxynaphthalene is converted by successive treatment with magnesium in the presence of ether (aided by periodical addition of ethyl bromide) and carbon dioxide into 2-*methoxy*-6-*naphthoic acid*, m. p. 209° after softening at 190° (corresponding *chloride*, m. p. 101°; *amide*, m. p. 216°). The chloride is transformed by zinc methyl iodide into 2-*methoxy*-6-*naphthyl methyl ketone*, m. p. 105°, which, with aluminium chloride and xylene, affords 2-hydroxy-6-naphthyl methyl ketone, m. p. 172°, identical with the compound obtained by Witt and Braun (*loc. cit.*), by heating β-naphthyl acetate with zinc chloride.

1-Hydroxy-2-naphthyl ethyl ketone is converted by hydrazine hydrate into the corresponding *ketazine*, $C_{26}H_{24}O_2N_2$, m. p. 232° (*acetyl* derivative, m. p. 139°). It is converted by concentrated sulphuric acid into the *azine* of 1-*hydroxy*-2-*propionylnaphthalene*-4-*sulphonic acid*, m. p. 234—240° (decomp.), which is hydrolysed by dilute acids to 1-*hydroxy*-2-*propionylnaphthalene*-4-*sulphonic acid*, m. p. 127° (decomp.) (more simply obtained by sulphonation of 1-hydroxy-2-naphthyl ethyl ketone). 4-*Bromo*-1-*hydroxy*-2-*naphthyl ethyl ketone*, m. p. 97°, and 4-*bromo*-1-*hydroxy*-2-*naphthyl α-bromoethyl ketone*, m. p. 138°, are prepared by brominating 1-hydroxy-2-naphthyl ethyl ketone or the corresponding 4-sulphonic acid. 5-*Bromo*-3-*keto*-2-*methyl*-6 : 7-*benzocoumaran* has m. p. 106°. The following compounds are prepared by

analogous methods: the *azines* of 1-hydroxy-2-naphthyl methyl ketone, m. p. above 300° (decomp.), and of the corresponding 4-sulphonic acid, m. p. 233—236° (decomp.) after darkening at 120°; 1-*hydroxy*-2-*acetylnaphthalene*-4-*sulphonic acid*, m. p. 127°, converted by bromine in glacial acetic acid solution into 4-bromo-1-hydroxy-2-naphthyl methyl ketone.

2-Ethoxy-1-naphthyl methyl ketone, m. p. 61°, is identical with the compound described by Witt and Braun as 2-ethoxy-3-naphthyl methyl ketone. The following compounds are incorrectly described in the literature as derivatives of 2-methoxy-3-naphthyl methyl ketone: 2-*ethoxy*-α-*naphthyl styryl ketone*, m. p. 90°; 2-*ethoxy*-α-*naphthyl* p-*methoxystyryl ketone*, m. p. 102°; 2-*ethoxy*-1-*naphthoylformic acid*, m. p. 162°; 2-*ethoxy*-1-*naphthoic acid*, m. p. 147°.

H. WREN.

Dioximes. XXVIII. G. PONZIO (Gazzetta, 1925, **55**, 698—705).—A mixture of finely-powdered β-phenylglyoxime and 4*N*-nitric acid is kept for 24 hrs. in the cold and is then diluted with water. The precipitate so obtained, when distilled in steam, gives β-*phenylglyoxime peroxide* (oximinophenylacetonitrile oxide), m. p. 108°. Hot nitric acid (*d* 1·4) oxidises it to *p*-nitrobenzoic acid. At 120° in a sealed tube, concentrated hydrochloric acid has no effect; no structure analogous to that of the hydrazoximes (Ponzio, A., 1898, i, 386) can, therefore, be assigned to it. Zinc dust and acetic acid give by reduction β-phenylglyoxime. Contrary to the precedent of Wieland and Semper (A., 1908, i, 108), β-phenylglyoxime peroxide is formulated

$$CPh(:NOH)\cdot C\overset{O}{\underset{N}{<}} \text{ or } CPh(:NOH)\cdot C:N:O.$$

From its close relationship with this compound, β-phenylglyoxime is thought to possess an *amphi*-structure. Benzenediazonium chloride converts β-phenylglyoxime into α-benzildioxime; this substance, moreover, generally resembles the β-glyoximes, and, in particular, exhibits the feature characteristic of these compounds of giving a complex nickel salt insoluble in dilute acetic acid. Hence α-benzildioxime is also believed to be *amphi* (Meisenheimer, A., 1922, i, 152). By the action of *p*-methoxybenzenediazonium chloride, β-phenylglyoxime is converted into α-*p*-methoxybenzildioxime, which is therefore also *amphi* (cf. Meisenheimer, Lange, and Lamparter, A., 1925, i, 1073). The α- differs from the β-phenylglyoxime in the structure of the oximino-groups.

W. E. ELLIS.

Hydroxymethylene-ketones. E. BENARY, H. MEYER, and K. CHARISIUS.—See this vol., 272.

Reactions of the *meso*-hydroxyanthrones. M. A. MATTHEWS (J.C.S., 1926, 236—245).—The action of acids and reducing agents on 10-hydroxyanthrone and 1- and 4-chloro-10-hydroxyanthrone is described and the mechanism of the reactions discussed. 10-Hydroxyanthrone is reduced by zinc and hydrochloric acid in glacial acetic acid to *dihydrodianthranyl*, m. p. 298—300°. This yields, on bromination, *dibromodihydrodianthranyl*, yellow, m. p. above 320°, and on nitration (*mono*)*nitrodihydrodianthranyl*, yellow, m. p. 305° (decomp.). Nitration of dichlorodihydrodianthranyl (m. p. 268°, not 288° as previously stated, J.C.S., 1923, **123**, 2549) is accompanied by oxidation, giving *dichlorodinitrodianthranyl*, orange-red, m. p. above 330°. 10-Hydroxy-10-phenylanthrone is similarly reduced to diphenyldianthranyl. Reduction of dianthranol under various conditions yields anthracene, anthrone, and dihydrodianthranyl. 1-*Chloro*-9-*anthranyl acetate*, yellow, m. p. 110—112°, and 4-*chloro*-9-*anthranyl acetate*, m. p. 124—126°, are obtained by acetylating the corresponding chloroanthrones. 1-*Chloro*-10-*bromoanthrone*, yellow, m. p. 165°, obtained by bromination of 1-chloroanthrone, gives on boiling with aqueous acetone, 1-*chloro*-10-*hydroxyanthrone*, m. p. 144—145°. 4-*Chloro*-10-*hydroxyanthrone* from 4-chloro-10-bromoanthrone has m. p. 144—145°, alone, or when mixed with the preceding compound. 10-*Chloroanthrone*, m. p. 225° (decomp.), prepared by the action of hydrogen chloride or hydrochloric acid on 10-hydroxyanthrone, or by direct chlorination of anthrone, is much more stable than 10-bromoanthrone. With pyridine, it gives 10-*hydroxyanthranyl*-9-*pyridinium chloride* (*anthronylpyridinium chloride*), m. p. 204° (decomp.). 4 : 10-*Dichloroanthrone*, m. p. 127—128°, is prepared by similar methods, but the action of hydrochloric acid on 1-chloro-10-hydroxyanthrone yields only 1-chloroanthraquinone and 1-chloroanthrone, whilst chlorination of 1-chloroanthrone leads to 4 : 4′-dichloro-9 : 9′-dianthrone. Anthraquinol is best prepared by boiling 10-hydroxyanthrone with water.

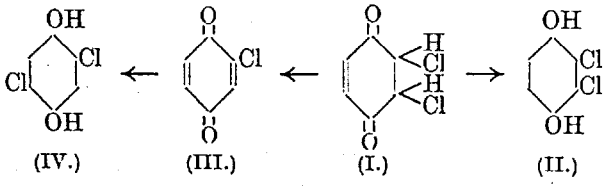
H. E. F. NOTTON.

Mechanism of substitution reactions in the aromatic nucleus. VI. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (Rec. trav. chim., 1926, **45**, 68—79).—The investigations on the behaviour of 1 : 5-dichloroanthracene dihalides towards various reagents (cf. A., 1925, i, 1140) have been extended to the 1 : 8-dichloroanthracene dihalides. The latter show less tendency to undergo the *cis*-type of reaction. Thermal decomposition of the anthracene dihalides may occur by loss either of halogen or of hydrogen halide, but conclusions concerning geometrical configuration based on this type of reaction are called into doubt, since different products result by heating the substance alone instead of in an inert solvent, several examples being given. When boiled with aqueous acetone and calcium carbonate, 1 : 8-dichloroanthracene dibromide may yield a *trans*-dihydroanthraquinol, but the only pure product isolated is 1 : 8 : 1′ : 8′-*tetrachloro*-9 : 9′-*dianthrone* (I), darkens at 280°, m. p. 310°, which is the sole product when the dichloride is heated with moist silver oxide. The action of alcoholic potassium hydroxide on 1 : 8-dichloroanthracene dichloride and dibromide yields, respectively, 1 : 8 : 10-trichloroanthracene, and 1 : 8-*dichloro*-10-*bromoanthracene*, m. p. 202°. Both these compounds on treatment with chlorine in carbon tetrachloride yield 1 : 8 : 10-*trichloroanthracene dichloride*, m. p. 185—186° (decomp.), which on hydrolysis yields 1 : 8 : 9-*trichloroanthrone*, m. p. 155°, which, in turn, heated with copper powder, gives (I). This on reduction yields 4 : 5-*dichloro*-9-*anthrone*,

m. p. 198°. The action of ethyl, *n*-butyl, and *iso*amyl alcohols, and of sodium acetate in glacial acid solution on 1 : 8-dichloroanthracene dichloride yields 1 : 8 : 10-trichloroanthracene and the dianthrone (I), together with products which are difficult to purify, but are probably 1 : 8-dichloroanthranyl alkyl ether and acetate, respectively. With phenol, 1 : 8 : 10-trichloroanthracene is the main product of the reaction. Hydrolysis of 1 : 8 : 10-trichloroanthracene dichloride with aqueous acetone and calcium carbonate yields 1 : 8 : 9-trichloroanthrone, whilst with alcohol, sodium acetate in acetic acid, and moist silver oxide, the products are 1 : 8-*dichloro*-9-*ethoxyanthrone*, m. p. 122°, 1 : 8-*dichloro*-9-*acetoxyanthrone*, m. p. 130°, and 1 : 8-*dichloro*-9-*hydroxyanthrone*, m. p. 221—222°, respectively. On treatment with diethylamine, piperidine, or quinoline, 1 : 8-dichloroanthracene dichloride and dibromide yield, respectively, 1 : 8 : 10-trichloroanthracene and 1 : 8-dichloro-10-bromoanthracene. Aniline yields 1 : 8-*dichloro*-10-*anilinoanthracene*, m. p. 213—215°, dimethylaniline yields the trihalogenoanthracene, together with 1 : 8-*dichloro*-10-*dimethylaminophenylanthracene*, m. p. 294—297°. The action of organic bases on 1 : 8 : 10-trichloroanthracene dichloride depends on the nature of the base. Piperidine yields mainly 1 : 8-*dichloro*-9-*piperidinoanthrone*, m. p. 186—188°, together with a small quantity of 1 : 8 : 10-trichloroanthracene; but with diethylamine the latter is the main product of the reaction, some 1 : 8-*dichloro*-9-*diethylaminoanthrone*, m. p. 113—114°, also being produced. Dimethylaniline yields 1 : 8 : 10-trichloroanthracene and 1 : 8-dichloro-10-dimethylaminophenylanthracene; aniline yields the dianthrone (I), whilst pyridine in the presence of acetic anhydride yields 1 : 8 : 9-*trichloroanthranylpyridinium chloride*, not melting below 300°. J. W. BAKER.

Preparation of tetrabenzoylperylene. H. PEREIRA, and COMP. NAT. DE MATIÈRES COLORANTES. —See B., 1926, 86.

***p*-Benzoquinone dichloride.** O. DIMROTH, H. EBER, and K. WEHR (Annalen, 1925, **446**, 132—147). —The isomerisation of *p*-benzoquinone dichloride (I) may take either of two courses:



(IV.) (III.) (I.) (II.)

By the action of acetic anhydride free from acetic acid, containing a little concentrated sulphuric acid, it is converted in 3 days at 65° into 2 : 3-dichloroquinol diacetate, m. p. 121°, hydrolysable to 2 : 3-dichloroquinol (II), m. p. 144°. When *p*-toluenesulphonic acid is used as catalyst in place of sulphuric acid, the product is 2 : 5-dichloroquinol diacetate, m. p. 141°, hydrolysable to 2 : 5-dichloroquinol (IV), m. p. 166°. *p*-Benzoquinone dibromide under varied conditions gives only 2 : 5- and never 2 : 3-dibromoquinol diacetate. β-Naphthaquinone dichloride and dibromide give 2-chloro- and 2-bromo-α-naphthaquinones, respectively, corresponding with the intermediate stage (III).

*cyclo*Hexa-1: 4-dione (1 : 4-diketo*cyclo*hexane), shown to contain no enol form by Meyer's bromine titration method, is quickly converted by acetic anhydride and sulphuric acid into 1 : 1 : 4 : 4-tetra-acetoxy*cyclo*hexane, m. p. 107°, subliming at 200—220° with partial decomposition, which is hydrolysed to the diketone by aqueous-alcoholic hydrochloric acid. Both the diketone and the tetra-acetate give quinol diacetate, m. p. 122°, when warmed with acetic anhydride and sulphuric acid, the latter being reduced to sulphur dioxide. The tetra-acetate is converted by acetic anhydride and *p*-toluenesulphonic acid at 50—60° in an inert atmosphere into 2 : 3- or 2 : 5-*dihydroquinol diacetate* (or a mixture of both), m. p. 94—95°. The analogy with benzoquinone dichloride suggests that a tetra-acetate may be formed during the conversion of (I) into (III) and (III) into (IV).

The reduction of *p*-benzoquinone dichloride by chromous chloride in a hydrogen atmosphere gives quinol, m. p. 169°. Stannous chloride and hydrochloric acid yield 2 : 3-dichloroquinol and chloroquinol, m. p. 104°. Hydrogen sulphide is without action at the ordinary temperature, whilst sulphur dioxide at 0° gives chloroquinol. With potassium iodide at 0°, the product is a *dichlorodihydroquinol*, m. p. 92° (impure).

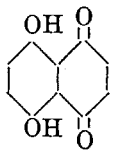
p-Benzoquinone dichloride is oxidised by permanganate at 0° to *iso*dichlorosuccinic acid, m. p. 175°, *i.e.*, the racemic form. It follows that the dichloride is a *trans*-compound. No *cis*-isomeride could be detected. The same *iso*dichlorosuccinic acid is obtained by the oxidation of toluquinone dichloride, of *methoxy*-p-*benzoquinone dichloride*, or of *acetamido*-p-*benzoquinone dichloride*, m. p. 91°. Methoxy-*p*-benzoquinone, m. p. 144—145°, is dimorphic and is prepared from methoxyquinol, m. p. 88—88·5°, obtained by a slight modification of Dakin's method from vanillin (Proc., 1909, 194). These results show that in the substituted *p*-benzoquinones addition of chlorine occurs at the double linking remote from the substituent, a reaction contrary to the theory of benzene substitution put forward by Böeseken and Holleman (A., 1923, i, 664).

C. HOLLINS.

Sulphonic acids of the arylamine derivatives of naphthaquinones. A. WAHL and R. LANTZ (Bull. Soc. chim., 1925, [iv], **37**, 1628—1637).—In oxidising the isomeride of 1-anilino-β-naphthol-4-sulphonic acid (cf. A., 1925, i, 910) with chromic acid in presence of aniline, a reddish-brown, amorphous powder is obtained. Evidence is adduced to show that this substance is 4-anilino-1-phenylimino-β-naphthaquinonesulphonic acid. Direct sulphonation of 2-anilino-4-phenylimino-α-naphthaquinone yields both a mono- and a di-sulphonic acid, whilst in the case of 4-anilino-2-hydroxy-α-naphthaquinone a monosulphonic acid is formed, the entering group taking the *meta*-position with respect to the anilino-group. A disulphonic acid was also prepared, and, in addition, the mono- and di-sulphonic acids of 2-

anilino-1 : 4-naphthaquinone. These derivatives exhibit marked tinctorial power towards animal fibres, but do not appear to be of any practical importance. H. J. EVANS.

Constitution of naphthazarin. O. DIMROTH and F. RUCK (Annalen, 1925, **446**, 123—131).—Since by the action of boroacetic anhydride a *bisdiacetoborate* is formed, naphthazarin must contain a hydroxyl group *ortho* to each carbonyl group (see following abstract), *i.e.*, it is 5 : 8-dihydroxy-1 : 4-naphthaquinone (annexed formula). The formulation accepted heretofore as 7 : 8-dihydroxy-1 : 4-naphthaquinone is based on the Liebermann–Kostanecki rule for mordant dyes, to which there are now numerous exceptions, and on the formation of naphthazarin from δ-tetranitronaphthalene (Will, A., 1895, i, 235, 668). The latter is now shown to be 1 : 4 : 5 : 8-tetranitronaphthalene.

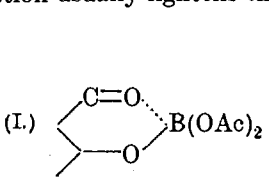


1 : 5-Dinitronaphthalene, nitrated by the method of Beilstein and Kuhlberg (A., 1873, 1138; Aguiar, A., 1872, 699) with mixed acid, gives 1 : 4 : 5-trinitronaphthalene ("γ"), m. p. 148—149°, which by further nitration by Will's method (*loc. cit.*) yields 1 : 4 : 5 : 7-("γ")- and 1 : 4 : 5 : 8-("δ")-tetranitronaphthalenes, separable by means of acetone. Nitration of 1 : 5-dinitronaphthalene with hot nitric acid in the absence of sulphuric acid gives a mixture of 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalenes, with a very small amount of an *isomeride*, m. p. 136—137°, and a minute quantity of a *substance*, m. p. 210°. 1 : 3 : 5-Trinitronaphthalene, m. p. 119·5°, is easily separated from the mixture in the form of its *compound*, $C_{10}H_5O_6N_3,C_{10}H_8O$, m. p. 146—148°, with β-naphthol. No trace of Will's 1 : 2 : 5-("δ")-trinitronaphthalene, m. p. 112—113°, is formed, but a mixture of 1 : 3 : 5- and 1 : 4 : 5-trinitronaphthalenes after two recrystallisations from formic acid melts constantly at 110—112°. δ-Tetranitronaphthalene is formed only from one of the trinitronaphthalenes, viz., the 1 : 4 : 5-isomeride, and is therefore 1 : 4 : 5 : 8-tetranitronaphthalene.

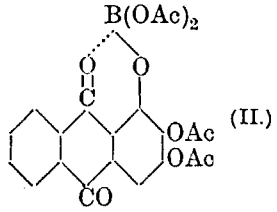
The new structure for naphthazarin is confirmed by its absorption spectra in sulphuric acid and in boroacetic anhydride, which closely resemble those of 1 : 4-dihydroxyanthraquinone derivatives.

C. HOLLINS.

Boroacetic anhydride as a reagent. II. O. DIMROTH [with R. SCHWEIZER, R. RUCHT, K. SAGSTETTER, J. HETZER, H. BERNZOTT, C. BAMBERGER, and O. REBMANN] (Annalen, 1925, **446**, 97—122).—It has already been shown (Dimroth and Faust, A., 1922, i, 155) that, whilst β-hydroxyanthraquinones react with boroacetic anhydride to give only acetates, α-hydroxyanthraquinones yield diacetoboric esters containing most probably the grouping (I). From an examination of the products of reaction of boroacetic anhydride with a large number of substances, it is now found that boric esters are formed in all cases where a hydroxy- or an amino-group is *ortho* to a carbonyl group or to other groups possessing residual valency, *e.g.*, nitrogen in 8-hydroxyquinoline. The formation of boric esters is accompanied by a deepening of the colour of the solution, whilst acetylation usually lightens the colour.



(I.)



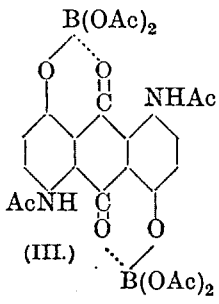
(II.)

Boroacetic anhydride (Pictet and Geleznov, A., 1903, i, 601) is shown to be the diacetate of pyroboric acid, $B(OAc)_2{\cdot}O{\cdot}B(OAc)_2$. It begins to decompose at 146°, melts at 150—152°, and by heating in a vacuum at 150—156° is converted into metaboric acetate, BO·OAc.

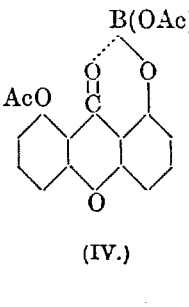
The following compounds are acetylated by pyroboric acetate in acetic anhydride solution, but give no boric esters: 2 : 3-dihydroxyanthraquinone, β-aminoanthraquinone, 2- and 4-hydroxyxanthones, 2-hydroxyphenanthraquinone (acetate, m. p. 215°), 2-aminophenanthraquinone (acetyl derivative, m. p. 315°), 3-hydroxyphenanthraquinone (acetate, m. p. 199—200°), 4-aminophenanthraquinone (acetyl derivative, m. p. 195°), 2-amino-3-hydroxyphenanthraquinone, *m*- and *p*-hydroxybenzoic acids (acetates, m. p. 127° and 185°, respectively).

1 : 2 : 3-Trihydroxyanthraquinone, when boiled for a short time with a solution of pyroboric anhydride in acetic anhydride, yields the *diacetoborate* of the diacetate (II). This is easily decomposed by cold water into 1-hydroxy-2 : 3-diacetoxyanthraquinone, m. p. 214°, which is also obtainable by partial acetylation of the trihydroxyanthraquinone.

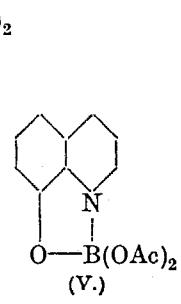
1-Aminoanthraquinone yields a "*boric* ester" of similar structure (NH in place of the α-oxygen atom), which, heated in a vacuum at 130—140° at the temperature of boiling xylene, slowly loses acetic anhydride to give the "*metaboric* ester" (1-anthraquinonylmetaboramide), $C_{14}H_7O_2{\cdot}NH{\cdot}B{:}O$. 1 : 4-*Bisdiacetoboramidoanthraquinone* ("diaminoanthraquinone diboroacetic ester") is more stable and does not lose acetic anhydride when heated. The 1 : 5-*isomeride* is also described. From 1 : 8-diaminoanthraquinone only the diacetyl derivative, m. p. 284°, is isolated, but the deepening of the colour indicates that "boric ester" formation has occurred. The "bisdiacetoboric ester" of 1-amino-4-hydroxyanthraquinone has already been described by Brass and Ziegler (A., 1925, i, 686). Diaminoanthrarufin (1 : 5-diamino-4 : 8-dihydroxyanthraquinone) gives the *bisdiacetoborate* (III), the structure of which is proved by its ready hydrolysis to diacetamidoanthrarufin, m. p. 270°.



(III.)



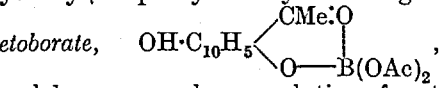
(IV.)



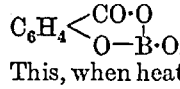
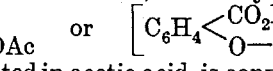
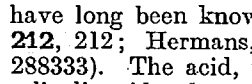
(V.)

1-Hydroxyxanthone gives a *diacetoborate*, and 1 : 8-dihydroxyxanthone the 8-acetoxy-derivative of this (IV), which is completely hydrolysed by water.

The *diacetoborate* from 1 : 4-dihydroxyphenanthraquinone gives on hydrolysis a *monoacetate*. From 1 : 4-aminohydroxyphenanthraquinone an acetylated *diboroacetate* is obtained. Alizarin-yellow-A (2 : 3 : 4-trihydroxybenzophenone) gives in the cold the *diacetoborate*, and, on keeping or warming, the *diacetoborate* of 2-hydroxy-3 : 4-diacetoxybenzophenone; hydrolysis of the latter yields 2-*hydroxy*-3 : 4-*diacetoxybenzophenone*, m. p. 119°.

Diacetoborates from 2-acetyl-α-naphthol and the 1 : 2- and 3 : 2-isomerides, from 2-benzoyl-α-naphthol, and from 2 : 4-diacetyl-α-naphthol are described. 1 : 8-Dihydroxy-β-naphthyl methyl ketone gives first a *diacetoborate*,  , and after several days a green-brown solution of acetylated diacetoborate, from which by hydrolysis there is obtained 8-acetoxy-2-acetyl-α-naphthol, m. p. 168—169° (cf. Lange, D.R.-P. 126199). Lange's "diacetyl derivative" of 1 : 8-dihydroxy-β-naphthyl methyl ketone has this m. p. and is the monoacetyl derivative; it is obtainable by acetylation at 0°. The true *diacetyl* derivative, prepared by acetylation at the ordinary temperature, has m. p. 146°. The *diacetoborate* of 8-acetoxy-2-acetyl-α-naphthol is prepared readily from the monoacetyl compound, more slowly from the diacetyl compound.

The oily 8-acetoxyquinoline (Skraup, A., 1883, 92), which forms with water a crystalline *hydrate*, and with 50% acetic acid a *compound*, $AcO\cdot C_9H_6N,AcOH$, m. p. 59—60°, crystallises when seeded and then has m. p. 55·5—56·5°. It gives an unusually stable *diacetoborate* (V).

Salicylic acid (and other *o*-hydroxy-acids) gives a well-crystallised, colourless *compound*, in which the molecular ratios of salicylic acid, boric acid, and acetic acid are 1 : 1 : 1; it may therefore be  or  . This, when heated in acetic acid, is converted into *borodisalicylic acid*,  , the salts of which have long been known (Jahns, Arch. Pharm., 1878, **212**, 212; Hermans, A., 1924, i, 728; cf. D.R.-P. 288333). The acid, which is readily prepared from salicylic acid and pyroboric acetate in ether or benzene, is at once hydrolysed by water. C. Hollins.

Production of [anthraquinone] dye intermediates. J. Thomas, and Scottish Dyes, Ltd.—See B., 1926, 121.

Isomeric terpineols and resolution of α-terpineol into optical antipodes. V. Paolini (Gazzetta, 1925, **55**, 804—811; cf. Fuller and Kenyon, A., 1925, i, 48).—Optically inactive α-terpineol, m. p. 35°, isolated by cooling commercial liquid terpineol, may be resolved into its optical isomerides by the following procedure. Treatment of the terpineol in toluene solution with metallic potassium yields the potassium derivative which, when treated with the theoretical quantity of phthalic anhydride, gives potassium terpenyl phthalate. Addition of dilute sulphuric acid then precipitates the terpenyl hydrogen phthalate, and treatment of this with strychnine yields a crystalline *l*-α-terpenyl strychnine phthalate, m. p. 207°, $[\alpha]_D$ −40·8°, which is readily converted into crystalline l-α-*terpinyl hydrogen phthalate*. Hydrolysis of the latter gives l-α-*terpineol*, m. p. 37—38°, b. p. 218° (corr.), d^{15} 0·935, $[\alpha]_D$ −98·5°. To obtain the corresponding *d*-compound, the mother-liquor from the *l*-terpinyl strychnine phthalate was treated with ammonia solution and then with silver nitrate, the resulting crystalline d-α-*terpinyl silver phthalate* being then converted into d-α-*terpinyl hydrogen phthalate*, m. p. 116°, $[\alpha]_D$ +40·5°, and this into d-α-*terpineol*, $[\alpha]_D$ +98·5°. T. H. Pope.

Isomeric α-terpineols. Active terpineols from active pinenes. V. Paolini (Gazzetta, 1925, **55**, 812—817).—The fraction of commercial oil of turpentine, b. p. 157—158°, d^{15} 0·80, $[\alpha]_D$ −35·5°, when hydrated by either alcoholic sulphuric acid or glacial acetic acid and zinc chloride, yields *l*-α-terpineol, which forms with strychnine and phthalic acid (see preceding abstract) a compound, m. p. 207°; hydrolysis of this yields an *l*-α-terpineol, $[\alpha]_D$ −98·32°, identical with that obtained by separation of the optical antipodes of inactive α-terpineol (*loc. cit.*). Similar treatment of *d*-pinene, $[\alpha]_D$ +29·5°, results in the formation of a terpineol, the strychnine phthalate of which, m. p. 207°, yields *d*-α-terpineol, $[\alpha]_D$ +95·0°, on hydrolysis. T. H. Pope.

Isomeric carvomenthols from carvacrol. V. Paolini (Gazzetta, 1925, **55**, 818—824).—The mixture of inactive α- and β-carvomenthols (hexahydrocarvacrols) prepared by Sabatier's method by Brunel (A., 1906, i, 81) may be resolved into its components by the author's cold esterification method, the hydrogen phthalate of the α-isomeride being readily soluble and that of the β-isomeride almost insoluble in light petroleum. Each of the two may then be resolved into the two optical antipodes via the carvomenthyl strychnine phthalates (cf. preceding abstracts).

β-*Carvomenthyl hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{19}$, has m. p. 125°; β-*carvomenthyl strychnine phthalate*, m. p. 148°, $[\alpha]_D$ (in alcohol) −14·72°; l-β-*carvomenthyl hydrogen phthalate*, m. p. 125°, $[\alpha]_D$ (in methyl alcohol) −3·70°; l-β-*carvomenthol*, an oily liquid, b. p. 218°, d^{15} 0·9082, n_D^{15} 1·4610, $[\alpha]_D$ −1·81°; d-β-*carvomenthyl hydrogen phthalate*, m. p. 125°, $[\alpha]_D$ +3·77°; d-β-*carvomenthol*, b. p. 218°, d^{15} 0·9081, n_D^{19} 1·461, $[\alpha]_D$ +1·79°.

α-*Carvomenthyl hydrogen phthalate* is syrupy, but α-*carvomenthyl silver phthalate* has m. p. 225°. The strychnine phthalates are difficult to separate, and the two α-carvomenthols were obtained only in an impure condition, the *l*-isomeride having $[\alpha]_D$ −2·70° and the *d*-isomeride, $[\alpha]_D$ +2·20°. T. H. Pope.

Caryophyllene series. I. G. G. Henderson, J. M. Robertson, and C. A. Kerr (J.C.S., 1926, 62—70).—Caryophyllene alcohol, m. p. 94—96°, prepared by hydrating β-caryophyllene with sulphuric and acetic acids (cf. Wallach and Walker, A., 1893, i, 101),

is stable towards hydrogen peroxide and potassium permanganate, and behaves towards bromine as a saturated substance, whence it is concluded that the hydrating agents have induced ring closure, giving rise to a tricyclic structure; this view is confirmed by the fact that the alcohol can be formed by the agency of formic acid, as also by its conversion into clovene. Its tricyclic nature is also indicated by the physical properties of the formate, viz., d_4^7 1·024, n_D^7 1·4998, and acetate, d_4^{17} 1·003, n_D^{17} 1·4919. The treatment of β-caryophyllene with sulphuric and acetic acids also yields an unsaturated *hydrocarbon*, $C_{15}H_{24}$, b. p. 110—114°/9 mm., d_4^{10} 0·9263, n_D^{10} 1·5010, $[\alpha]_{5790}^{18}$ −19·56°. To synthesise dicyclic hydroxy-derivatives of caryophyllene, caryophyllene dihydrochloride, m. p. 69°, $[\alpha]_D^{18}$ in ethyl alcohol +67° (prepared in dry ether at 0°), is treated with acetic acid and silver acetate, when the product, on hydrolysis with potassium hydroxide, yields an unsaturated, probably tertiary, *alcohol*, $C_{15}H_{25}\cdot OH$, b. p. 142—150°/10 mm., d_4^{17} 0·9632, n_D^{17} 1·5015 (*dibromide* prepared), for which the name *caryophyllol* is proposed, together with a saturated, stable *glycol*, $C_{15}H_{26}(OH)_2$, m. p. 173°. Caryophyllene chloride, m. p. 63° (Wallach and Walker, *loc. cit.*), is regarded as tricyclic because it is unchanged by heating with alcoholic sodium ethoxide or quinoline; by sodium acetate in acetic acid it is converted into caryophyllene *acetate*, b. p. 149—152°/10 mm., m. p. 40°. By treating caryophyllene dissolved in acetone with chlorocarbamide in presence of acetic acid and water, the (impure) *dichlorohydrin* of caryophyllene is obtained as an oil, which with acetic anhydride is converted into its (impure) *monoacetate*, b. p. 190—200°; on distilling this in a vacuum, it gives a saturated *compound*, $C_{15}H_{24}OCl_2$, b. p. 125—140°/1 mm. (the anhydride of the dichlorohydrin ?), the chlorine of which is not easily replaced.

F. M. Hamer.

Oxidation of sesquiterpenes with chromyl chloride and chromic acid. D. T. Gibson, J. M. Robertson, and J. Sword (J.C.S., 1926, 164—167; cf. *ibid.*, 1922, **121**, 2717; 1924, **125**, 107).—The action of chromyl chloride in carbon tetrachloride solution on cadinene, β-caryophyllene, and cedrene, gives additive *compounds*, $C_{15}H_{24},2{\cdot}5CrO_2Cl_2$, consisting presumably of $C_{15}H_{24},2CrO_2Cl_2$, contaminated with $C_{15}H_{24},3CrO_2Cl_2$, or perhaps $C_{15}H_{22},2CrO_2Cl$. None of these additive compounds, nor the chromyl chloride additive product of toluene, is acted on by dry ether (cf. Étard, A., 1881, 581). The additive compound from β-caryophyllene on decomposition with water yields a *ketone*, $C_{15}H_{24}O$, b. p. 100—110°/0·5 mm. (*semicarbazone*, m. p. 234°), an unsaturated *ketone*, $C_{15}H_{20}O_2$, b. p. 118°/1 mm., caryophyllene alcohol, and some chlorinated oxidation products, which are removed by prolonged treatment with zinc dust in alcoholic solution. Decomposition of the additive compound of cedrene gives a *compound*, $C_{15}H_{24}O$, b. p. 93°/0·15 mm., n^{15} 1·5462 (amorphous *semicarbazone* formed), which is probably a ketone, together with chlorinated products, whilst decomposition of that from cadinene yields a small amount of acid, together with a neutral *product*. Oxidation of cadinene with potassium dichromate and sulphuric acid gives acid products, whilst oxidation with chromic anhydride in acetic acid yields also an unsaturated *compound*, $C_{15}H_{24}O_2$, b. p. 180—196°/12 mm., $n_D^{8\cdot5}$ 1·5095, which polymerises on treatment with sodium.

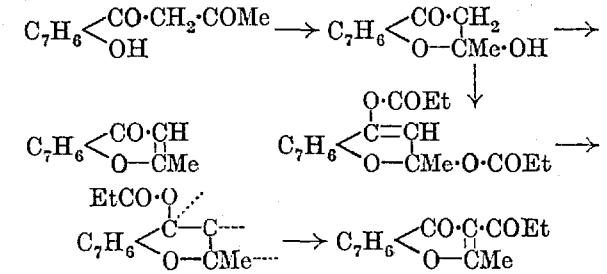
F. M. Hamer.

Higher terpene compounds. XXVII. Azulene. L. Ruzicka and E. A. Rudolph (Helv. Chim. Acta, 1926, **9**, 118—140).—A comparison of the physical constants and of the m. p. of the picrates and styphnates of the isomeric blue hydrocarbons, $C_{15}H_{18}$ (azulenes), obtained from various essential oils, and of their reduction products, has been made with a view to elucidate the structure of these hydrocarbons. The blue hydrocarbons obtained from oil of milfoil (cf. Kremers, A., 1923, i, 454) or from camomile oil, are identical, and for these the name *chamazulene* (d_4^{20} 0·9883 and 0·9881, respectively, from the two sources; picrate, m. p. 115°; styphnate, m. p. 95°) is suggested. A second isomeride, *guaiazulene* (d_4^{20} 0·9743; picrate, m. p. 122°; styphnate, m. p. 105°), is similarly obtained from the sesquiterpene guaiene (obtained by the action of formic acid on guaiacol; cf. Ruzicka, Pontalti, and Balas, A., 1923, i, 1217); whilst from *Eucalyptus globulus* oil, a third isomeride, *eucazulene*, is obtained, but was not investigated. Chamazulene is unattacked by formic acid at low temperatures, but on heating it polymerises to an amorphous product. Oxidation with potassium permanganate, in contradiction to the results of Kremers (*loc. cit.*), yields no trace either of acetone or of methylphthalic acid, the sole products being the lower fatty acids and carbon dioxide. Reduction of chamazulene with sodium and moist ether (or alcohol) yields only amorphous products (cf. Sherndal, A., 1915, i, 702; Kremers, *loc. cit.*), but when amyl alcohol is used, the product is *hexahydroazulene*, $C_{15}H_{24}$, b. p. 118—124°/11 mm., d_4^{20} 0·9177, n_D^{20} 1·5200, the physical constants of which show it to possess a structure similar to that of the sesquiterpenes. Oxidation of the hexahydro-derivative yields no products which could be characterised, whilst dehydrogenation with sulphur at 180° re-forms the original azulene. Catalytic reduction of chamazulene with colloidal platinum in acetic acid solution yields *octahydrochamazulene*, b. p. 119°/11 mm., d_4^{20} 0·8932, n_D^{20} 1·4856, which on dehydrogenation also yields the original chamazulene. Similarly, the catalytic reduction of guaiazulene yields the *octahydro*-derivative, b. p. 123—125°/11 mm., d_4^{20} 0·8872, n_D^{20} 1·4834, which similarly re-forms guaiazulene on dehydrogenation with sulphur. Mild catalytic reduction of guaiene yields the *dihydro*-compound, b. p. 124—125°/15 mm., d_4^{20} 0·8955, n_D^{20} 1·4894; energetic reduction yields the tetrahydro-derivative (cf. Semmler and Mayer, A., 1912, i, 479). On dehydrogenation, dihydroguaiazulene also yields guaiazulene. The molecular refraction values of all these reduction derivatives correspond with a dicyclic sesquiterpene structure, and the authors conclude that the colour of the azulenes is conditioned by a particular (as yet unknown) grouping of five double linkings in a dicyclic structure which corresponds closely, if it is not identical, with the sesquiterpene skeleton, and contains no aromatic ring (cf. Kremers, *loc. cit.*).

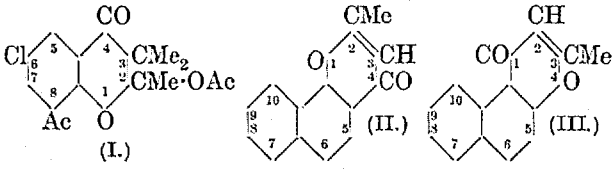
The ring structure, *per se*, is not responsible for the colour, but serves as a skeleton in which occurs the facile rearrangement of the double linkings, in which cause lies the difference between the isomeric azulenes.

The ultra-violet absorption spectra of chamazulene and guaiazulene have been determined and found to be identical, in spite of the fact that the two hydrocarbons are isomeric and not identical, and hence conclusions based on the similarity of absorption spectra (cf. Herzenberg and Ruhemann, B., 1926, 42) are invalid. J. W. BAKER.

Benzo-1 : 4-pyrones [chromones]. G. WITTIG [with F. BANGERT and H. E. RICHTER] (Annalen, 1925, **446**, 155—204).—The action of acetic anhydride and sodium acetate on β-diketones of the type of *o*-hydroxybenzoylacetone (*o*-acetoacetylphenol) provides a general method for the synthesis of 2-acetylbenzo-1 : 4-pyrones (cf. Wittig, A., 1924, i, 412). 2-Methylbenzo-1 : 4-pyrones are obtained in small amount as by-products. Since 3-acetoacetyl-*p*-cresol, heated with propionic anhydride and sodium propionate, gives 3-propionyl-2 : 6-dimethylbenzo-1 : 4-pyrone, the mechanism of the reaction is probably :



This is confirmed by the formation of the acetate of 6-chloro-2-hydroxy-8-acetyl-2 : 3 : 3-trimethylchromanone (I) by the action of acetic anhydride and sodium acetate on 4-chloro-2-*iso*butyrylphenol.



The synthesis is applicable to all phenols without exception, those with unsaturated substituents (Cl, NO_2, OH) reacting most rapidly and giving a smaller proportion of coumarin by-product.

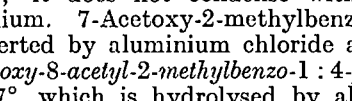
o-*Hydroxybenzoylacetone* (o-*acetoacetylphenol*), m. p. 90·5—91·5°, results in 65% yield from the action of sodium and ethyl acetate on *o*-acetylphenol. It is converted quantitatively by concentrated sulphuric acid or by glacial acetic acid containing a few drops of mineral acid into 2-methylbenzo-1 : 4-pyrone. With hot acetic anhydride and sodium acetate, it gives in 2 min. 3-*acetyl*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 88·5—89·5° (85% yield), which may be hydrolysed by aqueous sodium hydroxide to 2-methylbenzo-1 : 4-pyrone.

3-*Acetoacetyl*-2-*cresol*, m. p. 85—86°, prepared from 3-acetyl-2-cresol, ethyl acetate, and sodium, similarly gives 2 : 8-dimethylbenzo-1 : 4-pyrone, m. p. 111—112°; 4-*acetoacetyl*-3-*cresol*, m. p. 76—77°, from 4-acetyl-3-cresol, gives 2 : 7-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 97·5—98·5°, b. p. 192—193°/15 mm., and 3-*acetyl*-2 : 7-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 107·5—108·5°. The position of the acetyl group in 4-acetyl-3-cresol is proved by hydrolysis of the 2 : 7-dimethylbenzo-1 : 4-pyrone to 4-methylsalicylic acid. 3-*Acetyl*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 114·5—115·5°, from 3-acetoacetyl-*p*-cresol, and 3-*acetyl*-2 : 5 : 7-*trimethylbenzo*-1 : 4-*pyrone*, m. p. 112—113°, from 4-*acetoacetyl*-m-5-*xylenol*, m. p. 116—117°, which is also readily converted into 2 : 5 : 7-trimethylbenzo-1 : 4-pyrone, are described. 2-Acetyl-1-naphthol condenses with ethyl acetate and sodium to give 2-*acetoacetyl*-1-*naphthol*, m. p. 110·5—111·5°, from which 2-*methyl*-αβ-*naphtha*-1 : 4-*pyrone* (II), m. p. 174—174·5°, and the corresponding 3-*acetyl* derivative, m. p. 143—144°, are obtained in quantitative yield. In a similar manner, 1-*acetoacetyl*-2-*naphthol*, m. p. 152° (decomp.), gives 3-methyl-βα-naphtha-1 : 4-pyrone (III), m. p. 164°, and its 3-acetyl derivative, m. p. 156—157°.

Further details are given of the synthesis of benzo-1 : 4-pyrones and coumarins by the action of acetic anhydride and sodium acetate on *o*-acetylphenols (Wittig, A., 1924, i, 412). 3-Acetyl-2 : 6-dimethylbenzo-1 : 4-pyrone (from 3-acetyl-*p*-cresol) is isolated as a mixture of *mono-oxime*, m. p. 100—100·5°, and *dioxime*, m. p. 222—224° (easily separated by crystallisation from benzene), formed in the presence of acetic acid (2 : 6-dimethylbenzo-1 : 4-pyrone is oximated only in alkaline solution); the residue, treated in ethereal solution with hydrogen chloride, gives the oxonium chloride of 2 : 6-dimethylbenzo-1 : 4-pyrone, and 4 : 6-dimethylcoumarin is obtained on evaporation of the ether. The yields of the products in this example are 50%, 14%, and 24%, respectively. In other cases, the reaction product is hydrolysed with 2*N*-sodium hydroxide to convert acetylbenzo-1 : 4-pyrones into benzo-1 : 4-pyrones, which are isolated as oxonium chlorides. 2-Acetylphenol (*o*-hydroxyacetophenone) gives a little 3-acetyl-2-methylbenzo-1 : 4-pyrone directly on distillation of the product in a vacuum, but as 2-methylbenzo-1 : 4-pyrone gives no solid oxonium chloride, the sodium ethoxide method (*loc. cit.*) is used for the main separation. The following products, in addition to those already mentioned (*loc. cit.*), are described : 2 : 8-Dimethylbenzo-1 : 4-pyrone and 4 : 8-dimethylcoumarin, m. p. 112—113° (from 3-acetyl-*o*-cresol); 2 : 7-dimethylbenzo-1 : 4-pyrone and 4 : 7-dimethylcoumarin, m. p. 132° (from 4-acetyl-*m*-cresol); 2 : 5 : 7-trimethylbenzo-1 : 4-pyrone [*hydrochloride*, m. p. 152° (decomp.)] and 3-acetyl-2 : 5 : 7-trimethylbenzo-1 : 4-pyrone (from 4-acetyl-*m*-5-xylenol; no trimethylcoumarin is formed); 3-acetyl-2-methyl-αβ-naphtha-1 : 4-pyrone (the only product isolable from 2-acetyl-1-naphthol); 3-methyl-βα-naphtha-1 : 4-pyrone and its 3-acetyl derivative (from 1-acetyl-2-naphthol).

The acetate of *p*-nitrophenol decomposes when treated with aluminium chloride, but 6-*nitro*-2-*acetylphenol* (3-nitro-2-hydroxyacetophenone), m. p. 98·5—99·5°, is obtained in 10% yield by nitration of *o*-acetylphenol. 5-*Nitro*-3-*acetyl*-p-*cresol*, m. p. 130—130·5°, prepared from 3-acetyl-*p*-cresol (yield

77%), is converted by acetic anhydride and sodium acetate into 8-*nitro*-3-*acetyl*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 146·5—147·5°. 5 : ?-*Dinitro*-3-*acetyl*-p-*cresol*, m. p. 147—147·5°, is obtained by further nitration or from 3-acetyl-*p*-cresol. 2-Acetylquinol (2 : 5-dihydroxyacetophenone), m. p. 197·5—198·5°, from quinol diacetate and aluminium chloride, gives with acetyl chloride a diacetate, which is converted by acetic anhydride and sodium acetate into 6-*acetoxy*-3-*acetyl*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 120—121°. 6-*Hydroxy*-3-*acetyl*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 215—216°, and 6-hydroxy-2-methylbenzo-1 : 4-pyrone, m. p. 241—242°, are obtained by hydrolysis. 4 : 6-Diacetylresoreinol, m. p. 177—178°, gives only tarry products; it does not condense with ethyl acetate and sodium. 7-Acetoxy-2-methylbenzo-1 : 4-pyrone is converted by aluminium chloride at 50—120° into 7-*hydroxy*-8-*acetyl*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 186—187°, which is hydrolysed by alcoholic sodium ethoxide to 2 : 4-*diacetylresorcinol*, m. p. 88—89°, and gives, by treatment with acetic anhydride and sodium acetate, 3-acetyl-2 : 6-dimethylbenzodi-1 : 4-pyrone, m. p. 210—211°,



The reaction is further extended to higher *o*-acylphenols. p-*Chlorophenyl propionate*, b. p. 234—236°, is converted by aluminium chloride into 4-*chloro*-2-*propionylphenol*, m. p. 56·5—57·5°, from which the *propionate*, b. p. 170°/14 mm., is prepared by the action of propionyl chloride and calcium chloride. The phenol or its propionate reacts with acetic anhydride and sodium acetate to give 6-chloro-2 : 3-dimethylbenzo-1 : 4-pyrone, m. p. 106—107°; with propionic anhydride and sodium propionate to give 6-*chloro*-3-*methyl*-2-*ethylbenzo*-1 : 4-*pyrone*, m. p. 66—67°; and with chloroacetyl chloride and sodium chloroacetate to give 6-*chloro*-3-*methyl*-2-*chloromethylbenzo*-1 : 4-*pyrone*, m. p. 125·5—126·5°. 3 : 6-Dimethylflavone, m. p. 93°, is obtained from 3-propionyl-*p*-cresol, benzoic anhydride, and sodium benzoate. 4-*Chloro*-2-*butyrylphenol* (5-chloro-2-hydroxybutyrophenone), m. p. 49—50°, prepared from p-*chlorophenyl butyrate*, b. p. 249—251°, condenses with acetic anhydride and sodium acetate to give 6-*chloro*-2-*methyl*-3-*ethylbenzo*-1 : 4-*pyrone*, m. p. 103—104°. 6-*Methyl*-3-*ethylflavone*, m. p. 73—74°, 6-*methyl*-3-n-*propylflavone*, m. p. 77—78°, and 6-*methyl*-3-iso*propylflavone*, m. p. 150°, are prepared from 3-butyryl-, 3-*n*-valeryl-, and 3-*iso*valeryl-*p*-cresols, respectively. 5-*Chloro*-2-*hydroxyphenyl benzyl ketone* (4-chloro-2-phenylacetylphenol), m. p. 66—67°, b. p. 280—285°/30 mm., prepared from *p*-chloroanisole, phenylacetyl chloride, and aluminium chloride, gives with acetic anhydride and sodium acetate 6-*chloro*-3-*phenyl*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 127—128°, and with benzoic anhydride and sodium benzoate 6-*chloro*-2 : 3-*diphenylbenzo*-1 : 4-*pyrone*, m. p. 178—179° (*oxime*, m. p. 206—206·5°). 3-Phenylacetyl-*p*-cresol similarly yields 3-*phenyl*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 91°, and 2 : 3-*diphenyl*-6-*methylbenzo*-1 : 4-*pyrone*, m. p. 170°; and with cinnamic anhydride and sodium cinnamate 3-*phenyl*-2-*styryl*-6-*methylbenzo*-1 : 4-*pyrone*, m. p. 179°, isolated as perchlorate. 3 : 6-*Dichloro*-2-*methylbenzo*-1 : 4-*pyrone*, m. p. 155·5—156·5°, from 4-chloro-2-chloroacetylphenol; 3-*chloro*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 145—146°, with 3-*hydroxy*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 188—189°, from 3-chloroacetyl-*p*-cresol. The hydroxybenzo-1 : 4-pyrone is also synthesised, in the form of its *acetate*, m. p. 119·5—120·5°, from 3-*bromoacetyl*-p-*cresol*, m. p. 45·5—46·5°, which itself is prepared from p-*tolyl bromoacetate*, b. p. 180—181°/60 mm. 4-*Chloro*-3-*acetoxycoumarone*, m. p. 30·5—31°, b. p. 165—167°/20 mm., obtained by the action of acetic anhydride and sodium acetate on 4-chlorocoumaranone, is converted by hot 30% sulphuric acid into 2-keto-1 : 2′-dehydro-1 : 2′-bis-4-chlorocoumaran (Fries and Pfaffendorff, A., 1911, i, 149), m. p. 210—211° (rapidly heated), or 321° when heated slowly. The *semicarbazone* of 4-chlorocoumaranone melts at 237—238° (decomp.).

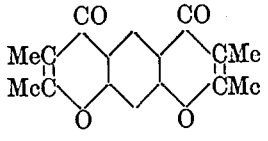
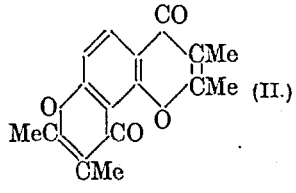
4-Chloro-2-acetylphenol, heated with acetyl chloride and calcium chloride, gives the *acetate*, b. p. 156—157°, together with some 6-chloro-3-acetyl-2-methylbenzo-1 : 4-pyrone. The phenol or its acetate reacts with propionic anhydride and sodium propionate to give a mixture, from which by the sodium ethoxide method of separation are obtained 6-*chloro*-3 : 4-*dimethylcoumarin*, m. p. 140—141°, and 6-*chloro*-2-*ethylbenzo*-1 : 4-*pyrone*, m. p. 137—138°, in the ratio 4 : 1. 6-*Chloro*-4-*methyl*-3-*ethylcoumarin*, m. p. 120—125°, and 6-*chloro*-3-*butyryl*-2-*propylbenzo*-1 : 4-*pyrone*, m. p. 65—66°, from the phenol by the action of butyric anhydride and sodium butyrate, and 6-chloroflavone, m. p. 181°, 6-chloro-3-benzoylflavone, and 4-*chloro*-2-*benzoylacetylphenol*, m. p. 107—108° (*benzoate*, m. p. 128·5—129·5°), by the action of benzoyl chloride and sodium benzoate. 6-Methylflavone, b. p. 235°/12 mm., is obtained from 3-acetyl-*p*-cresol. 4-Chloro-2-acetylphenol condenses with ethyl formate and sodium to give the *hydroxymethylene*-derivative, $OH{\cdot}C_6H_3Cl{\cdot}CO{\cdot}CH{:}CH{\cdot}OH$, m. p. 148—149°, which is converted by dissolution in concentrated sulphuric acid into 6-chlorobenzo-1 : 4-pyrone, m. p. 137—138°.

The benzo-1 : 4-pyrone–coumarin synthesis may be made to yield only coumarins under determined conditions. Thus 4-chloro-2-acetylphenol, heated for 2 hrs. at 180° with phenylacetyl chloride and sodium phenylacetate, gives 6-*chloro*-3-*phenyl*-4-*methylcoumarin*, m. p. 190·5—191·5°, without any benzo-1 : 4-pyrone. 6-*Chloro*-4-*phenylcoumarin*, m. p. 147—148°, is readily obtained by the action of acetic anhydride and sodium acetate on 4-*chloro*-2-*benzoylphenol*, m. p. 93—94°, which with phenylacetyl chloride and sodium phenylacetate yields 6-*chloro*-3 : 4-*diphenylcoumarin*, m. p. 163·5—164°.

In connexion with the discussion of the mechanism of the synthesis, the following compounds are described: 4-*acetoacetyl*-m-5-*xylenyl methyl ether*, m. p. 50—60°; 6-*chloro*-4-*acetyl*-m-*tolyl methyl ether*, m. p. 79—80°; 6-*chloro*-4-*acetyl*-m-*tolyl acetate*, m. p. 35—36°, b. p. 165—167°/12 mm.; 6-*chloro*-3 : 4 : 7-*trimethylcoumarin*, m. p. 162—163°; 5-*acetyl*-o-*tolyl acetate*, m. p. 60—61° (the *propionate*, b. p. 168—169°/14 mm., gives a *semicarbazone*, m. p. 192—193°); 3-*bromoacetyl*-p-*tolyl acetate* (?), b. p. 150—210°/12 mm.; 3-*propionyl*-2 : 6-*dimethylbenzo*-1 : 4-*pyrone*, m. p. 81—82° (from 3-acetoacetyl-*p*-cresol, propionic anhydride, and sodium propionate); 6-*chloro*-2-

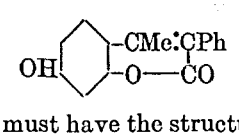
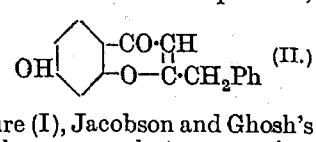
acetoxy-8-*acetyl*-2 : 3 : 3-*trimethylchromanone*, m. p. 79·5—80°, b. p. 176—179°/12 mm. (from 4-chloro-2-*iso*butyrylphenol); 5-*chloro*-3-*acetylsalicylic acid*, m. p. 173—174°. C. HOLLINS.

Preparation of benzodi-4-pyrones. G. WITTIG [with H. E. RICHTER] (Ber., 1926, **59**, [*B*], 116—119).—Resorcinol is converted by propionyl chloride into the *dipropionate*, b. p. 297—298°, which is transformed when heated with zinc chloride into 4 : 6-*dipropionylresorcinol*, m. p. 125—126°. The latter compound with acetic anhydride and sodium acetate at 170° affords 1 : 6 : 3 : 4-*benzo*-2′ : 3′ : 2″ : 3″-*tetramethyldi*-4′ : 4″-*pyrone* (I), m. p. 271—272°, whereas with benzoic anhydride and sodium benzoate it yields 1 : 6 : 3 : 4-*benzo*-2′ : 2″-*diphenyl*-3′ : 3″-*dimethyldi*-4′ : 4″-*pyrone*, m. p. 261—261·5°. 6-Propionylresorcinol is transformed by acetic anhydride and

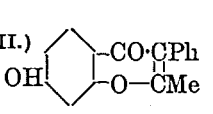
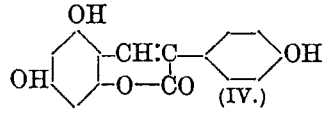
(I.)   (II.)

sodium acetate at 160—170° into 7-*hydroxy*-2 : 3-*dimethylchromone*, m. p. 257—258°, which with propionic anhydride and sodium propionate gives the corresponding *propionate*, m. p. 75·5—76·5°. The latter compound suffers displacement of the propionyl group when heated with aluminium chloride at 120—130°, affording thereby 7-*hydroxy*-8-*propionyl*-2 : 3-*dimethylchromone*, m. p. 161·5—162°, converted by acetic anhydride and sodium acetate at 170° into 1 : 6 : 2 : 3-*benzo*-2′ : 3′ : 2″ : 3″-*tetramethyldi*-4 : 4′-*pyrone* (II), m. p. 188—191°. The position of the propionyl group in 7-hydroxy-8-propionyl-2 : 3-dimethylchromone is shown by the transformation of it (or of 1 : 6 : 2 : 3-benzo-2′ : 3′ : 2″ : 3″-tetramethyldi-4 : 4′-pyrone) by sodium ethoxide into 2 : 6-*dipropionylresorcinol*, m. p. 82°. H. WREN.

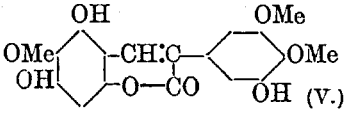
Phenylcoumarins. G. BARGELLINI (Gazzetta, 1925, **55**, 945—951).—Since some of the compounds prepared by the author (cf. A., 1925, i, 1442; and following abstract) and regarded as coumarin derivatives are identical with compounds described by Jacobson and Ghosh as chromones (J.C.S., 1915, **107**, 424, 959, 1051; 1916, **109**, 105), the author is preparing various 3-phenylcoumarins by condensing different *o*-hydroxybenzaldehydes with sodium phenylacetate for making further comparisons. As regards the 3-phenyl-4-methylcoumarins, condensation of 2 : 4-dihydroxyacetophenone with phenylacetic acid might yield either compound (I) or (II), whereas that of the ester or nitrile of α-phenylacetoacetic acid and resorcinol might give either (I) or (III). Since both condensations result in the same product,

(I.)  (II.) 

this must have the structure (I), Jacobson and Ghosh's compounds being, not chromones, but coumarins. Robinson and Baker (*ibid.*, 1925, **127**, 1981, 2340) have reached this conclusion by another way. Investigation of the decomposition of some of these compounds by concentrated potassium hydroxide solution gives results identical with those obtained

(III.)   (IV.)

by Jacobson and Ghosh. With the 3 : 4-disubstituted coumarins, this decomposition is interpretable according to the scheme: $C_6H_4<\begin{matrix}CR{:}CR'\\ O—CO\end{matrix}\longrightarrow Ph{\cdot}OH+$ $OH{\cdot}CR{:}CR'{\cdot}CO_2H$. If R is an aryl or alkyl group and R′ a hydrogen atom, this hydroxy-acid decomposes further into either $R{\cdot}CO_2H$ and $Me{\cdot}CO_2H$ or R·COMe and CO_2; that is, 4-phenylcoumarins decompose like flavones. If, on the other hand, R and R′ are two alkyl or aryl groups, the ketonic acid, $R{\cdot}CO{\cdot}CHR'{\cdot}CO_2H$, yields CO_2 and the corresponding ketone, such as benzyl methyl ketone, deoxybenzoin, etc. If, again, R is a hydrogen atom and R′ an alkyl or aryl group, the aldehydo-acid, $CHO{\cdot}CHR'{\cdot}CO_2H$, gives formic acid and an alkyl- or aryl-acetic acid; thus 3-phenyl-4-hydroxycoumarin gives phenylacetic and formic acids and resorcinol. These considerations lead to the suggestion that Finnemore's prunetin (A., 1910, ii, 1102), Perkin's genistein (J.C.S., 1899, **75**, 830; 1900, **77**, 1310), and other natural products which yield phenylacetic acid or its hydroxyl derivatives, together with phenols, are 3-phenylcoumarins; all the properties of prunetol and of genistein are, indeed, in accord with the formula IV, and Laire and Tiemann's irigenin (A., 1894, i, 47) has probably the annexed formula (V). T. H. POPE.

 (V.)

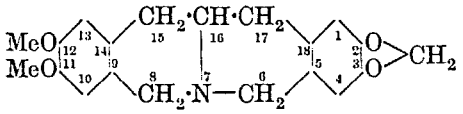
3-Phenyl-4-methylcoumarins. G. BARGELLINI (Atti R. Accad. Lincei, 1925, [vi], **2**, 261—266).—The compounds here described are all obtained by condensing a hydroxyacetophenone with sodium phenylacetate in acetic anhydride (cf. Bargellini, A., 1925, i, 1442). They dissolve in hot dilute alkali and are reprecipitated unaltered by acids; hence they are assumed to be coumarins, although from the condensation of 2 : 4-dihydroxyacetophenone with sodium acetate in acetic anhydride both coumarins and chromones are produced (Kostanecki, A., 1901, i, 222; Kostanecki and Lloyd, *ibid.*, 735). From 2 : 4-dihydroxyacetophenone 7-*acetyl*-3-*phenyl*-4-*methylcoumarin*, m. p. 180—182°, is produced; hydrolysis with concentrated sulphuric acid or alcoholic ammonia yields 7-*hydroxy*-3-*phenyl*-4-*methylcoumarin*, m. p. 225°; *benzoyl* derivative, m. p. 190—192°; *methyl ether* by the action of methyl sulphate and sodium hydroxide on the alcoholic solution or directly from 2-hydroxy-4-methoxyacetophenone by condensation with sodium phenylacetate and acetic anhydride, m. p. 101—102°. From 2 : 5-dihydroxyacetophenone 6-*acetyl*-3-*phenyl*-4-*methylcoumarin* is obtained, m. p. 170—173°; 6-hydroxy-3-phenyl-4-

methylcoumarin, m. p. 248°; *methyl ether* by methylation or condensation of 2-hydroxy-5-methoxyacetophenone, m. p. 150—151°; this compound is reduced by the Zeisel reaction to the corresponding hydroxycoumarin. Condensation of 2 : 3 : 4-trihydroxyacetophenone yields 7 : 8-*diacetyl*-3-*phenyl*-4-*methylcoumarin*, m. p. 207—208°; 7 : 8-*dihydroxy*-3-*phenyl*-4-*methylcoumarin*, m. p. 265—274° (decomp.); *dimethyl ether*, m. p. 166—168°. From 2-acetyl-α-naphthol 3-*phenyl*-4-*methyl*-αβ-*naphthacoumarin*, m. p. 215—216°, is obtained. W. E. ELLIS.

Esters of 2-quinolone-4-carboxylic acid. E. THIELEPAPE.—See B., 1926, 141.

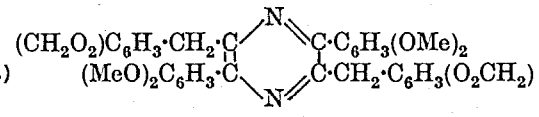
***iso*Quinoline group. VI. Synthesis of derivatives of paraberine.** R. CAMPBELL, R. D. HAWORTH, and W. H. PERKIN, jun. (J.C.S., 1926, 32—43).—The synthesis of 2 : 3-*methylenedioxy*-11 : 12-*dimethoxy*-6 : 15 : 16 : 17-*tetrahydroparaberine* (I) has been effected, but this system of rings is produced

(I.)



with difficulty, as compared with the case of formation of the tetrahydroberberine type. 6 : 7-Dimethoxy-4-dihydro*iso*quinoline is not available as the starting point in the synthesis, since it is not obtained by the action of formaldehyde on ω-aminoacetoveratrone, nor by treating the *N*-formyl derivative of the base with phosphorus oxychloride, whilst *N*-phenacetyl-ω-aminoacetoveratrone with phosphorus oxychloride yields 5-veratryl-2-benzyloxazole; this failure to close the *iso*quinoline ring is attributed to the presence of the carbonyl group. 3 : 4-Dimethoxyphenyl 3 : 4-methylenedioxystyryl ketone is reduced by hydrogen in the presence of colloidal palladium to 3 : 4-dimethoxyphenyl 3 : 4-methylenedioxy-β-phenylethyl ketone, m. p. 102—103° (*oxime*, m. p. 119—121°), which on treatment with methyl nitrite and sodium ethoxide yields its iso*nitroso*-derivative, m. p. 137°. With alkaline reducing agents this gives the *pyrazine* derivative (II), m. p. 205°, but

(II.)



by anhydrous stannous chloride and dry hydrogen chloride in absolute alcohol at −10° the *iso*nitroso-compound is reduced to the *chlorostannate*, from which is obtained the *hydrochloride*, m. p. 218—219° (decomp.), of 3 : 4-dimethoxyphenyl 3 : 4-methylenedioxy-β-phenyl-α-aminoethyl ketone (*picrate*, m. p. 213°). The amine condenses with formaldehyde and hydrochloric acid in methyl-alcoholic solution to form 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzoyl*)-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline* (III), m. p. 137°; *hydrochloride* (anhyd.), m. p. 232—234° (decomp.), and also $+2H_2O$, *oxime*, m. p. 205—209° (decomp.), *picrate*, m. p. 157—158° (decomp.), *benzoyl* derivative, m. p. 187—188°. When this substance, dissolved in ethyl alcohol containing potassium acetate, is oxidised with iodine, it yields 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzoyl*)iso*quinoline* (IV), m. p. 222° [*sulphate*, *oxime*, m. p. 234—236° (decomp.)], from which, by fusion with potassium hydroxide, veratric acid is obtained. The base, m. p. 222°, is reduced by zinc and acetic acid to 6 : 7-*methylenedioxy*-3-(α-*hydroxy*-3′ : 4′-*dimethoxybenzyl*)iso*quinoline* (V), m. p. 153° [*picrate*, m. p. 195° (decomp.)], which on treatment with hydrobromic acid and zinc in presence of acetic acid yields the *picrate*, m. p. 206—207°, of 6 : 7-methylenedioxy-3-(3′ : 4′-dimethoxybenzyl)*iso*quinoline. Reduction of (III), (IV), and (V) tends to give amorphous bases, but the electrolytic reduction of (IV) in hot, dilute sulphuric acid gives 6 : 7-*methylenedioxy*-3-(3′ : 4′-*dimethoxybenzyl*)-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, which is also amorphous [*hydrochloride*, m. p. 220—222° (decomp.), *hydriodide*, m. p. 226° (decomp.), *nitrosoamine*, m. p. 128°]; this on treatment with formaldehyde and hydrochloric acid gives a very small yield of 2 : 3-*methylenedioxy*-11 : 12-*dimethoxy*-6 : 15 : 16 : 17-*tetrahydroparaberine* (I), m. p. 221—222°; *hydrochloride*, m. p. 236—238°, *picrate*, m. p. 199—201° (decomp.), *methiodide*, m. p. 268°, *methochloride*, m. p. 260° (decomp.). The base (I) resembles tetrahydroberberine and tetrahydro-ψ-berberine in crystallising well, in giving sparingly soluble salts, and in the stability of its methiodide to boiling alcoholic potassium hydroxide. But it is dissimilar, in that treatment with iodine yields a *hydriodide*, m. p. 225—226°, which may be converted into the *hydrochloride*, $(+\frac{1}{2}H_2O)$, m. p. 120°, of an amorphous *base*, $C_{20}H_{19}O_4N$, m. p. 180—190° [a 2 : 3-*methylenedioxy*-11 : 12-*dimethoxydihydroparaberine* (6 : 17 or 6 : 15)]. F. M. HAMER.

Substituted pyrrolealcohols, pyrrolealdehydes, and aminopyrrole. H. FISCHER and A. STERN (Annalen, 1926, **446**, 229—241).—When the appropriate aldehydes are reduced (*a*) with platinum-black and hydrogen in alcoholic solution, or (*b*) with aluminium amalgam in moist ethereal solution, the following compounds are obtained: *ethyl* 2 : 5-*dimethyl*-4-*hydroxymethylpyrrole*-3-*carboxylate*, m. p. 131°; *ethyl* 2 : 4-*dimethyl*-5-*hydroxymethylpyrrole*-3-*carboxylate*, m. p. 119°; *ethyl* 2 : 4-*dimethyl*-3-*hydroxymethylpyrrole*-5-*carboxylate*, m. p. 146°. By heating the first two to 150°, water and formaldehyde are eliminated with formation of dipyrrylmethanes, which are also obtained if the aldehydes are reduced with platinum-black in acetic acid solution. When pyrrolealdehydes are treated with hydrogen sulphide in alcoholic solution, the corresponding thioaldehydes are formed: *ethyl* 4-*thioformyl*-2 : 5-*dimethylpyrrole*-3-*carboxylate*, m. p. 231°; *ethyl* 3-*thioformyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 246·5°; *ethyl* 4-*thioformyl*-1-*phenyl*-2 : 5-*dimethylpyrrole*-5-*carboxylate*, m. p. 241°; *ethyl* 4-*thioformyl*-1-p-*tolyl*-2 : 5-*dimethylpyrrole*-3-*carboxylate*, m. p. 246°. The attempted preparation of an aminopyrrole by the reduction of 3-*carbethoxy*-1 : 2 : 5-*trimethylpyrrole*-4-*azobenzene*-*sulphonic acid* was unsuccessful. *Ethyl* 3-*amino*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 125·5°, is obtained by the reduction of the nitropyrrole, using aluminium amalgam in moist ethereal solution. It forms a *picrate*, m. p. 191°, a *hydrochloride*, m. p.

291°, and on diazotisation and coupling with β-naphthol it yields *5-carbethoxy-2 : 4-dimethylpyrrole-3-azo-β-naphthol*, m. p. 234°. It is converted by the action of methyl sulphate into *ethyl 3-dimethylamino-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 87°. The normal behaviour of this aminopyrrole throws doubt on the structure of the supposed aminopyrroles isolated by Fischer and Rothweiler (A., 1923, i, 391).

R. W. WEST.

Complex salts of quinoline, metallic chlorides, water, and hydrogen chloride. W. M. DEHN (J. Amer. Chem. Soc., 1926, **48**, 275—277).—The following complex salts were prepared by dissolving quinoline (1 mol.) in concentrated hydrochloric acid, adding the metallic chloride (1 mol.), heating the mixture until dissolution was complete, with addition, if necessary, of more hydrochloric acid, and allowing crystallisation to take place spontaneously, or evaporating where necessary. Type $2QHCl,MCl_2,2H_2O$: *copper*, orange-red, m. p. 110° after softening at 90°; *cobalt*, dark blue, m. p. 118° (anhydrous, m. p. 155° after softening at 125°); *nickel*, yellow, turning green at 125°, m. p. not below 250°; *zinc*, m. p. 119°; *calcium*; and *strontium*, hygroscopic, m. p. not below 250°; type $QHCl,MCl_2$: *lead*, m. p. not below 250°; ferric (cf. Brosbach, A., 1890, 643); type $2QHCl,MCl_2$: *cadmium*, m. p. not below 250°; type $QHCl,MCl_3,2H_2O$: *arsenic*, m. p. 145° after softening at 120°; *antimony*, m. p. 198°; *bismuth*, m. p. 212°; type $QHCl,MCl_2,H_2O$: *manganese*, faintly pink, m. p. not below 250°.

F. G. WILLSON.

Complex salts of quinoline, mercuric halides, water, and hydrohalogen acids. W. M. DEHN (J. Amer. Chem. Soc., 1926, **48**, 277—282).—The following salts were obtained from the appropriate components in non-aqueous solvents such as alcohol, acetone, acetonitrile, or acetic anhydride. Type (I), Q,Hg,X (X=halogen): chloride, m. p. 223·5° (cf. Hofmann, Ann. Chim. Phys., 1843, [iii], **9**, 173), converted by quinoline into type (V), by hydrochloric acid into type (VIII), and by quinoline hydrochloride into type (VI): type (II), QHX,HgX_2 : *bromide*, m. p. 121°, by dehydration of the corresponding dihydrate; *iodide*, yellow, m. p. 147°, decomposing in aqueous solution into mercuric iodide and $2QHI,HgI_2$; type (III), QHX,HgX_2,H_2O: none obtainable; type (IV), $QHX,HgX_2,2H_2O$: *bromide*, m. p. 118° after softening at 100°; type (V), Q_2HgX_2 : chloride (cf. Pesci, A., 1896, i, 186), m. p. above 200° after softening at 145°, indicating dissociation into quinoline and the salt of type (I); *bromide*, m. p. 185° after softening at 145°; *iodide*, m. p. 154° after softening at 145°; type (VI), Q_2HX,HgX_2 : *chloride*, m. p. 142°; *bromide*, m. p. 147°; *iodide*, yellow, m. p. 106°, decomposed by water into quinoline and QHI,HgI_2; type (VII), $2QHX,HgX_2$: *chloride*, m. p. 130° after softening at 95°, hydrolysing to type (I) with water, and affording type (VIII) with hydrochloric acid; *bromide*, m. p. 118° after softening at 70°; *iodide*, yellow, m. p. 160° after softening at 110°, melting in water with partial formation of QHI,HgI_2; type (VIII), $2QHX,HgX_2,2H_2O$: chloride (cf. Borsbach, A., 1890, 643), m. p. 91°, yielding type (I) with water or aqueous sodium hydrogen carbonate, and type (VI) with alcoholic quinoline; *bromide*, m. p. 120° after softening below 100°; iodide not obtainable; type (IX), $2QHX,HgX_2$: chloride, m. p. 160°, yielding type (I) with boiling water, type (VIII) with hydrochloric acid, type (VII) with quinoline hydrochloride, type (VI) with quinoline, and type (VII) with hydrogen chloride in acetone, owing to the formation of an acetone–mercuric chloride condensation product (cf. Auld and Hantzsch, A., 1905, i, 742); *bromide*, m. p. 145°; iodide not obtainable. The results obtained indicate that definite conditions are required for the formation of any particular type of salt, and that the types obtainable are specific, to some extent, for the individual halogens.

F. G. WILLSON.

Preparation of quinolinic acid and certain of its derivatives. E. SUCHARDA (Rocz. Chem., 1925, **5**, 449—452).—See A., 1925, i, 1317.

Reaction of quinolinic anhydride with aromatic hydrocarbons and aluminium chloride. C. M. JEPHCOTT (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 28).—A continuation of previous work. Naphthalene in benzene solution afforded α- and β-*naphthoylpicolinic acids*, m. p. 155° and 145°, respectively (*hydrochlorides* and *methyl* esters prepared). Acenaphthene in benzene solution afforded *4-acenaphthoylpicolinic acid* (decomp. 168—170°), which forms no hydrochloride, but gives a *hydrate*, m. p. 121°, and *methyl* ester, m. p. 112—114°.

J. S. CARTER.

Complex molybdates with organic bases. C. DI CAPUA (Gazzetta, 1925, **55**, 909—916).—The following compounds have been prepared. *Cobalt pyridine molybdates* : $MoO_3,CoO,4C_5H_5N$; $MoO_3,CoO,2C_5H_5N,2H_2O$; $MoO_3,CoO,C_5H_5N,2H_2O$; $MoO_3,CoO,1{\cdot}5C_5H_5N$.

Cobalt hexamethylenetetramine molybdates : $MoO_3,CoO,C_6H_{12}N_4,2H_2O$; $5MoO_3,2CoO,2C_6H_{12}N_4,12H_2O$; $3MoO_3,CoO,C_6H_{12}N_4,6H_2O$; $6MoO_3,3CoO,2C_6H_{12}N_4,12H_2O$; $3MoO_3,CoO,C_6H_{12}N_4,9H_2O$.

Cobalt guanidine molybdates : $12MoO_3,12CoO,CH_5N_3,22H_2O$; $7MoO_3,7CoO,2CH_5N_3,18H_2O$; $2MoO_3,CoO,2CH_5N_3,4H_2O$.

Nickel pyridine molybdate, $MoO_3,NiO,5C_5H_5N,H_2O$.

Nickel hexamethylenetetramine molybdates : $8MoO_3,3NiO,2C_6H_{12}N_4,36H_2O$; $8MoO_3,2NiO,3C_6H_{12}N_4,16H_2O$; $6MoO_3,3NiO,2C_6H_{12}N_4,16H_2O$.

Nickel guanidine molybdate, $6MoO_3,NiO,5CH_5N_3,12H_2O$.

Magnesium hexamethylenetetramine molybdate, $MoO_3,MgO,C_6H_{12}N_4,10H_2O$.

Manganese hexamethylenetetramine molybdate, $3MoO_3,2MnO,C_6H_{12}N_4,5H_2O$.

Manganese guanidine molybdate, $12MoO_3,12MnO,CH_5N_3,18H_2O$.

T. H. POPE.

Action of *s*-tetrabromoethane on organic bases. J. D. FULTON (J.C.S., 1926, 197—199).—When 2 or 3 mols. of *s*-tetrabromoethane are

added to 1 mol. of a tertiary amine, a colourless additive compound is formed, which on recrystallisation tends to change to the hydrobromide of the base. These additive compounds are decomposed by water, and converted by auric bromide into the bromoaurate of the corresponding base; the bromoaurates of nicotine and quinoline are abnormal. Nicotine (*bromoaurate*, $C_{10}H_{14}N_2,2HBr,AuBr_3$, m. p. 183°) gives the *compound* $C_{10}H_{14}N_2,2HBr,2C_2H_2Br_4$, softens at 140°, m. p. 178—180° (decomp.), $[\alpha]^{17}_{\text{Hg green}}$ in alcohol +3·21°, which on repeated recrystallisation, or by reaction of equimolecular proportions of nicotine and tetrabromoethane, gives the *compound* $(C_{10}H_{14}N_2,2HBr)_2,C_2H_2Br_4$, m. p. 182—183° (decomp.), $[\alpha]^{17}_{\text{Hg green}}$ in alcohol +6·96°; pyridine (*bromoaurate*, m. p. 318—319°) gives the *compound* $C_5H_5N,HBr,C_2H_2Br_4$, m. p. 108—109°; quinoline [*bromoaurate*, $(C_9H_7N,HBr)_2,AuBr_3$, m. p. 171—172°], gives the *compound* $(C_9H_7N,HBr)_2,C_2H_2Br_4$, softens at 115°, m. p. 136°; *iso*quinoline (*bromoaurate*, m. p. 223°) gives its *hydrobromide*, m. p. 207°, together with the *compound* $(C_9H_7N,HBr)_2,C_2H_2Br_4$, m. p. 155—156°; lutidine, b. p. 153—156°, gives the *compound* $(C_7H_9N,HBr)_2,C_2H_2Br_4$, m. p. 135—140°; α-picoline gives the *compound* $C_6H_7N,HBr,C_2H_2Br_4$, m. p. 104—105°. Tetrabromoethane does not react with antipyrine or pyrrole, whilst with piperidine, coniine, homopiperonylamine, menthylamine, hexamethylenetetramine, and phenylhydrazine, it yields hydrobromide only. F. M. HAMER.

Action of mercuric salts on dialkylbarbituric acids. I. Phenylethyl, diethyl, and butylethyl derivatives. P. FLEURY (Bull. Soc. chim., 1925, [iv], **37**, 1656—1668).—Excess of an acid solution of mercuric sulphate, added to an aqueous or an aqueous-alcoholic solution of phenylethylbarbituric acid, forms a *precipitate* the composition of which is practically constant and is represented by

$$2{\cdot}5HgO,3C_4H_2O_3N_2PhEt.$$

This precipitation is sufficiently complete to be used in determining the concentration of a solution of the acid and furnishes a method of separating the latter. Washing with distilled water changes the composition to $2HgO,3C_4H_2O_3N_2PhEt$, but renewed contact with acid mercuric sulphate solution transforms this substance into the original compound. In the case of diethylbarbituric acid, the composition of the precipitate, which is soluble in excess of the reagent, varies with the acidity of the latter. From acid solution the *compound* $2HgO,3C_4H_2O_3N_2Et_2$ is obtained, whilst from neutral solution

$$2{\cdot}5HgO,3C_4H_2O_3N_2Et_2$$

is precipitated. The composition of the last-named is unchanged on washing with water. The precipitate obtained from ethylbutylbarbituric acid varies in composition with the acidity of the reagent; moreover, the quantity of mercury fixed by the acid increases as the concentration of the latter diminishes, although variation appears to be between the limits $2{\cdot}0—2{\cdot}5HgO,3C_4H_2O_3N_2EtBu$. These substances appear to be unchanged by water. H. J. EVANS.

Derivatives of 3-methyl-5-pyrazolone. H. J. BACKER and W. MEYER (Rec. trav. chim., 1926, **45**, 82—99).—Various alkyl, urethane, and carbamide derivatives of 3-methyl-5-pyrazolone have been prepared, and the action of fuming nitric acid on them has been investigated. The alkyl derivatives are obtained by the condensation of hydrazine with the appropriate alkylated acetoacetic ester in an aqueous medium, the reaction proceeding much more readily if the methyl esters are employed, and thus are obtained: 3-methyl-5-pyrazolone, m. p. 269° (divergent values given in the literature); 3 : 4 : 4-trimethyl-5-pyrazolone, m. p. 109·5° (von Rothenburg, A., 1895, i, 686, gives 268°); 3-methyl-4-ethyl-5-pyrazolone, m. p. 227·5° (Locquin, A., 1902, i, 705, gives 190—196°); 3-*methyl*-4 : 4-*diethyl*-5-*pyrazolone*, m. p. 105·5°; 3 : 4-*dimethyl*-4-*ethyl*-5-*pyrazolone*, m. p. 76—77°. Two methods are available for the preparation of the urethane derivatives, (1) the introduction of a carbalkoxyl group into the pyrazolone by the action of the appropriate alkyl chloroformate in the presence of alkali; (2) the condensation of a substituted acetoacetic ester with the alkyl hydrazinecarboxylate hydrochloride. By the first method are obtained: ethyl 3-methyl-5-pyrazolone-1-carboxylate, m. p. 203° (cf. Gatmann, Dissertation, Heidelberg, 1903, 32); *propyl* 3-*methyl*-5-*pyrazolone*-1-*carboxylate*, m. p. 120°; *ethyl* 3 : 4-*dimethyl*-5-*pyrazolone*-1-*carboxylate*, m. p. 184·5°; *propyl* 3 : 4-*dimethyl*-5-*pyrazolone*-1-*carboxylate*, m. p. 149°; *ethyl* 3-*methyl*-4-*ethyl*-5-*pyrazolone*-1-*carboxylate*, m. p. 170°; *propyl* 3-*methyl*-4-*ethyl*-5-*pyrazolone*-1-*carboxylate*, m. p. 126°. Methyl hydrazinecarboxylate hydrochloride (Diels and Fritzsche, A., 1911, i, 957) condenses with ethyl ethylacetoacetate to yield *ethyl ethylacetoacetate-carbomethoxyhydrazone*, m. p. 94°, which when heated above its m. p. is converted into 3-methyl-4-ethyl-5-pyrazolone. *Propyl hydrazinecarboxylate hydrochloride*, m. p. 51° (from propyl chloroformate and hydrazine hydrate in methyl-alcoholic solution), with benzaldehyde yields a *benzylidene*-derivative, m. p. 145°, and when heated with ethyl ethylacetoacetate in a sealed tube at 110° yields propyl 3-methyl-4-ethyl-5-pyrazolone-1-carboxylate (above), but when heated at 160° yields only 3-methyl-4-ethyl-5-pyrazolone. Carbamide derivatives of the pyrazolones are obtained from the semicarbazones of the substituted acetoacetic esters. The product obtained depends somewhat on whether semicarbazide itself or its hydrochloride is employed, and the use of methyl or ethyl esters, the latter alternative in each case favouring the direct formation of the pyrazolone derivative. Thus are obtained: *methyl acetoacetate semicarbazone*, m. p. 152—153° (decomp.), which, with concentrated ammonia, is converted into 3-methyl-5-pyrazolone-1-carbamide (cf. Thiele and Strange, A., 1895, i, 251), *semicarbazones* of methyl methylacetoacetate, m. p. 138°; ethyl methylacetoacetate, m. p. 86°; methyl ethylacetoacetate, m. p. 98°, and ethyl ethylacetoacetate, m. p. 80°; the corresponding pyrazolones 3-*methyl*-5-*pyrazolone*-1-*carbamide*, m. p. 192°; 3 : 4-*dimethyl*-5-*pyrazolone*-1-*carbamide*, m. p. 194° (decomp.), which on heating above its m. p. or on boiling its aqueous solution for 1 hr. is converted into 3 : 4-dimethyl-5-pyrazolone; 3-*methyl*-4-*ethyl*-5-*pyrazolone*-1-*carbamide*, m. p. 161—162°, which is hydrolysed to 3-methyl-4-ethyl-5-pyrazolone only after its aqueous solution

has been boiled for several hours. On treatment with fuming nitric acid at —15°, 3-methyl-5-pyrazolone yields 4-nitro-3-methyl-5-pyrazolone (cf. Betti, A., 1901, i, 533); ethyl and propyl 3-methyl-5-pyrazolone-1-carboxylate, treated with fuming nitric acid at 0°, yield, respectively, *ethyl 4-nitro-3-methyl-5-pyrazolone-1-carboxylate*, m. p. 172° (decomp.) (also obtained by the action of ethyl chloroformate on 4-nitro-3-methyl-5-pyrazolone), and *propyl 4-nitro-3-methyl-5-pyrazolone-1-carboxylate*, m. p. 157° (also by the action of propyl chloroformate on the 4-nitropyrazolone). 3 : 4-Dimethyl- and 3 : 4 : 4-trimethyl-5-pyrazolone do not react with nitric acid, whilst ethyl 3 : 4-dimethyl-5-pyrazolone-1-carboxylate, ethyl 3-methyl-4-ethyl-5-pyrazolone-1-carboxylate, and 3 : 4-dimethyl-5-pyrazolone-1-carbamide yield the corresponding pyrazolone, the carbalkoxyl or carbamide groups being eliminated. On treatment with nitrous anhydride in alcoholic suspension, 3 : 4-dimethyl-5-pyrazolone yields *1-nitroso-3 : 4-dimethyl-5-pyrazolone*, which is stable at 0°, but decomposes at the ordinary temperature. Nitrosation of 3-methyl-5-pyrazolone yields 4-iso*nitroso-3-methyl-5-pyrazolone*, m. p. 229° (*silver* derivative described).

J. W. BAKER.

Preparation of 1-phenyl-2 : 3-dimethyl-5-pyrazolone. K. T. HERBST.—See B., 1926, 108.

Thioesters of pyrazolone series. E. SCHERING.—See B., 1926, 141.

Pyrazolone azo dyes. BRITISH DYESTUFFS CORP., LTD., ETC.—See B., 1926, 85.

Ether-substituted derivatives of ethyl malonate and barbituric acid. A. J. HILL and D. T. KEACH.—See this vol., 271.

Reduction of 2 : 5-diketopiperazine. M. GAWRILOFF (Bull. Soc. chim., 1925, [iv], **37**, 1651—1656).—The action of sodium and amyl alcohol on diketopiperazine results in the formation of ammonia (50%), aminoethanol (21%), and piperazine (15%). In addition, amylamine and amylethanolamine are also formed, presumably from the amyl alcohol. By reason of the slight solubility of diketopiperazine in ethyl alcohol, this substance was found to be unsuitable as a medium for the reaction, but a small yield of aminoethanol was obtained (cf. Cohn, A., 1900, i, 466; Hoyer, A., 1902, i, 352; Heimrod, A., 1914, i, 327).

H. J. EVANS.

Desmotropic forms of diketopiperazines, their formation, and combination with amino-acids. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1925, **149**, 298—301).—An unsaturated form of leucylglycyl anhydride is obtained by heating leucylglycyl anhydride with the molecular quantity of tyrosine in glycerol. This product may be methylated. If ordinary leucylglycyl anhydride is heated with the molecular quantity of inactive leucine, the same unsaturated product is obtained.

Leucylglycyl anhydride is formed when the two amino-acids are heated together with glycerol at 190°.

H. D. KAY.

Action of phenylcarbimide on diketopiperazines. M. LUDTKE (Z. physiol. Chem., 1925, **150**, 215—219).—By boiling the diketopiperazines with phenylcarbimide (3—5 mols.), the following were obtained as well-crystallised compounds in good yields: 1 : 4-*di*(*phenylcarbamyl*)-2 : 5-*diketopiperazine*, becomes yellow at 220° and brown (decomp.) towards 270°; 1 : 4-*di*(*phenylcarbamyl*)-2 : 5-*diketo*-3-*methylpiperazine*, m. p. 158—159° (corr.), and 1 : 4-*di*(*phenylcarbamyl*)-2 : 5-*diketo*-3-*benzylpiperazine*, m. p. 154° (corr.) (decomp.). These compounds did not give the picric acid reaction.

H. I. COOMBS.

1 : 2-Methylacetyl derivatives of indazole. K. VON AUWERS and H. G. ALLARDT (Ber., 1926, **59**, [*B*], 90—95).—A further contribution to the chemistry of the labile and stable acylindazoles (cf. A., 1925, i, 1460).

The additive products from 2-methylindazole and acetyl iodide at atmospheric temperature and 50°, respectively, melt indefinitely at about 90°, but behave somewhat differently towards water, in which one dissolves and can be recovered unchanged, whereas the other is decomposed into 2-methylindazole and the compound, m. p. 41°, regarded previously as "stable 2-acetylindazole." The first product undergoes the same change when warmed with water. The same substances, in addition to much free indazole, are obtained when either compound is distilled under diminished pressure. It appears therefore that the primary additive product has the constitution $\left[C_6H_4\langle\begin{matrix}CH\\NAc\end{matrix}\rangle NMe\right]I$, and that the acetyl derivative obtained from it is 1-acetylindazole. This conclusion is supported by the observation that acetylindazole, m. p. 41°, and methyl iodide give an additive compound similar to that just described, whereas acetylindazole, m. p. 170°, regarded previously (A., 1924, i, 1348) as the 1-derivative, reacts quite differently.

The additive products from 1-methylindazole and acetyl iodide are not invariably uniform in character, but are sharply differentiated from those just described, since they are smoothly decomposed by water into 1-methylindazole and acetic acid and distil almost unchanged in a vacuum. It follows, therefore, that the stable acetylindazole, m. p. 41°, cannot be a 2-derivative, since, if this were the case, it must apparently be formed from the compound $\left[C_6H_4\langle\begin{matrix}CH\\NMe\end{matrix}\rangle NAc\right]I$; the non-appearance of the labile acetylindazole, m. p. 106°, among the products of fission is not surprising, since acyl groups are retained with little firmness in position 2. The addition of methyl iodide to acetylindazole, m. p. 106°, could not be studied owing to absence of reaction at the atmospheric temperature and decomposition of the reactant when heated.

Stable 1-*o*-nitrobenzoylindazole does not appear to react with methyl iodide at 100°, whereas the isomeric, labile 2-*o*-nitrobenzoylindazole is partly transformed into 1 : 2-dimethylindazolium iodide. This salt is also formed, amongst other products, from ethyl indazole-1-carboxylate and methyl iodide.

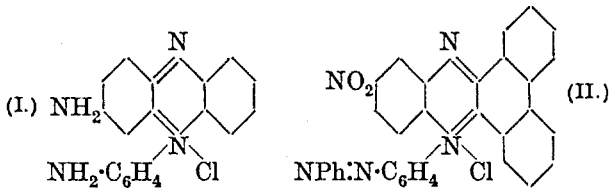
H. WREN.

Indazyl-fatty acids. K. VON AUWERS and H. G. ALLARDT (Ber., 1926, **59**, [*B*], 95—100).—Ethyl bromoacetate reacts with indazole at 100—120° with almost exclusive production of ethyl indazole-2-acetate, whereas at higher temperatures the isomeric 1-derivative is produced subordinately or even predominatingly; in the presence of alkali alkoxide, both isomerides are formed. *Indazyl-1-acetic acid*, m. p. 185—186°, *ethyl indazyl-2-acetate*, b. p. 175—177°/11 mm., m. p. 54—54·5° (*picrate*, m. p. 164·5°), and *indazyl-2-acetic acid*, m. p. 257° (decomp.), are described; the latter substance is converted by methyl iodide into 1 : 2-dimethylindazolium iodide. The isomeric indazylacetic acids break down into carbon dioxide and the corresponding methylindazole when distilled under diminished pressure; the reaction takes place more smoothly with the 2- than with the 1-derivative. Indazole and ethyl α-bromopropionate react in a similar manner, affording *ethyl 1-indazyl-α-propionate*, b. p. 153—155°/11 m., non-crystalline 1-indazyl-α-propionic acid (*silver* salt), *ethyl 2-indazyl-α-propionate*, b. p. 172°/11 mm. (*picrate*, m. p. 141—142°), and *2-indazyl-α-propionic acid*, m. p. 209° (decomp.). The latter acid decomposes above its m. p. into carbon dioxide and 2-ethylindazole. Indazole and ethyl α-bromo*iso*butyrate at 140° afford *2-ethylindazole*, m. p. 40—41°, d_4^{20} 1·076, n_{He}^{20} 1·591, in moderate yield; it appears probable that the formation of the compound is due to partial hydrolysis of the ester by hydrogen bromide liberated in the initial stage of the change and alkylation of unchanged indazole by the ethyl bromide thus produced rather than to pyrogenic decomposition of ethyl 2-indazyl-α-*iso*butyrate. Indazole and β-bromopropionic acid at 210° yield *indazyl-β-propionic acid*, m. p. 148—149° (*picrate*, m. p. 170°), which decomposes when distilled under diminished pressure into indazole and acrylic acid. It remains uncertain whether it is a 1- or 2-derivative. H. WREN.

Synthetic indigo. R. LEPETIT.—See B., 1926, 121.

Synthesis of δ-pyrindigotin. E. SUCHARDA (Rocz. Chem., 1925, **5**, 453—458).—See A., 1925, i, 1331.

Transformation of 2 : 4-dinitro-4′-phenylazodiphenylamine into phenazine derivatives. A. BERETTA (Gazzetta, 1925, **55**, 711—713).—2 : 4-Dinitro-4′-phenylazodiphenylamine (A., 1924, i, 221) is reduced with tin and hydrochloric acid on the water-bath at a temperature not exceeding 70°. When the liquid is clear, cold water is added until the temperature has fallen to 40°, and the tin is then precipitated with zinc dust. After neutralising the liquid with calcium carbonate, it is oxidised with potassium dichromate and sulphuric acid, filtered, and the filtrate saturated with sodium chloride. The *aminophenosafranine* (I), which is precipitated, m. p. above 360°, dyes cotton mordanted with tannin and potassium antimonyl tartrate a tint similar to that given by ordinary phenosafranine (cf. Barbier and Sisley, A., 1905, i, 840). By condensing 2 : 4-dinitro-4′-phenylazodiphenylamine with phenanthraquinone, nitrophenylazoflavinduline is formed. The former is dissolved in the least possible quantity of hot alcohol, slightly acidified with hydrochloric



acid, and poured into a saturated solution of phenanthraquinone in glacial acetic acid at 100°. After heating for some time on the water-bath, the liquid is allowed to evaporate spontaneously to a small bulk; it is filtered and *nitrophenylazoflavinduline chloride* (II), m. p. 146—148°, is precipitated by hydrochloric acid. W. E. ELLIS.

Pyrogenic transformation of *o*-aminoazo-compounds into triazoles. G. B. CRIPPA (Gazzetta, 1925, **55**, 706—711).—Certain arylazo-β-naphthylamines are transformed into triazoles by boiling, not only in nitrobenzene solution, but also in various other liquids in the presence of copper or iron powder. In accordance with the observed formation of primary amine and *o*-diamine, the reaction is assumed to follow Charrier's equation (A., 1910, i, 287). In the presence of either copper or iron, the minimum reaction temperature is 155°; iron is slightly less favourable than copper. Resinification is avoided if the reaction is completed below 300°. The time necessary for complete change varies with the solvent from 10 min. in vaseline oil (b. p. 280°) to 8 hrs. in naphthalene and 50 hrs. in turpentine, whilst in xylene no change is observed after boiling for 70 hrs. 2′ : 4′ : 5′-Trimethylphenylazo-1-amino-2-naphthalene is boiled with a seventh of its weight of copper powder in vaseline oil for 15 min. After the liquid has been filtered and cooled, crude 2-N-2′ : 4′ : 5′-*trimethylphenyl*-1 : 2-*naphthatriazole* separates from it. When freed from 1 : 2-naphthylenediamine by boiling water and from traces of other bases by dilute hydrochloric acid, this product gives crystals, m. p. 102°. By steam distillation of the vaseline oil, ψ-cumidine is obtained. W. E. ELLIS.

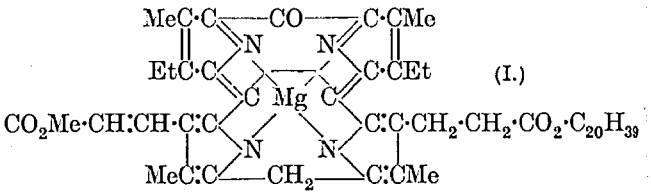
***o*-Aminoazo-compounds and 1 : 2 : 3-acenaphthatriazoles.** G. CHARRIER and A. BERETTA (Gazzetta, 1925, **55**, 745—754).—On oxidation with cupric ammonium sulphate (Schmidt and Hagenböcker, A., 1921, i, 897) 2-phenylazo-3-aminoacenaphthene (Sachs and Mosebach, A., 1910, i, 726) is converted into 2-N-*phenyl*-2 : 3-*acenaphtha*-1 : 2 : 3-*triazole*, m. p. 186°. The corresponding *quinone*, m. p. 268°, is obtained by oxidation with potassium dichromate in acetic acid; *monophenylhydrazone*, m. p. 254°. Alkaline potassium permanganate oxidises the acenaphthatriazole to 2-N-*phenyl*-3 : 4-*triazolenaphthalic acid*, m. p. 218°. The following new compounds obtained by the above methods are also described: 3-*amino*-2-o-*tolylazoacenaphthene*, m. p. 175°; 2-N-o-*tolyl*-2 : 3-*acenaphthatriazole*, m. p. 100°; 2-m-*tolylazo*-3-*aminoacenaphthene*, m. p. 171°; 2-N-m-*tolyl*-2 : 3-*acenaphthatriazole*, m. p. 181°; 3-*amino*-2-p-*tolylazoacenaphthene*, m. p. 154°; 2-N-p-*tolyl*-2 : 3-*acenaphthatriazole*, m. p. 198°; 3-*amino*-

2-s-*ψ-cumylazoacenaphthene*, m. p. 170°; 2-N-*ψ-cumyl*-2 : 3-*acenaphthatriazole*, m. p. 150°; 3-*amino*-2-p-*nitrophenylazoacenaphthene*, m. p. 195°; 3-*amino*-2-p-*chlorophenylazoacenaphthene*, m. p. 184°; 2-N-p-*chlorophenyl*-2 : 3-*acenaphthatriazole*, m. p. 223°; 3-*amino*-2-p-*bromophenylazoacenaphthene*, m. p. 185°; 2-N-p-*bromophenyl*-2 : 3-*acenaphthatriazole*, m. p. 231°. W. E. ELLIS.

Dioximes. XXVII. G. PONZIO and G. PEROLIO (Gazzetta, 1925, **55**, 688—698).—The action of phenylhydrazine on phenylchloroglyoxime yields a symmetrical derivative of 2 : 3 : 4 : 5-tetrahydrotetrazine, $C_{14}H_{12}ON_4$ (cf. Ponzio and Avogadro, A., 1923, i, 472, 855). Slightly more than 2 mols. of phenylhydrazine are added to 1 mol. of phenylchloroglyoxime, powdered, and suspended in alcohol, and the action is completed at 50—60°. The new compound, m. p. 174—175°, is concluded to be 3-*keto*-2 : 6-*diphenyl*-2 : 3 : 4 : 5-*tetrahydrotetrazine* (I); it is slightly basic and gives a hydrochloride. The *monoacetyl* derivative, m. p. 161°, is formed by acetic anhydride in the cold, and the *diacetyl* derivative, m. p. 174°, by boiling with acetic anhydride and fused sodium acetate. When (I) is oxidised in 50% acetic acid with chromium trioxide, 3-*keto*-2 : 6-*diphenyl*-2 : 3-*dihydrotetrazine*, m. p. 264—265°, is obtained. The reduction of (I) with zinc dust and acetic acid gives 2 : 6-*diphenyl*-2 : 3 : 4 : 5-*tetrahydrotetrazine*, m. p. 86°. On oxidation of the latter with chromium trioxide in acetic acid, 2 : 6-*diphenyl*-2 : 3-*dihydrotetrazine*, m. p. 238—239°, is formed. When phenylchloroglyoxime is treated with *p*-bromophenylhydrazine under the conditions of the formation of (I), 3-*keto*-6-*phenyl*-2-p-*bromophenyl*-2 : 3 : 4 : 5-*tetrahydrotetrazine*, m. p. 189—190°, is formed; *diacetyl* derivative, m. p. 169—170°. If *p*-tolylchloroglyoxime (Avogadro, A., 1924, i, 54) is substituted for phenylchloroglyoxime in the reaction with phenylhydrazine, 3-*keto*-2-*phenyl*-6-p-*tolyl*-2 : 3 : 4 : 5-*tetrahydrotetrazine*, m. p. 190—191°, is formed (the same compound is obtained from p-*tolylchlorodiacetylglyoxime*); *diacetyl* derivative, m. p. 170°. The following related compounds are formed as in the previous cases: 3-*keto*-2-*phenyl*-6-p-*tolyl*-2 : 3-*dihydrotetrazine*, m. p. 265°; 2-*phenyl*-6-p-*tolyl*-2 : 3 : 4 : 5-*tetrahydrotetrazine*, m. p. 104°; 2-*phenyl*-6-p-*tolyl*-2 : 3-*dihydrotetrazine*, m. p. 259°. W. E. ELLIS.

Constitution of spermine. II. Methylation of spermine. H. W. DUDLEY and O. ROSENHEIM (Biochem. J., 1925, **19**, 1032—1033; cf. A., 1925, i, 294).—Spermine was completely methylated by treatment with potassium hydroxide and methyl iodide. After removing the excess of methyl alcohol, methyl iodide, and iodides, the decamethylspermine was converted into the sparingly soluble mercurichloride. This was decomposed with hydrogen sulphide and the picrate of the methylated base was obtained by adding excess of sodium picrate. The following salts were prepared: *decamethylspermine chloroaurate*, $C_{20}H_{50}N_4,4AuCl_4$, m. p. 278—280° (decomp.); *decamethylspermine chloroplatinate*, $C_{20}H_{46}N_4,2H_2PtCl_6$, m. p. 286—288° (decomp.); *decamethylspermine tetrapicrate*, $C_{20}H_{50}N_4,4C_6H_2O_7N_3$, m. p. 272—274° (decomp.); *decamethylspermine mercurichloride*, m. p. 268°. Spermine thus takes up ten methyl groups, forming the quaternary ammonium base $C_{20}H_{50}N_4(OH)_4$; two of its nitrogen atoms are therefore primary whilst the other two are secondary. S. S. ZILVA.

Efficiency of photosynthesis by *Chlorella*. E. Q. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 292—294).—The structure (I), which agrees with analytical data within the usual limits, is suggested for chlorophyll-*a*. This contains two conjugated chains of 11 atoms each, similar to that contained in the cation of malachite-green, and would therefore be expected to absorb 2 quanta of red light. Further, as the differences between chlorophylls-*a* and -*b* do not involve these chains, only a slight difference in the wave-length absorbed by the two modifications

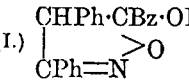
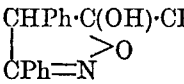


is to be expected. The energy of 4 quanta of light absorbed (174·4 Cal./mol.) is sufficient to cause the chlorophyll to pass through a cycle of four reactions, according to the following scheme, in which R represents the group $C_{55}H_{72}O_4N_4Mg$: $RO+H_2O+2$ quanta $\lambda 666\ \mu\mu \longrightarrow R+H_2O_2$; $R+CO_2 \longrightarrow RCO_2$; RCO_2+H_2O+2 quanta $\lambda 640\ \mu\mu \longrightarrow RCO+H_2O_2$; $RCO+H_2O \longrightarrow RO+CH_2O$. The nett result of this cycle is the conversion of 1 mol. of carbon dioxide and 3 mols. of water into 2 mols. of hydrogen peroxide and 1 mol. of formaldehyde, for which 171·0 Cal./mol. are required. As 6 mols. of formaldehyde are required to produce 1 mol. of dextrose, the heat of combustion of which (dissolved) is 674 Cal./mol., the maximum possible efficiency of this synthesis thus becomes 64·4%, as compared with Warburg and Negelein's figures of 59—63·5% (cf. A., 1923, ii, 718). F. G. WILLSON.

Substituted dihydropentazines. New series of cyclic nitrogen compounds. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1926, 113—117).—Benzaldehyde-2 : 4-dibromophenylhydrazidine, prepared from ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone (A., 1925, i, 929), is converted by nitrous acid into 1-(2 : 4-*dibromophenyl*)-4-*phenyltetrazole*, m. p. 127°, which is also obtained by heating benzaldehyde-2 : 4-dibromophenylhydrazone and phenyl azide in presence of alcoholic sodium ethoxide; similarly, ω-bromo-*m*-nitrobenzaldehyde-2 : 4-dibromophenylhydrazone gives 1-(2 : 4-*dibromophenyl*)-4-m-*nitrophenyl*-1 : 2 : 3 : 5-*tetrazole*, m. p. 215°. ω-Bromobenzaldehyde-2 : 4-dibromophenylhydrazone reacts with hydrazine hydrate in alcoholic solution to form ω-*hydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 123° (decomp.) [*hydrochloride*, m. p. 188° (decomp.); *sulphate*, decomp. without melting], which with benzaldehyde yields ω-*benzylidenehydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p.

126°, with *p*-nitrobenzaldehyde yields ω-p-*nitrobenzylidenehydrazinobenzaldehyde*-2 : 4-*dibromophenylhydrazone*, m. p. 194°, and with ω-bromobenzaldehyde-2 : 4-dibromophenylhydrazone yields (probably) *hydrazobenzaldehyde*-2 : 4-*dibromophenylhydrazone* ($C_6H_3Br_2$·NH·N:CPh·NH·)$_2$, (αβ-*dibenzoylhydrazine*-2 : 4-*dibromophenylhydrazone*), m. p. 237°. By nitrous acid, ω-hydrazinobenzaldehyde-2 : 4-dibromophenylhydrazone is converted into 1-(2 : 4-*dibromophenyl*)-5-*phenyl*-1 : 4-*dihydropentazine*, m. p. 172° (decomp.), which decomposes when heated, giving rise to benzonitrile, but is unchanged by heating with acetylene in presence of acetone. F. M. HAMER.

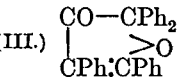
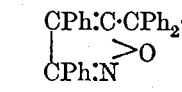
***iso*Oxazoline oxides. IV. Benzoyldiphenyl-*iso*oxazoline oxide.** E. P. KOHLER (J. Amer. Chem. Soc., 1925, **47**, 3030—3036; cf. A., 1924, i, 1239).—αγδ-Triphenylbutanetrione oxime is obtained in 85—90% yield by treating α-bromo-γ-nitro-βγ-diphenylpropiophenone with aqueous 5% sodium hydroxide in presence of methyl alcohol and ether (cf. A., 1924, i, 998). It is stable only in solid form. In chloroform solution, a trace of acid rapidly converts it into a purple *anhydride*, whilst boiling with methylalcoholic sodium methoxide affords a quantitative yield of 5-*hydroxy*-5-*benzoyl*-3 : 4-*diphenyl*isooxazoline (I), m. p. 123°, previously assumed to be 4-benzoyl-2 : 3-diphenyl*iso*oxazoline oxide (*loc. cit.*). The formulæ for the sodium and benzoyl derivatives of

(I.)  (II.) 

this compound are amended in accordance with the new structure. When treated with excess of magnesium phenyl bromide, (I) affords *diphenyl*-3 : 4-*diphenyl*-5-isooxazolylcarbinol (II), m. p. 170—171°, together with 3-*keto*-2 : 2 : 4 : 5-*tetraphenyl*-2 : 3-*dihydrofuran* (III), the latter being also obtained when (II) is heated above its m. p. When treated with ozone in chloroform, or with chromic acid in glacial acetic acid at 90°, (III) yields benzoic acid and *γ-hydroxy-αγγ-triphenylbutane-αβ-dione*,

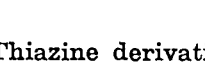
Bz·CO·CPh_2·OH,

yellow, m. p. 150°, which, on further oxidation, yields benzoic and benzilic acids. When the proportion of magnesium phenyl bromide applied in the

(III.)  (IV.) 

above Grignard reaction is limited to 1 mol., the product is 2 : 3-*diphenyl*-5-*diphenylcarbinyl*isooxazolidine (IV), m. p. 157—158°, which resembles triphenylcarbinol in that it cannot be benzoylated, but readily forms ethers (*methyl ether*, m. p. 182—183°). F. G. WILLSON.

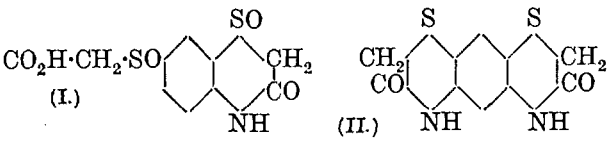
Quaternary salts of benzoxazoles. L. M. CLARK (J.C.S., 1926, 232—235).—The benzoxazolonium salts are less stable than the benzthiazolonium salts and give rise to pseudo-bases which are *o*-acylaminophenols and cannot be reconverted into the quaternary salts. Addition of 1 mol. of potassium hydroxide to an aqueous solution of benzoxazole methiodide, m. p. 202° (decomp.), forms o-*formylmethylaminophenol*, m. p. 103—104° (hydrolysable to *o*-methylaminophenol, m. p. 95—96°). 1-Methylbenzoxazole methiodide, m. p. 196° (decomp.) (*methoperchlorate*, m. p. 173°), is converted similarly, or by the action of silver oxide, or of water only, into *o*-acetylmethylaminophenol, whilst 1-*phenylbenzoxazole methiodide*, m. p. 196° (decomp.), is converted into *o*-benzoylmethylaminophenol, m. p. 164° (*urethane*, m. p. 144°). A carbinol base may be formed intermediately, but treatment of 1-phenylbenzoxazole methiodide with sodium hydroxide and methyl sulphate yields no derivative of such a base, but only o-*benzoylmethylaminoanisole*, m. p. 115° (also prepared by benzoylation of *o*-methylaminoanisole). F. M. HAMER.

4-Keto-3-*p*-xylyl-2-thiothiazolidone and some of its derivatives. R. M. HANN (J. Washington Acad. Sci., 1926, **16**, 31—35).—*Ammonium* p-*xylyldithiocarbamate*, $C_6H_3Me_2$·NH·CS_2NH_4, prepared in 80% yield by the interaction of *p*-xylidine, ammonia, and carbon disulphide, condenses with ethyl bromoacetate in absolute alcohol to give a 70% yield of 4-*keto*-3-p-*xylyl*-2-*thiothiazolidone*,  m. p. 119—120° (corr.). The *benzylidene*- (m. p. 188—189°, corr.), *cinnamylidene*- (m. p. 194—195°, corr.; *dibromide*, m. p. 119—120°, corr.), p-*hydroxy*-m-*methoxybenzylidene*- (m. p. 155—156°, corr.), and 5-*bromo*-4-*hydroxy*-3-*methoxybenzylidene*- (m. p. 192—193°, corr.) derivatives are described. C. HOLLINS.

Thiazine derivatives of nitro-2 : 4-phenylenedithioglycollic acid. II. C. FINZI and ERMINIA PAGLIARI (Gazzetta, 1925, **55**, 859—868).—In the benzoketodihydrothiazines the hydrogen atoms of the nuclear methylene-group are readily replaceable by halogen atoms, but 2-keto-2 : 3-dihydrothiazine-6-thiolacetic acid (A., 1919, i, 75) is insoluble in the cold in solvents commonly used in halogenations, and when heated the halogen derivatives readily decompose. Zahn's method of chlorination (A., 1923, i, 375) gives a mixture of products from which the chloro-compound could not be separated. The action of bromine in acetic acid solution gives, however, 3 : 3-*dibromo*-2-*keto*-2 : 3-*dihydrothiazine*-6-*thiolacetic acid*, m. p. 220° (decomp.), which easily loses its halogen.

The reactivity of the methylenic hydrogen of the thiazine ring is more evident in the corresponding sulphones, both sulphazone (cf. Claasz, A., 1912, i, 389) and sulphazone-6-sulphonacetic acid being capable of coupling with diazo-derivatives to form azo colouring matters. The observations of Claasz on "thionylindigo" (*ibid.*, 513) and those of Barnett and Smiles on the sulphoxide corresponding with thiodiphenylamine (J.C.S., 1910, **97**, 186, 362) lead to the conclusion that colouring power is due to the quinonic linking and not to the characteristic grouping of the molecule. 2-*Keto*-2 : 3-*dihydrothionylazine*-6-*sulphoxyacetic acid* (I), m. p. 210°, prepared by reduction of 4-nitro-*m*-phenylenedisulphoxyacetic acid by means of tin and hydrochloric acid, exhibits no quinonoid behaviour and is unable to

couple with diazo-derivatives. Its 7-*nitro*-derivative, m. p. 264° (decomp.), when reduced with tin and hydrochloric acid, forms *bisketodihydrothiazine* (II),



which remains solid at 300°. It has not been found possible to prepare the sulphoxide and sulphone corresponding with this ketothiazine, since oxidation of the latter or of 2-keto-2 : 3-dihydrothiazine-6-thiolacetic acid results in rupture of the thiazine ring and nitration of either the sulphoxide or the sulphone of this acid yields no definite nitro-product. Further, nitration of *m*-phenylenedisulphonacetic acid (cf. A., 1914, i, 1132) yields its 4 : 6-*dinitro*-derivative, m. p. 215°, which, when very dry, may explode at 207°.

Oxidation of 4-nitro-*m*-phenylenedithiolacetic acid by hydrogen peroxide in acetic acid solution yields (1) readily 4-*nitro*-m-*phenylenedisulphoxyacetic acid*, m. p. 199°, which gives 2-keto-2 : 3-dihydrothionylazine-6-sulphoxyacetic acid (see above), and (2) with more difficulty 4-nitro-*m*-phenylenedisulphonacetic acid, m. p. 228° (Finzi and Bottiglieri, A., 1919, i, 75, gave m. p. 199°).

Phenyl 4-*nitro*-m-*phenylenedithiolacetate*, prepared by treating the acid with phenol in presence of phosphorus oxychloride, has m. p. 96—98°. *m*-Phenylenedisulphonacetic acid, formerly (A., 1914, i, 1132) described as amorphous, forms crystals ($+H_2O$), m. p. 115° or 187° (anhydrous). T. H. Pope.

Thiazoles. VIII. Condensation of *o*-aminophenyl mercaptan [*o*-aminothiophenol] and *o*-aminophenyl disulphide with acid chlorides, anhydrides, and esters. M. T. Bogert and A. Stull (J. Amer. Chem. Soc., 1926, **48**, 248—254).—When boiled with ethyl oxalate, *o*-aminophenyl disulphide affords *ethyl oxanilate* o-*disulphide*, $(\cdot S\cdot C_6H_4\cdot NH\cdot CO\cdot CO_2Et)_2$, light yellow, m. p. 104° (cf. Hofmann, A., 1880, 884), which is converted, by the action of ammonia and aniline, into the corresponding *diamide*, m. p. about 240° (decomp.), and *dianilide*, m. p. 229—230° with slight darkening, respectively, and on reduction with sodium and alcohol, yields benzthiazole-1-carboxylic acid, m. p. 107° (decomp.) (Hofmann, A., 1887, 1039; Reissert, A., 1904, i, 990). Bis-1 : 1′-benzthiazolyl, m. p. 300·5° (cf. Lauth, A., 1896, i, 326), is obtained when zinc *o*-aminophenylmercaptide is heated with oxalyl chloride. *Succinanilic acid* o-*disulphide*, $(\cdot S\cdot C_6H_4\cdot NH\cdot CO\cdot[CH_2]_2\cdot CO_2H)_2$, m. p. 167—168° after becoming yellow and sintering at 155—158°, is obtained by heating together *o*-aminophenyl disulphide and succinic anhydride, glutaric anhydride affording similarly *glutaranilic acid* o-*disulphide*, m. p. 155—156° with slight darkening, decomp. at 160—161°. *Camphoranilic acid* o-*disulphide*, greenish-yellow, m. p. 229° (decomp.), and *maleanilic acid* o-*disulphide*, m. p. 200—201° (decomp.), losing water at a slightly higher temperature with formation of a brown resin, are obtained analogously. Condensation of *o*-aminophenyl disulphide with phthalic anhydride at 120—135° affords o-*phthalimidophenyl* o-*disulphide*, $(\cdot S\cdot C_6H_4\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4)_2$, m. p. 219°, whilst zinc *o*-aminophenylmercaptide (*o*-aminothiophenoxide) reacts with terephthalyl chloride with formation of 1 : 1′-(p-*phenylene*)-*bisbenzthiazole*, m. p. 263° (cf. Hofmann, A., 1880, 884). Condensation of *o*-aminophenyl disulphide with pyromucyl chloride (cf. Baum, A., 1904, i, 910) affords *pyromucylanilide* o-*disulphide*, yellow, m. p. 160·5°, which, on reduction with tin and hydrochloric acid, yields 1-α-furylbenzthiazole, m. p. 105° (cf. Bogert and Stull, this vol., 183), which is also obtained by heating zinc *o*-aminophenylmercaptide with pyromucyl chloride. α-Thienoyl chloride affords analogously *α-thienanilide* o-*disulphide*, pale yellow, m. p. 154°, which, on reduction with tin and hydrochloric acid, yields 1-α-*thienylbenzthiazole*, m. p. 99·5°, a compound possessing a marked tea-rose or geranium odour, which is also obtained by heating zinc *o*-aminophenylmercaptide with α-thienoyl chloride.

F. G. Willson.

Preparation of 1-thiolbenzthiazole. E. Azzalin (Gazzetta, 1925, **55**, 895—899).—Various methods for preparing 1-thiolbenzthiazole (cf. Romani, A., 1922, i, 466; Bruni and Levi, A., 1924, i, 1000) are given. A good yield is obtained when ammonium phenyldithiocarbamate, which probably acts as the thiol tautomeride, is heated with a slight excess of sulphur in a sealed tube at 250° : $NPh:C(SH)\cdot NH_4S + S=C_6H_4<\begin{matrix}N\\S\end{matrix}>C\cdot SH + NH_3 + H_2S$. The formation of 1-thiolbenzthiazole from thiocarbanilide and sulphur apparently takes place with intermediate formation of phenylthiocarbimide, but this method is uneconomical owing to the production of aniline in large proportion. 1-Thiolbenzthiazole may be obtained in about 80% yield by heating aniline with a carbon disulphide solution of sulphur in a sealed tube at 260°, thiocarbanilide being formed as an intermediate product; no waste products are formed in this process. T. H. Pope.

Additive compounds of tin and titanium halides with organic bases. G. Scagliarini and E. Brasi (Atti R. Accad. Lincei, 1925, [vi], **2**, 269—274).—When a cold saturated chloroform solution of caffeine is gradually added to a cold saturated solution of stannic chloride in the same solvent, the *compound* $4SnCl_4,3C_8H_{10}O_2N_4,CHCl_3$ is formed. Under similar conditions, now in chloroform and now in bromoform, the following *compounds* were formed : $2SnBr_4,3C_8H_{10}O_2N_4,3CHCl_3$; with hexamethylenetetramine, $SnI_4,4C_6H_{12}N_4,5CHBr_3$; $SnI_4,5C_6H_{12}N_4,8CHBr_3$; $TiCl_4,12C_6H_{12}N_4,3CHCl_3$; $TiI_4,4C_6H_{12}N_4,5CHBr_3$.

W. E. Ellis.

Resolution of *dl*-dicentrine. R. D. Haworth, W. H. Perkin, jun., and J. Rankin (J.C.S., 1926, 29—32).—By treating synthetic *dl*-dicentrine, m. p. 181° (corr.) (A., 1925, i, 1314), with *d*-tartaric acid in absolute alcoholic solution, l-*dicentrine hydrogen*

d-*tartrate* crystallises, whilst the bases liberated from the residue on treatment with *l*-tartaric acid yield d-*dicentrine hydrogen* l-*tartrate*; these salts give *d*- and *l*-dicentrine, m. p. 169° (corr.), $[\alpha]_D^{15}$ in chloroform +64·1° and −63·5°, respectively. By heating 6′-nitroveratrylnorhydrohydrastinine with formaldehyde, formic acid, and water, 6-nitrohomoveratrole and hydrohydrastinine are produced.

F. M. HAMER.

Comparison of boldine dimethyl ether with glaucine. K. WARNAT (Ber., 1926, **59**, [*B*], 85—86; cf. this vol., 185).—The identity of boldine dimethyl ether with glaucine is established by direct comparison of the bases, their salts, and the products obtained during the degradation of the bases by Hofmann's method. H. WREN.

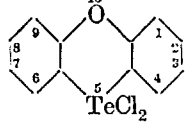
Preparation of sodium methylarsinate etc. (MISS) M. G. TAVERNARI.—See B., 1926, 106.

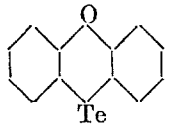
Bismuth compounds. II. E. MASCHMANN (Arch. Pharm., 1925, **263**, 721—726; cf. A., 1925, i, 527).—The following more complicated compounds have been prepared, generally by mixing solutions of the sodium salts with bismuth chloride, or nitrate, in hydrochloric acid or a solution containing lævulose or mannitol. Basic *bismuth* 3-*amino*-4-*hydroxyphenylarsinate*, $C_6H_7O_5NAsBi$, and basic *bismuth* 3-*acetamido*-4-*hydroxy*-5-*oxymercuriphenylarsinate*, are insoluble in water. A soluble product is obtained by converting 3-amino-4-hydroxyphenylarsinic acid into its dihydroxypropyl derivative (D.R.-P. 412171) and preparing a bismuth *complex* from this. Other soluble products described are *sodium bismuth* o-*carboxyphenylglycerate* (from β-naphthaquinone by oxidation with calcium hypochlorite), *sodium bismuth caffeate* (3 : 4-dihydroxycinnamate), *bismuth alizarin*, $C_{14}H_7O_5Bi$ (a yellow powder, soluble in sodium hydroxide), and *sodium bismuth* 7-*iodo*-8-*hydroxyquinoline*-5-*sulphonate*, $(C_9H_4O_4NISNa)_3Bi$.

W. A. SILVESTER.

Selenium organic compounds. VI. Bromine, sulpho-, and mercury derivatives of 2 : 4-diphenylselenophen and experiments with some related compounds. M. T. BOGERT and C. N. ANDERSEN (J. Amer. Chem. Soc., 1926, **48**, 223—231; cf. A., 1923, i, 240).—By the action of phthalic anhydride and aluminium chloride on 2 : 5-dimethylselenophen (cf. Paal, A., 1885, 1205; Zoppellari, A., 1895, ii, 249) in boiling carbon disulphide, *phthaloyl*-2 : 5-*dimethylselenophen*, pale yellow, m. p. 155·5°, is obtained. 2 : 4-*Diphenyl*-3 : 5-*dimethylthiophen*, m. p. 163·8°, is obtained when propiophenoneanil, m. p. 53° (cf. Reddelien, A., 1910, i, 746), is heated with sulphur for 6 hrs. at 240°. n-*Butyrophenoneanil*, pale yellow, b. p. 198—202°/25 mm., affords similarly a compound, m. p. 286°, probably 2 : 4-*diphenyl*-3 : 5-*diethylthiophen*. The corresponding selenophens could not be prepared analogously. Treatment of 2 : 4-diphenylselenophen with the appropriate proportions of bromine in glacial acetic acid yields *dibromo*-2 : 4-*diphenylselenophen*, m. p. 86·7°, and *tribromo*-2 : 4-*diphenylselenophen*, straw-coloured, m. p. 126·7°. When the latter is treated with sodium and methyl iodide in ether, a *compound*, $C_{17}H_{11}Br_3Se$, m. p. 139·8°, is produced, the constitution of which is uncertain. *Tetrabromo*-2 : 4-*diphenylselenophen*, m. p. 176·5°, is obtained by the action of bromine on the diphenyl derivative in boiling alcohol in direct sunlight. 2 : 4-*Diphenylselenophentetrasulphonic acid*, m. p. above 300°, is produced by the action of chlorosulphonic acid on diphenylselenophen at 0° in suspension in light petroleum. 2 : 4-Diphenylselenophen-5-mercurichloride (cf. A., 1923, i, 240) yields the above tribromodiphenylselenophen when boiled with bromine water, whilst treatment with potassium bromide in acetone affords the corresponding *mercuribromide*, m. p. 215°, and *mercury di*-5-(2 : 4-*diphenyl*)*selenophen*, m. p. 236·7°, the latter being also produced by the action of sodium iodide or sodium cyanide on the above 5-mercurichloride, or of potassium bromide on the 5-mercuribromide. When boiled with mercuric bromide in acetone, the above mercury diselenophen yields the 5-mercuribromide, whilst mercuric iodide yields similarly 2 : 4-*diphenylselenophen*-5-*mercuri*-*iodide*, m. p. 176°, which reddens rapidly on exposure to light. 2 : 4-*Diphenylselenophen*-5-*mercuricyanide*, m. p. 256·4°, is obtained similarly by the action of sodium cyanide. F. G. WILLSON.

Cyclic organo-metallic compounds. I. Compounds of tellurium. H. D. K. DREW (J.C.S., 1926, 223—231).—When tellurium tetrachloride and diphenyl ether are heated in chloroform solution, hydrogen chloride is eliminated, giving a 90% yield of p-*phenoxyphenyltelluritrichloride* (I), softens at 154°, m. p. 156—157°, together with pp′-*diphenoxydiphenyltelluridichloride*, m. p. 157—158°, which is also obtained by heating (I) with diphenyl ether at 160°, and is unchanged by heating at 210°. By aqueous potassium metabisulphite, (I) is reduced to pp′-*diphenoxydiphenyl ditelluride*, softens at 85°, m. p. 87—88°, which gives rise to an amorphous *oxide* on exposure to air, and with bromine gives a *bromide*, m. p. near 180°, whilst by warm, concentrated nitric acid it is converted into *pp*′-dinitrodiphenyl ether. When (I) is heated to 200°, the product is 5 : 5-*dichlorophenoxtellurine* (II), m. p. 265°, which is obtained in 50% yield by heating tellurium tetrachloride and diphenyl ether at 200°. It is colourless below 100°, but yellow above, and is stable to heat, but slowly hydrolysed by boiling water. As regards

(II.) 



(III.)

the mechanism of its formation, it is suggested that (I) undergoes change into *o*-phenoxyphenyltelluritrichloride, which then condenses to form (II). An attempt to prepare the *o*-compound by heating (I) at 160° led to the production of an impure *compound*, decomp. 125°, which is reduced to a *substance* resembling a ditelluride. By concentrated nitric acid, (II) is converted into p-*phenoxyphenyltelluritrinitrate*, which yields *pp*′-dinitrodiphenyl ether; this reaction may indicate the *p*-structure of (II). By aqueous potassium metabisulphite, (II) is converted quan-

*

titatively into *phenoxtellurine* (III), m. p. 78—79°, which is stable and colourless; with bromine in chloroform solution, (III) gives 5 : 5-*dibromophenoxtellurine*, decomp. 290°, and similarly 5 : 5-*di-iodophenoxtellurine*, decomp. about 270°, whilst warm, concentrated nitric acid converts it into *phenoxtellurine*-5 : 5-*dinitrate*, decomp. about 258°.

F. M. HAMER.

Mercuration of nitrobenzene. J. JÜRGENS (Rec. trav. chim., 1926, **45**, 61—67).—When nitrobenzene is treated with mercuric nitrate in accordance with the method of Dimroth (A., 1902, i, 656), all three isomeric nitrophenylmercuric chlorides are obtained, the yields being *o*- 52·6%, m. p. 187° (Dimroth, *loc. cit.*, gives 182°), *m*- 38·5%, and *p*- 8·9%, the determination being made by means of a thermal analysis of the mixture of monobromonitrobenzenes obtained on treatment of the product with bromine water. A small quantity (about 1%) of a dimercurated compound which yields 1 : 2-dibromo-3(?)-nitrobenzene on treatment with bromine water is also obtained. On boiling with aqueous sodium chloride, either with or without previous treatment with hydrogen sulphide, the *o*-compound is converted into an *o*-dinitrodiphenyl mercury *compound*, $(C_6H_4{\cdot}NO_2)_2Hg$, m. p. 206°. J. W. BAKER.

Mercuration of nitrobenzene and substitution in the benzene nucleus. O. DIMROTH (Annalen, 1925, **446**, 148—154).—Holleman (A., 1923, i, 664; cf. Jürgens, preceding abstract) by the action of mercuric acetate on nitrobenzene obtained *o*-, *m*-, and *p*-compounds in the ratio 5 : 4 : 1. This is now confirmed, 60% of *o*- and *p*-compounds and 40% of *m*-compound being obtained. The mechanism of mercuration is discussed and the conclusion is reached, contrary to Holleman's views, that the type of substitution (*o*-, *p*-, or *m*) in the benzene ring depends, not only on the nature of the substituent present, but also on that of the entering group. Conformity to Körner's rule and other generalisations has only been observed because the entering groups (halogen, nitro-, sulpho-) have hitherto been of one type.

For the determination of isomeric nitrophenyl mercurichlorides the mixture is converted into bromonitrobenzenes, which react with hydrazine hydrate in methyl alcohol at 110°. The *o*- and *p*-compounds lose their bromine as hydrobromic acid (determined as silver bromide), whilst the *m*-compound is reduced to *m*-bromoaniline.

From the reaction product of mercuric acetate with nitrobenzene practically pure *o*- and *m*-nitrophenyl mercurichlorides may be isolated in small quantity by a long series of crystallisations. No *p*-compound was isolated. C. HOLLINS.

A mercuri-organic compound of phenyl-β-naphthylamine. G. ROSSI and B. CECCHETTI (Gazzetta, 1925, **55**, 869—872).—In aqueous alcoholic solution, phenyl-β-naphthylamine reacts with mercuric acetate rendered slightly acid with acetic acid to form *mercuriphenylnaphthylamine*,

$$Hg<\begin{matrix}C_6H_4\\C_{10}H_6\end{matrix}>NH,2EtOH,$$

m. p. 173°. T. H. POPE.

Structure of proteins. Physical and chemical properties of diketopiperazines. Fumaric acid as a hydrolytic product of gelatin. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1926, **151**, 114—125). **Comparative oxidation experiments.** E. ABDERHALDEN and H. QUAST (*ibid.*, 145—150).—Diketopiperazines are completely neutral substances and cannot form salts with acids or bases; when a diketopiperazine is dissolved in sodium hydroxide at p_H 11·4, the opening of the ring does not proceed to completion, but equilibrium is attained after many hours at about p_H 8·5. Long keeping in faintly alkaline solution leads to disappearance of the picric acid reaction for diketopiperazines from silk peptone and caseinogen, but not from blood-serum or its heat-coagulable protein; the disappearance of the picric acid reaction runs parallel with an increase in the "formol" titration figure. Diketopiperazines are adsorbed by bone charcoal from 0·05*M*-aqueous solution to the extent of nearly 40%, whilst the corresponding peptides are only adsorbed to 7—8%. Potassium mercuric iodide and sodium hydroxide precipitate diketopiperazines, but not peptides or amino-acids (except tryptophan and histidine) from aqueous solution. On vacuum distillation of the ester mixture obtained from the products of sulphuric acid hydrolysis of gelatin there was isolated, from the fraction boiling at 100—130°, methyl fumarate in a yield of 0·5% of the original protein. Oxidation of silk peptone with zinc permanganate yielded, with different preparations, 2·5—3·9% of oxamide and large quantities of oxalic acid; the yield of oxamide did not vary much with the temperature of the reaction. Leucylglycine, when oxidised with zinc permanganate, gave oxalic and *iso*valeric acids, but no oxamide, whilst leucylglycine anhydride, under similar conditions, gave much oxamide. The occurrence of oxamide as an oxidation product may therefore be regarded as definite evidence of the presence of a diketopiperazine linking in the original compound. Treatment of a solution of silk peptone with dilute sodium hydroxide caused an increase in the amino-nitrogen, as indicated by "formol" titration, and a simultaneous reduction in the yield of oxamide on oxidation.

C. R. HARINGTON.

Silk fibroin. R. BRILL (Annalen, 1925, **446**, 307—308).—The results of the *X*-ray investigation of fibroin (A., 1923, i, 102) are discussed and an analogy is indicated between the supposed structure of the unit silk crystal and that of the diketomethylpiperazine compounds obtained by Bergmann, Miekeley, and Kann (A., 1925, i, 1474). R. W. WEST.

Porphyrins from blood pigments. III. A. PAPENDIECK (Z. physiol. Chem., 1925, **150**, 261—266).—An improved method for reducing hæmatin by hydrazine and glacial acetic acid is given. Better results are obtained if the reduction is carried out in the cold (cf. A., 1925, i, 711). In extracting α-hæmatoporphyroidin with chloroform, the solvent must be free from alcohol, otherwise partial esterification takes place. The composition for α-hæmatoporphyroidin or the hæmaterindicarboxylic acid of Küster (A., 1913, i, 1005) agrees best with the formula

$C_{34}H_{34}O_4N_4$. When alcohol-free chloroform is used in the extraction of this compound, it dissolves readily and completely in dilute alkalis, and can be made to yield a *dimethyl* ester, m. p. 221°.

H. I. COOMBS.

Action of benzoyl peroxide on a dimethyl-(chloro)hæmin. W. KÜSTER and W. RUFF (Z. physiol. Chem., 1926, **151**, 98—113).—After the prolonged action, in the cold, of benzoyl peroxide on a sample of dimethyl(chloro)hæmin, there was obtained, besides one-third of the starting material unchanged, a *product* having two hydrogen atoms less and showing an entirely different absorption spectrum; on treatment with hydrochloric acid, the new substance split off its iron more readily than the original material, and a porphyrin was formed which was not identical with hæmatoporphyrin; on treatment with pyridine, the dehydrogenated product lost only 60% of its halogen, and chlorine could not be reintroduced into the resulting substance with hydrochloric acid in methyl alcohol; with aniline it lost 75% of its chlorine, which, in this case, could be reintroduced. The dehydrogenated compound took up two atoms of bromine, and the resulting additive product, on treatment with sodium carbonate, lost both bromine and chlorine, yielding a compound with a free hydroxyl group, whereas the original compound did not lose its chlorine under such conditions; similarly one bromine atom could be eliminated from the bromine additive product by boiling with methyl alcohol, which could not be done with dibromodimethylhæmin. In view of these results, it is thought that the action of the benzoyl peroxide consisted in the removal of two hydrogen atoms from the side-chain, converting the existing ethylene linking into an acetylene one; this might account for the loosening of the combination with iron, and for the effects observed with the bromine additive product, provided that an interchange of the positions of the halogen atoms is assumed.

C. R. HARINGTON.

Chlorocruorin, a pigment related to hæmoglobin. H. M. FOX (Proc. Roy. Soc., 1926, **B**, **99**, 199—220).—Chlorocruorin, which occurs in the blood plasma of certain polychæte worms (Lankester, J. Anat. Physiol., 1867, **2**, 114; 1870, **3**, 119), shows differences from hæmoglobin greater than those between specific hæmoglobins. The oxidised and reduced forms are almost the same colour (red, concentrated; green, dilute), but differ spectroscopically as oxyhæmoglobin differs from hæmoglobin. Oxychlorocruorin is deoxygenated by living tissue more rapidly than oxyhæmoglobin, and the affinity for oxygen is increased by an increase in p_H. Specific chlorocruorins of different oxygen affinity are present in *Myxicola, Spirographis, Sabella, Branchiomma*; that of *Myxicola* may be saturated with oxygen at the ordinary atmospheric (partial) pressure, whilst the others take up more when oxygen is bubbled through their diluted solutions. The specific chlorocruorins differ in the position of the α-band axis in the absorption spectra. The affinity of chlorocruorin for carbon monoxide is greater than its affinity for oxygen. *Carbonylchlorocruorin* is more readily dissociated by light than carbonylhæmoglobin. *Metachlorocruorin* (brownish-green) is prepared by the action of potassium ferricyanide on oxychlorocruorin, and differs considerably from methæmoglobin spectroscopically. Weak acids convert oxychlorocruorin into *chlorocruorohæmatin* (reddish-brown in acid, greenish-brown in alkali). *Chlorocruorohæmin* and *chlorocruorochromogen* are prepared by the methods used for hæmin and hæmochromogen, and their absorption spectra are described. The α absorption band is the same for the chromogens from different chlorocruorins, but differs from that of the hæmochromogens of hæmoglobin, helicorubin, actiniohæmatin, and part of the cytochrome complex. Hence the hæmatin group of chlorocruorin is probably not the same as that of these pigments. It contains iron, probably united to a different porphyrin. The protein portion of the chlorocruorin molecule is not displaced by ammonia. A hybrid *pigment* is readily made by mixing hæmatin solution with an alkaline solution of the protein from chlorocruorin. *Chlorocruoroporphyrin*, prepared by Nencki's method for hæmatoporphyrin or by a modification of Laidlaw's method, shows absorption bands more to the red than those given by other porphyrins. Its solubility in chloroform classes it with the oöporphyrin group.

C. HOLLINS.

Analysis of proteins. V. Van Slyke's method of determination of nitrogen distribution. R. H. A. PLIMMER and J. L. ROSEDALE (Biochem. J., 1925, **19**, 1004—1014).—A critical investigation of the discrepancies arising at the various stages of the Van Slyke method. Modifications and simplifications are introduced, especially in the determination of the amide and humin nitrogen and in the treatment of the phosphotungstate fraction. S. S. ZILVA.

Analysis of proteins. VI. Distribution of nitrogen in the proteins of eggs. R. H. A. PLIMMER and J. L. ROSEDALE (Biochem. J., 1925, **19**, 1015—1019).—Utilising their simplified method (see preceding abstract), the authors have determined the nitrogen distribution in the proteins of eggs. The results are tabulated and compared with the figures obtained by other workers. S. S. ZILVA.

Analysis of proteins. VII. Direct determination of arginine. R. H. A. PLIMMER and J. L. ROSEDALE (Biochem. J., 1925, **19**, 1020—1021).—Arginine determined directly in solutions of hydrolysed proteins by boiling with sodium hydroxide gives a higher value than if determined in the diamino-fraction precipitated by phosphotungstic acid. On treating the monoamino-fraction in the same way, a value is obtained representing the difference. The arginine value of a protein is therefore the sum of the figures obtained from the diamino- and monoamino-fractions, or the figure obtained directly, assuming that no other amino-acid behaving like arginine is present in proteins. S. S. ZILVA.

Interaction of free amino-nitrogen and dextrose. H. BORSOOK and H. WASTENEYS (Biochem. J., 1925, **19**, 1128—1137).—Protein derivatives react with dextrose in alkaline solution, as is shown by the reduction of free amino-nitrogen. The reduction is

not the result of a synthetic process and carbamide, cyanic acid, and ammonia are not formed. The mixture of dextrose and protein derivative acquires the property of reducing methylene-blue in approximately neutral solution. With glycine and peptone the reduction of methylene-blue is accelerated by phosphate. With albumin an equal velocity of reduction is obtained without phosphate. The reduction of methylene-blue by incubated peptone and dextrose is accelerated by washed muscle. Preliminary incubation with dextrose increases the yield of ammonia after oxidation with hydrogen peroxide. S. S. ZILVA.

Potentiometric titration (diazotisation) of amines. E. MÜLLER and E. DACHSELT (Z. Elektrochem., 1925, **31**, 662—666).—Aniline and other aromatic amines in hydrochloric acid solution may be accurately titrated with concentrated sodium nitrite solution, with suitable cooling, using a platinum electrode and a standard calomel electrode. An average potential of +0·58 volt, independent of the amine, is found at the end-point. Titrations may be conveniently carried out by applying a compensating voltage of the above amount to the electrode circuit and titrating until a sensitive galvanometer indicates zero. W. A. CASPARI.

Determination of arsenic and silver in silver arsenobenzenes. U. CAZZANI.—See B., 1926, 107.

Development of organic analysis from Lavoisier to Pregl. C. WEYGAND (Z. angew. Chem., 1925, **38**, 881—885).—An historical account of the development of the accuracy of combustion analysis. T. S. WHEELER.

Biochemistry.

Carbon dioxide production and duration of life of *Drosophila* cultures. J. H. NORTHROP (J. Gen. Physiol., 1926, **9**, 319—324).—Since the total quantity of carbon dioxide produced during its lifetime by each individual is greater at 15° than at 26° or 30°, and is much greater in the light than in the dark, the duration of life of *Drosophila* is not determined by the time required to produce a limiting amount of carbon dioxide. C. P. STEWART.

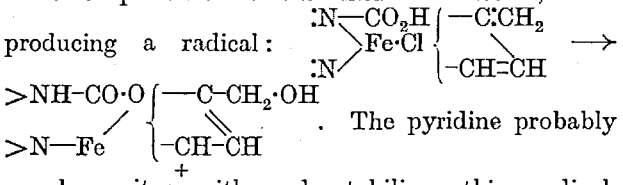
Tests for blood. Oxydase and hæmochromogen reactions of yeast and plant seeds. O. SCHUMM (Z. physiol. Chem., 1925, **150**, 276—286).—Certain chemical or chemical-spectroscopic tests for blood which depend on highly sensitive oxydase or hæmochromogen reactions—such as the benzidine and pyridine–hæmochromogen tests—must be interpreted with caution when dealing with material of unknown origin and composition, since yeast and plant seeds give positive reactions. Support is given to Keilin's view (A., 1925, i, 1112) that cytochrome is a normal constituent of many parts of plants. Although the author has not been able to obtain the true blood pigment (oxyhæmoglobin-, methæmoglobin-, or hæmoglobin-) spectra from yeast extracts, he obtained a pigment which he could not safely differentiate from hæmatin. H. I. COOMBS.

Oxygen content of methæmoglobin. Dissolved methæmoglobin and hæmoglobin in corpuscles. M. NICLOUX and J. ROCHE (Compt. rend. Soc. Biol., 1925, **93**, 275—278; from Chem. Zentr., 1925, II, 1292).—Methæmoglobin, either in corpuscles or in laked blood, has an oxygen content half that of oxyhæmoglobin. G. W. ROBINSON.

Formation of methæmoglobin. VII. [Action of] nitrite. R. MEIER (Arch. exp. Path. Pharm., 1926, **110**, 241—264).—In alkaline solution, oxyhæmoglobin is only slightly affected by the presence of nitrite, an excess of 20—50 times resulting in the formation of a mixture of oxyhæmoglobin and alkaline methæmoglobin, and of 100—1000 times, a mixture of alkaline methæmoglobin and nitrogen dioxide–hæmoglobin. In neutral and faintly acid solutions, with pigment and nitrite in molecular proportions, methæmoglobin only results, whilst with smaller amounts of nitrite a mixture of oxyhæmoglobin and methæmoglobin, and with larger amounts of nitrite a mixture of methæmoglobin and nitrogen dioxide–hæmoglobin, is formed. In the experiments in which methæmoglobin only is obtained, one-fourth of the oxygen combined with the hæmoglobin is liberated and an amount of nitrite disappears equivalent to the oxyhæmoglobin. In acute poisoning of cats with nitrite or nitrous fumes, much methæmoglobin is formed, but on keeping this is completely converted into nitrogen dioxide–hæmoglobin. P. W. CLUTTERBUCK.

Blood pigments. IV. Sulphæmoglobin. F. HAUROWITZ (Z. physiol. Chem., 1926, **151**, 130—144).—Crystalline sulphæmoglobin has been obtained by alternate introduction of oxygen and hydrogen sulphide into a 20% solution of pure horse hæmoglobin and subsequent addition of 20% alcohol to the ice-cold solution; the crystals have a similar appearance to those of hæmoglobin; details are given of the absorption spectrum. An accurate determination of the sulphur content could not be obtained owing to the difficulty of getting rid of adsorbed sulphur; the iron in sulphæmoglobin is still in organic combination. Pure selenium hydride is without action on hæmoglobin, the effects observed by Clarke and Hurtley (A., 1907, i, 992) having been due to the presence of traces of hydrogen sulphide; the assumption by these observers of a carbon monoxide–sulphæmoglobin is also shown to be an error due to the unnoticed formation of methæmoglobin. The action of nitric oxide on reduced hæmoglobin in absence of oxygen gives nitric oxide–hæmoglobin; with oxyhæmoglobin methæmoglobin is produced by the action of the small quantities of

nitrogen peroxide formed, and with excess of nitric oxide passes into the nitric oxide compound; with carbon monoxide–hæmoglobin the nitric oxide compound is obtained with no intermediate formation of methæmoglobin (cf. Anson and Mirsky, J. Physiol., 1925, **60**, 100). C. R. HARINGTON.

Hæmochromogen and hæmoglobin. W. KÜSTER (Ber., 1925, **58**, [*B*], 2851—2854; cf. A., 1925, i, 992).—A solution of hæmin in 1·5% sodium hydroxide free from air deposits red needles when preserved at a low temperature in the presence of nitrogen; the isolation of the substance has not yet proved possible, but its spectrum in air-free solvents is identical with that of hæmochromogen. The production of the hæmochromogen spectrum in solutions of hæmin in pyridine and in alkaline solutions in the presence of reducing agents (Küster, Chem. Zelle Gewebe, 1924, **12**) is due to the alkali hydroxide alone, which causes the hydroxy-group produced in union with the iron atom to migrate to the most reactive position in the hæmin molecule, thus producing a radical:  . The pyridine probably merely unites with and stabilises this radical, whereas the reducing agent is active only in preventing the atmospheric oxidation of the very sensitive hæmochromogen. The observation appears particularly important for the explanation of the absorption of oxygen and carbon monoxide by hæmoglobin, since the capacity of the latter and of hæmochromogen to combine with carbon monoxide is the same, and if hæmochromogen is regarded as containing a radical, the radical nature of hæmoglobin must be regarded as established. H. WREN.

Blood. IV. Origin of hæmins from hæmoglobin-*A* and the existence of two forms of hæmoglobin, *Aa* and *Ab*. W. KÜSTER [with G. SCHMID, W. RUFF, W. HEESS, and R. HUTTENLOCHER] (Z. physiol. Chem., 1926, **151**, 56—85).—It is suggested that hæmoglobin exists as a tribasic acid, in which two of the acid carboxyl groups are derived from the globin part of the molecule, and the other is one of the two present in the prosthetic part of the molecule. These two carboxyl groups of the prosthetic group are not identical, and thus two hæmoglobins are possible, according to which carboxyl group is ionised. The various theoretically possible hæmins and methyl- and dimethyl-hæmins are discussed. It is assumed that where the two hæmin carboxyl groups exist as betaines, the halogen is not ionisable, *e.g.*, in a dimethyl(bromo)hæmin which is described. An attempt is made to correlate the various products obtained experimentally by the authors, with those theoretically possible. W. O. KERMACK.

Lactic acid in blood. J. COLLAZO and J. SUPNIEVSKI (Compt. rend. Soc. Biol., 1925, **92**, 367—369; from Chem. Zentr., 1925, II, 411).—The normal lactic acid content of the blood of rabbits is 0·048%. It is appreciably increased by injection of dextrose, acetaldehyde, hydrazine, phenylhydrazine, alanine, and insulin, decreased by arabinose, pituitary extract, acetates (sodium acetate, ethyl acetate, etc.), and inappreciably affected by lævulose, phloridzin, guanidine, and adrenaline. G. W. ROBINSON.

Combined sugar in blood. M. BUFANO (Arch. Farm. sperim. Sci. aff., 1925, **40**, 235—250).—A solution of blood-albumin at the same concentration as in blood is hydrolysed by Condorelli's method (A., 1925, i, 714), and its reducing power then compared with that of an unhydrolysed solution of equal concentration. Deproteinised blood plasma and also a solution of glycogen of the same concentration as in blood are similarly tested. In every case the increase in the reducing power is insufficient to account for the proportion of combined blood-sugar deduced from hydrolyses of blood by Condorelli's method. Further reasons for believing in the existence of combined blood-sugar are: firstly the variability of the proportion of combined sugar in the blood of a rabbit after insulin treatment; secondly, Condorelli's method of hydrolysis is far too gentle to affect the protein. It is concluded that about one-third of the blood-sugar is combined, chiefly with the protein of the serum (according to Condorelli with the globulin), but so loosely that it can be liberated without decomposing the protein. W. E. ELLIS.

Relationship of the constituents of blood and cerebrospinal fluid. L. S. KUBIE and G. M. SHULTS (J. Exp. Med., 1925, **42**, 565—591).—When due allowances are made, the amounts of sugar, chloride, and non-protein nitrogen in cerebrospinal fluid correspond generally with the amounts in blood, but factors other than the concentration in the blood affect the distribution of a substance.

CHEMICAL ABSTRACTS.

Post-mortem blood and spinal fluid. G. W. PUCHER and L. A. BURD (Buffalo Gen. Hosp. Bull., 1925, **3**, 11—13).—The quantities of uric acid, amino-acids, and carbon dioxide in post-mortem spinal fluid are less than those in the blood.

CHEMICAL ABSTRACTS.

Changes in the blood constituents accompanying gastric secretion. Chloride. R. K. S. LIM and T. G. NI (Amer. J. Physiol., 1926, **75**, 475—486).—A fall in the chloride concentration of the blood accompanies gastric secretion. The fall is related in extent to the degree of dehydration rather than to the rate of excretion of chloride. Prolonged secretion resulted, in one case, in a loss of 49% of the total chloride of the body. The secreting cells are largely independent of the level of blood chloride.

R. K. CANNAN.

Distribution of ions in blood-serum. III. P. RONA and G. MELLI (Biochem. Z., 1925, **166**, 242—250; cf. A., 1911, ii, 302; 1923, i, 728; 1925, i, 95).—The non-dialysable calcium of serum represents 31—39% of the total calcium. The addition of a small amount of lecithin to the collodion of the cell causes an increase to more than 50% in the non-dialysable calcium. The anomalous positive osmosis

of physiological saline towards serum in collodion thimbles is reversed when 0·1—0·01*N*-thorium nitrate is employed as the external solution.

E. C. SMITH.

Connexion between vegetative nervous system and potassium and calcium ions of serum. S. LEITES (Biochem. Z., 1925, **166**, 47—54).—The ratio of the concentrations of potassium and calcium in the serum serves as an index of the equilibrium between the two subdivisions of the vegetative nervous system, but the absolute value of the potassium concentration can give no indication of the preponderating influence of either branch over the other. Section of one vagus at the neck, or of both vagi below the diaphragm, causes a temporary lowering of the coefficient K/Ca, which recovers after a certain interval. Removal of the solar plexus and division of the splanchnic nerves result in a fall in serum-calcium. E. C. SMITH.

Hæmolysis. I. Mechanism of hæmolysis by hydrogen ions and hydroxyl ions. R. MOND (Pflüger's Archiv, 1925, **208**, 574—594; from Chem. Zentr., 1925, II, 1292).—Hæmoglobin is enclosed by a membrane of plasma the impermeability of which must first be overcome by substances causing hæmolysis. If, however, such substances cause coagulation of the hæmoglobin particles to compound aggregates, the hæmolysis is not evident. Heat-coagulated hæmoglobin dissolves in hot, dilute ethyl alcohol on the alkaline side of its isoelectric point, but is precipitated on cooling. Heat-coagulated globin dissolves slowly at, and on the acid side of its isoelectric point. The stromata of corpuscles have an isoelectric point between p_H 5·5 and 3·0, according to the salt concentration and the nature of the ions. A slight decrease in p_H from neutrality causes hæmolysis; on the alkaline side there is a wide zone of resistance. The point at which hæmolysis sets in is affected by salts according to their effect on the isoelectric point of the stromata. The maximum resistance to hæmolysis by ether and ethyl alcohol is at the neutral point. The hæmolytic effect of saponin increases proportionally with decrease in p_H.

G. W. ROBINSON.

Isoelectric zone of typhoid agglutinin. R. OTTENBERG and F. A. STENBUCK (J. Gen. Physiol., 1926, **9**, 345—350).—The isoelectric point of typhoid agglutinin lies between p_H 4·4 and p_H 4·6.

C. P. STEWART.

Sensitisation by albumins and pseudoglobulins from normal and immune sera. H. FREUNDLICH and W. BECK (Biochem. Z., 1925, **166**, 190—201).—The authors have confirmed the results of Reitstötter (A., 1923, i, 393) on the sensitisation of ferric hydroxide sols by the pseudoglobulins of normal and immune sera, and extended the investigation to diphtheria, dysentery, and tetanus, with positive results, the result being negative, however, with swine erysipelas. Sensitisation occurs when the concentration of the pseudoglobulin is 0·1%, but a concentration of 0·6% is necessary for the detection of any difference between the normal and immune sera. The p_H of the pseudoglobulin is 6·1—6·3 in each case; the effect therefore is not due to p_H difference. A similar sensitisation takes place with Mo_2O_5,H_2O sols, but not with slightly acid gold sols. The effect of a series of cations on sensitisation with serum-albumin is given.

E. C. SMITH.

Cytological evidence of presence of cholesterol in the normal eye. A. DEHORNE (Compt. rend., 1926, **182**, 341—343).—Histological evidence is adduced to show that lipins and cholesterol, probably united with protein, occur in all the transparent tissues of the eye of various species. In pathological conditions (*e.g.*, senile cataract), separation of the lipins from the compound takes place, it is suggested, forming opaque lipoid deposits. L. F. HEWITT.

Lipin content of the corpus luteum. HERMSTEIN (Arch. Gynäkol., 1925, 739—770).—The total lipin content was approximately constant, but was slightly higher just before the menses; after the menses more fatty acids, neutral fat, and soaps are present. At the height of development the corpus luteum contains chiefly cholesterol, cholesterol esters, and phosphatides, the last-named constituent being abundant in all phases. CHEMICAL ABSTRACTS.

Comparative physiology of animal extractives and alkaloids. F. KUTSCHER and D. ACKERMANN (Z. Biol., 1926, **84**, 181—192).—The paper reviews the extensive work from Kutscher's laboratory in this field and discusses the physiological significance of the distribution amongst animals of purines, derivatives of glyoxaline and of guanidine, and of methylated substances. R. K. CANNAN.

Skin skeleton of insects. I. H. SCHMALFUSS and H. WERNER (Ber., 1925, **58**, [*B*], 2763—2764).—Extraction of the wing-sheath of the cockchafer with boiling alcohol yields a material which, in aqueous solution, gives a dark green colour with ferric chloride, becoming dark red on addition of sodium carbonate. Similar results are obtained with the aqueous extract of the wing-sheath. Ferment test-paper (Schmalfuss, A., 1923, ii, 783) is coloured brown in a few minutes by the aqueous extract. The presence of an *o*-dihydroxybenzene is thus established. H. WREN.

Effect of alkaloids and salts on vital staining. I. Studies with living tissue. A. BORNSTEIN and E. RÜTER (Pflüger's Archiv, 1925, **207**, 596—613; from Chem. Zentr., 1925, II, 472).—The dyes used were neutral-red, Nile-blue, and methylene-blue; the alkaloids were quinine, strychnine, atropine, novocaine, caffeine, theophylline, and pilocarpine. Paramœcia were strongly decolorised by alkaloids and by ammonium chloride, but scarcely affected by neutral salts and hydrochloric acid. Similar results were obtained with leucocytes and erythrocytes. Muscle and flower petals were decolorised by certain of the alkaloids, by neutral salts, and by hydrochloric acid. The permeability of cells for different toxic substances has an important effect on their behaviour.

G. W. ROBINSON.

Effect of alkaloids and salts on vital staining. II. E. RÜTER and A. BORNSTEIN (Pflüger's Archiv, 1925, **207**, 614—623; from Chem. Zentr., 1925, II, 472; cf. preceding abstract).—The basic dyes neutral-red, Nile-blue, and methylene-blue are displaced from

protoplasm by alkaloids. Although the process can be followed microscopically, the specific effect of each alkaloid is not evident. Neutral salts can also displace dyes from living cells. Similar, although not necessarily analogous, effects can be observed with organic and inorganic absorbents. G. W. ROBINSON.

Relation of the filterability of dyes to their excretion and behaviour in the animal body. A. GROLLMAN (Amer. J. Physiol., 1926, **75**, 287—293).—The ability of the frog's kidney to eliminate dyes introduced into the blood-stream is determined in great part by their filterability as measured by their ultrafiltration through collodion membranes. The contrary results in the literature are due to failure to establish true equilibrium during ultrafiltration by reason of adsorption of dye by the collodion. The salts of serum may change the degree to which dyes will filter. R. K. CANNAN.

Analysis of sweat. R. E. BARNEY (J. Amer. Med. Assoc., 1925, **85**, 1373—1375).—In senile eczema, but not in psoriasis, there is an apparent diminution in the output of the nitrogenous constituents of the sweat. CHEMICAL ABSTRACTS.

Urine formation in the kidneys of frogs. VII. Excretion of non-electrolytes. F. WANKELL (Pflüger's Archiv, 1925, **208**, 604—616; from Chem. Zentr., 1925, II, 1371—1372).—Solutions of the following compounds are concentrated on passing through the frog's kidney: carbamide, thiocarbamide, monosodium urate, hypoxanthine, glycine (acid reaction), alanine (acid reaction), aspartic acid, glutamic acid, lysine, arginine, guanidine, creatinine, hippuric acid, lactamide. The following compounds pass through without change of concentration: asparagine, glutamine, creatine, glucosamine, *d*- and *l*-mannose, *d*- and *l*-arabinose, *l*-dextrose, *d*-lævulose, sucrose, lactose, raffinose. The following compounds are partly retained: *d*-galactose, *d*- and *l*-xylose, *d*-ribose, glycine (? neutral reaction), alanine (? neutral reaction). *d*-Dextrose is completely retained. Concentration apparently takes place in the case of nitrogenous compounds, but not in the case of any carbohydrate. G. W. ROBINSON.

Source of errors in the determination of glycuronic acid in urine. M. BRÜLÉ, H. GARBAN, and A. AMER (Compt. rend. Soc. Biol., 1925, **92**, 1216—1218; from Chem. Zentr., 1925, II, 1375).—In certain cases when glycuronic acid is known to be present, the Tollens test is negative or the violet coloration is only obtained when, after hydrolysis with hydrochloric acid and cooling, more naphthoresorcinol is added. Other sources of error are the presence of hexamethylenetetramine or large amounts of dextrose. G. W. ROBINSON.

Hydrogen-ion concentration of human fæces. G. SCHAUDT (Biochem. Z., 1925, **166**, 136—154).—The p_H of fæces normally lies between 8·4 and 5·2. Liquid fæces are of lower p_H than solid. Karlsbad salts and sodium dihydrogen phosphate *per os* cause an increase in acidity, but disodium hydrogen phosphate and sodium hydrogen carbonate *per os* or intravenously have no effect on the p_H. On mixed diet the fæces are alkaline, but on fat diet practically neutral. No definite connexion exists between the p_H of urine and that of the fæces. On fat diet, the urinary p_H varies between 6·0 and 7·0, on protein diet between 5·0 and 7·0. E. C. SMITH.

Presence of copratin and detection of blood in fæces. O. SCHUMM [with W. DANKMEIER] (Z. physiol. Chem., 1926, **151**, 126—129).—The presence of copratin (this vol., 87) could not be demonstrated in human bile, although the hæmochromogen reaction was positive; the same applies generally to meconium, although here sometimes copratin was definitely present; it is pointed out that the presence of copratin or chloroform-soluble porphyrin in the fæces may be the only sign of "occult" hæmorrhage in certain cases. Comparison of the pyridine blood test with Weber's test and the benzidine reaction has shown the former to be a sensitive and certain method for the detection of hæmatin. C. R. HARINGTON.

Lipoid partition in blood in health and disease. B. L. OSER and W. G. KARR (Arch. Int. Med., 1925, **36**, 507—515).—In human plasma and corpuscles variations in the lipoid phosphorus in normal cases, greater than are usually stated to occur, were found. The ratio of cholesterol to phosphorus was inconstant. H. J. CHANNON.

Lipin content of blood in relation to cell resistance. A. GRIGAUT, M. DEBRAY, and W. E. FURSTNER (Compt. rend. Soc. Biol., 1925, **92**, 935—937; from Chem. Zentr., 1925, II, 477).—Data are given for the content of lipins and fat in the blood of various mammals. In certain cases of icterus a correlation is observed between cholesterol content and cell resistance. Both are diminished in hæmolytic icterus and frequently increased in jaundice due to retention of bile. G. W. ROBINSON.

Utilisation of glucosone by the diabetic. S. J. THANNHAUSER and M. JENKE (Arch. exp. Path. Pharm., 1926, **110**, 300—316).—A very impure syrup containing chiefly glucosone (cf. A., 1888, i, 1267), prepared by the action of hydrogen peroxide on lævulose in presence of iron, was administered to severe cases of diabetes and shown to be completely utilised. The sugar excretion was not increased, the acetone substances completely disappeared, the urine became alkaline, and the alveolar carbon dioxide tension increased. The disturbance in the diabetic is due not so much to the inability to convert dextrose after glycogenolysis into a utilisable form, as to the inability to convert dextrose into glucosone, which is then utilised for the synthesis of glycogen. Glucosone forms glycogen even more readily then lævulose. It cannot, however, be recommended for therapeutic use until obtainable in pure form. P. W. CLUTTERBUCK.

Curve of inorganic blood phosphates during the sugar tolerance test. Significance in diagnosis and prognosis. F. W. HARTMAN and A. BOLLINGER (J. Amer. Med. Assoc., 1925, **85**, 653—656).—Seven charts of curves are constructed from the data on inorganic blood phosphates and sugar in a series of clinical cases. The effects of insulin on

phosphate utilisation are comparable with those on carbohydrate utilisation. Abnormal carbohydrate metabolism may be divided into seven groups by means of the blood phosphate curve. Slight abnormalities and the functionless pancreas are readily identified through the phosphate curve. Abnormal carbohydrate metabolism associated with the pituitary, and possibly with the suprarenals, may be recognised. CHEMICAL ABSTRACTS.

Blood chemistry of the new-born. O. H. SHERMAN, G. W. PUCHER, and H. R. LOHNES (Amer. J. Dis. Children, 1925, **30**, 496—503).—Inanition fever is accompanied by marked acidosis and marked increase of blood urea and amino-acids. CHEMICAL ABSTRACTS.

Quantitative changes in tissue glycogen, blood sugar, plasma, inorganic phosphates, and in blood lactic acid in canine histamine shock. E. K. CHAMBERS and K. W. THOMPSON (J. Infect. Dis., 1925, **37**, 229—231).—The results were similar to those for anaphylaxis (McCullough and O'Neill, this vol., 192). CHEMICAL ABSTRACTS.

Melanotic pigment. B. BRAHN (Virchow's Arch., 1924, **253**, 661—664; from Chem. Zentr., 1925, II, 1289).—In the urine of patients with melanotic tumours there was found, in addition to melanin, a colourless substance which was changed into melanin by oxidation with potassium persulphate. The ferric chloride reaction for melanin in urine is less specific than the brown coloration with potassium persulphate. The melanin of urine contains less nitrogen and has a stronger vaso-constrictor action than melanins hitherto obtained. It contains no sulphur. G. W. ROBINSON.

Prevention and cure of tetany by oral administration of strontium. W. W. SWINGLE and W. F. WENNER (Amer. J. Physiol., 1926, **75**, 378—391).—Tetany can be prevented or relieved by the continuous administration of strontium lactate. The strontium acts by decreasing the permeability of the gut to calcium excretion and by reducing the excitability of the motor nerves. Thyroparathyroidectomised dogs treated for 40 days with strontium readjusted themselves to lack of the parathyroids and recovered permanently. R. K. CANNAN.

Results of thyroidectomy. E. ABDERHALDEN (Pflüger's Archiv, 1925, **208**, 476—486; from Chem. Zentr., 1925, **II**, 1290).—Parenteral administration of telluric acid, which is without effect on normal guinea-pigs, causes death where thyroidectomy has been performed. In such animals, methyl telluride is formed, but to a smaller extent than in normal animals. Anatomical differences, and differences in gaseous exchanges, in reaction to adrenaline, and in body temperature are also observed. G. W. ROBINSON.

Uric acid in normal and pathological plasma. Relationship between free and total uric acid. C. M. JONES (Compt. rend. Soc. Biol., 1925, **93**, 298—299; 299—300; from Chem. Zentr., 1925, II, 1292).—The uric acid content of normal plasma is 32—49 mg. per litre, of which approximately 70% is in the free state. The uric acid content of plasma was also investigated in hepatic, renal, and spinal disease. G. W. ROBINSON.

Residual nitrogen content of blood in its relationship with renal insufficiency and uræmia. O. KLEIN (Zentr. inn. Med., 1925, **46**, 411—413; from Chem. Zentr., 1925, II, 411).—In the absence of kidney disease the residual nitrogen in blood is generally less than 45 mg.%, and never more than 50 mg.%. The upper limit is attained with diets very rich in protein shortly after meals and after sweating. Increase of residual nitrogen to 50—80 mg.% occurs during fever, with or without albuminuria, in gangrene, and in stasis during the stage of resorption of œdema, in acute and chronic nephritis. In the gravest kidney diseases with disturbance of function the figure exceeds 80 mg.%, whilst in true uræmia it is always greater than 100 mg.% G. W. ROBINSON.

Breakdown of proteins in frogs after extirpation of the liver. S. J. PRZYLECKI (Arch. internat. Physiol., 1925, **24**, 27—40; from Chem. Zentr., 1925, II, 1371).—Fasting frogs, after extirpation of the liver, excrete as much total nitrogen as normal animals. The carbamide quotient decreases, whilst the ammoniacal nitrogen increases. It is concluded that frogs after the removal of the liver can still deaminise amino-acids and synthesise carbamide. G. W. ROBINSON.

Nitrogen and sulphur metabolism in the dog. M. FAY and L. B. MENDEL (Amer. J. Physiol., 1926, **75**, 308—329).—The ratio of urinary nitrogen to sulphur varies with the individual animal as well as with the dietary protein. When a deviation of the urinary ratio from the food ratio persisted, it was in the direction of a higher value. Following a period of starvation, there is a greater retention of the sulphur of the food than of the nitrogen. R. K. CANNAN.

Conversion of insoluble compounds containing phosphorus and calcium into soluble, and their absorption in the alimentary canal. W. M. ARISTOWSKY (Biochem. Z., 1925, **166**, 55—70).—After administration of milk to dogs, chyme from a fistula in the ileum is practically calcium- and phosphorus-free, whereas that from a fistula in the jejunum contains large quantities of calcium and phosphorus. Absorption is somewhat delayed when bread is added to the meal. In the case of meat, which contains much phosphorus and little calcium, the phosphorus is largely absorbed in the ileum, but the calcium is excreted. The small intestine therefore acts as an excretory organ for calcium only, and that only on meat diet. The excretion of calcium and phosphorus probably takes place in the large intestine. E. C. SMITH.

Digestibility of lichenin. A. WALLERSTEIN (Biochem. Z., 1925, **166**, 157—161).—Administration of pure lichenin to mice resulted, in two cases, in a utilisation of 64% and 53%. E. C. SMITH.

Chemistry of rigor. H. J. DEUTICKE (Z. physiol. Chem., 1925, **149**, 259—297).—Although there is a marked increase in the lactic and phosphoric acids of a muscle in rigor, the production of these acids

is not the immediate cause of rigor. Acid production leads to changes in the physical properties of the muscle colloids, which changes are reversible *in vivo*, and more difficultly reversible in the isolated organ. Beyond a certain point, even although rigor is not yet evident, the change of which the inception is accompanied by acid production becomes irreversible, and even if a portion of the acid is removed from the muscle, rigor nevertheless sets in.

The changes in the properties of the muscle colloids are exemplified by the incapability of muscle which has been kept or allowed to go into rigor to esterify free phosphoric acid in presence of fluoride ions. The muscle nevertheless still retains its power to hydrolyse hexosediphosphoric acid to lactic acid. It cannot, however, hydrolyse glycogen, because it is unable to transform this polysaccharide into the essential intermediate hexosephosphoric ester. H. D. KAY.

Control of blood pressure with hepatic extract. A. A. JAMES, N. B. LAUGHTON, and A. B. MACALLUM (Amer. J. Physiol., 1926, **75**, 392—398).—Extracts of liver reduce hypertension in rabbits induced by certain pressor substances and reduce the normal blood pressure over long periods. The active substance is ether-soluble and is neither choline nor histamine. R. K. CANNAN.

Nitrogen output of isolated frog's muscle under the action of substances causing contraction. O. RIESSER (Pflüger's Archiv, 1925, **208**, 522—528; from Chem. Zentr., 1925, II, 1373).—Fresh gastrocnemius muscle in Ringer's solution with abundant supply of oxygen produced 0·0175% of its weight of nitrogen in 3 hrs. In the subsequent period, the output fell to 0·005—0·006%. Fatigue, potassium chloride contracture, isotonic sucrose solution, or narcosis by 4—10% of ethyl alcohol did not affect the output of nitrogen. An appreciable increase in nitrogen output as the result of muscular injury resulted from contraction induced by hydrochloric acid, sodium hydroxide, chloroform, or bromoacetic acid. G. W. ROBINSON.

Influence of histamine on the intestinal secretion of the dog. W. KOSKOWSKI (J. Pharm. Exp. Ther., 1926, **26**, 413—419).—Histamine introduced parenterally into dogs causes after one minute an increase in the amount of intestinal juice secreted, and also in the invertase and amylase activity of the juice. The invertase of intestinal juice has an optimum p_H of about 6·0, and appears to be an endoferment, as the action of the juice becomes much more marked after disintegration of cell-elements by grinding with glass. The amylase activity is then similarly increased. W. O. KERMACK.

Blood and symptomatic changes following the intravenous administration of a variety of agents and solutions. P. J. HANZLIK, F. DE EDS, and M. L. TAINTER (Arch. Int. Med., 1925, **36**, 447—506).—Intravenous injections into dogs of solutions of various concentrations of sodium chloride, sucrose, dextrose, urea, agar, gum acacia, gelatin, copper sulphate, calcium chloride, sodium iodide and salicylate, arsphenamine, and peptone, and of suspensions of barium sulphate and fuller's earth have been made. The effect of these substances on dilution of the blood, its p_H, carbon dioxide, lactic acid, phosphate, ammonia, sugar, and urea content have been studied. H. J. CHANNON.

Pharmacological action of cæsium salts. F. KÜLZ and I. PAULS (Arch. exp. Path. Pharm., 1926, **110**, 351—363).—A study of the action of cæsium salts on skeletal muscle, respiratory activity, the intestine, and the isolated frog's heart shows that cæsium in its physico-chemical properties and its pharmacological action is similar to the quaternary ammonium bases. P. W. CLUTTERBUCK.

Pharmacological action of complex metallic compounds of the metalammonium type. F. KÜLZ (Arch. exp. Path. Pharm., 1926, **110**, 342—350).—The same pharmacological action is possessed both by metallic hexammine compounds and by compounds of the types $[Cr(carbamide)_6]Cl_3$ and $[Cr_3(fatty\ acid)_6(OH)_2]Cl$. It appears, therefore, that the action of such complex substances is a function of the molecule as a whole, and not of the ammonia grouping, as originally suggested by Ostwald (A., 1922, i, 498). P. W. CLUTTERBUCK.

Cathode rays as substitutes of potassium. H. ZWAARDEMAKER and T. P. FEENSTRA (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 650—655).—The hearts of eels and frogs, perfused in Ringer's solution which has been deprived of its potassium, until they have ceased to beat for a period of about 15 min., may be made to beat again by exposure to cathode rays of the correct penetrating power. J. W. BAKER.

Physiological action of light. V. Increase in uric acid in blood irradiated directly. F. C. KOCH and C. I. REED (Amer. J. Physiol., 1926, **75**, 351—357).—Irradiation of blood for 1½ hrs. with a carbon arc resulted in an average increase of 38% in the uric acid concentration determined by a modification of Folin's method. This increase was not due to uric acid alone, and possibly indicated the formation of a precursor of melanin (dihydroxyphenylalanine). R. K. CANNAN.

Effect of light on nitrogen metabolism. G. FONTÈS and A. YOVANOVITCH (Compt. rend. Soc. Biol., 1925, **93**, 269—270; from Chem. Zentr., 1925, II, 1293).—Exclusion of light decreases nitrogen metabolism nearly to the level attained during sleep. The decrease in nitrogen metabolism during sleep in light is less than the corresponding decrease in darkness. G. W. ROBINSON.

Physiological action of darkness, daylight, and of carbon arc radiation. I. Effects of darkness on metabolism in the dog. II. Effect of carbon arc radiation on metabolism in the dog. H. S. MAYERSON, L. GUNTHER, and H. LAURENS (Amer. J. Physiol., 1926, **75**, 399—420, 421—442).—I.—A period of darkness extending from 18 to 28 days acted initially as a stimulus to metabolism in adult dogs. There was a return to normal within the period, and a prolonged stay in the dark was without further effect on the composition of blood or urine. There was retention of calcium and of phosphorus.

II.—Irradiation with moderate intensities increased

the endogenous nitrogen metabolism, stimulated the absorption of calcium and phosphorus from the intestine, and depressed the blood-sugar. Similar results followed when animals were taken from darkness into room-light or from light into darkness. Any deviation from the usual in radiant energy supply acts as a stimulus to these metabolic processes.

R. K. CANNAN.

Biological action of *X*-rays. III. Sensitisation to Röntgen rays by thorium salts. P. ELLINGER and O. GANS (Arch. exp. Path. Pharm., 1926, **110**, 295—299).—Injection into rats of various protein precipitants, viz. tannic acid, concentrated nitric acid, aluminium chloride, and silver nitrate, does not cause any noteworthy increase in sensitivity to *X*-rays, and the authors' original view that the increased sensitivity after injection of thorium nitrate is due to a physical, and not to a chemical–colloidal effect is maintained.

P. W. CLUTTERBUCK.

Acute and chronic poisoning by heavy metals. I. Poisoning by manganese compounds. H. HANDOVSKY, H. SCHULZ, and M. STAEMMLER (Arch. exp. Path. Pharm., 1926, **110**, 265—280).—Acute poisoning occurs only when the concentration of manganese in the blood suddenly becomes very high and is accompanied with nervous disturbances. In chronic poisoning, this high concentration is not reached, nervous symptoms are not observed, the liver is chiefly attacked, and death occurs usually with smaller amounts than in acute poisoning, the lethal doses being for the former 40 mg./kg. and for the latter 50 mg./kg. In the chronic condition, manganese citrate is more rapidly absorbed and more poisonous than the chloride. About 50% of the manganese injected is excreted in the fæces, but only traces appear in the urine. Considerable amounts are found in bone, bile, pus, and ascitic fluid. In the organs, most manganese is deposited in the spleen and brain, a variable quantity in the liver, and only a little in the lungs. Manganese is found in muscle only after injection of the chloride, and not of complex organic salts of manganese. Fatty degeneration of the liver, heart, and kidney sometimes occurs.

P. W. CLUTTERBUCK.

Narcotic action of propylene. J. T. HALSEY, C. REYNOLDS, and W. A. PROUT (J. Pharm. Exp. Ther., 1926, **26**, 479—490).—The narcotic action of propylene on mice, cats, dogs, and men is more than twice as powerful as that of ethylene, and its lethal concentration is about two-thirds as great again as that at which narcosis is induced.

W. O. KERMACK.

Pharmacology of pinocamphone, verbanone, verbenone, and camphor. V. Chemical constitution and physiological action. R. SIEGEL (Arch. exp. Path. Pharm., 1926, **110**, 364—385).—Concentrations of 100×10^{-6} to 5×10^{-6} of verbanone, verbenone (in c.c.), and of camphor (g.) are very injurious when perfused through the surviving heart of the guinea-pig. The respiratory activity of rabbits, reduced to one-half to one-third of the normal by injection of 3—6 mg. morphine per kg., is increased up to normal values by intravenous injection of 3—5 mg/kg. of verbanone, verbenone, pinocamphone, and camphor. No simple connexion between chemical constitution and physiological properties was found (cf. A., 1914, i, 347).

P. W. CLUTTERBUCK.

Effect of ether and chloroform on the action of acetylcholine and pilocarpine on the intestine. H. RYDIN (Compt. rend. Soc. Biol., 1925, **92**, 654—657; from Chem. Zentr., 1925, II, 413).—Ether and chloroform in low concentrations increase the effect of subsequent moderate doses of acetylcholine; ether similarly increases the effect of pilocarpine. Both narcotics increase the motor effect of acetylcholine on the intestine and its inhibitory effect on the heart.

G. W. ROBINSON.

Effect of chloral hydrate and chloral-formamide on the intestinal action of parasympathetic stimulants. H. RYDIN (Compt. rend. Soc. Biol., 1925, **92**, 658—661; from Chem. Zentr., 1925, II, 413; cf. preceding abstract).—Chloral hydrate and chloral-formamide behave similarly to chloroform and ether in increasing the effect on the intestine of acetylcholine and pilocarpine. G. W. ROBINSON.

Effect of trichloro*iso*propyl alcohol and trichloro*iso*butyl alcohol on the intestinal action of parasympathetic stimulants. H. RYDIN (Compt. rend. Soc. Biol., 1925, **92**, 662—664; from Chem. Zentr., 1925, II, 413; cf. preceding abstracts).—Trichloro*iso*propyl alcohol and trichloro*iso*butyl alcohol do not increase the effect of acetylcholine on the intestine. Trichloro*iso*butyl alcohol increases the effect of pilocarpine alone. In fairly large doses, both narcotics may actually decrease the intestinal effect of acetylcholine and pilocarpine. Moderate amounts of the narcotics mentioned in this and the preceding abstracts can increase the automatic activity of isolated surviving mammalian intestine preparations. G. W. ROBINSON.

Bacterial chemotherapy with reference to mercury dyes. G. W. RAIZISS, M. SEVERAC, and J. C. MOETSCH (J. Pharm. Exp. Ther., 1926, **26**, 447—459).—Rabbits experimentally infected with *Staphylococcus aureus* are beneficially influenced by the intravenous injection of the following compounds 48 or 72 hrs. after infection: metaphen, mercurochrome, 565 (mercury derivative of rose-bengal 3*B*), and benzurin (mercury derivative of benzopurpurin-4*B*). The results with the last compound were particularly promising. W. O. KERMACK.

Chemotherapy of bacterial infections. I. Action of acriflavine, gentian-violet, and mercurochrome in experimental bacterial infections. E. L. WALKER and M. A. SWEENEY (J. Pharm. Exp. Ther., 1926, **26**, 461—467).—Therapeutic effects are obtained by the use of acriflavine, gentian-violet, and mercurochrome, in acute infections of mice by *Staphylococcus aureus* and *Streptococcus pyogenes hæmolyticus*, particularly if these chemicals are brought into immediate contact with the invading bacteria. None of them is effective against the gram-negative Friedländer bacillus. W. O. KERMACK.

Bactericidal properties of the quinone group. S. HILPERT (Biochem. Z., 1925, **166**, 71—88).—Chloranil, suspended in gelatin, serum, or water, has a specific bactericidal action on *Staphylococcus*, but no action on *Bacillus coli*. Chloranilic acid is disinfectant only in solutions of greater acidity than p_H 3. Since *Staphylococcus* is more sensitive to acid than *B. coli*, the bactericidal action of chloranil is probably due to the liberation of hydrochloric acid during its hydrolysis to chloranilic acid. Dichloronaphthaquinone and diehloroindoquinone behave similarly to chloranil. Benzoquinone is more actively bactericidal towards *B. coli* than towards *Staphylococcus*. The action is probably not due to oxidation, since homologous methyl-substituted quinones are progressively less active, but may be due to condensation with the primary amino-groups of the cell proteins, forming compounds analogous to anilinoquinone. This action is similar to the effect of benzoquinone on dry, powdered skin. In each case a red condensation product and quinol are formed, according to the equation $2C_6H_4O_2+NH_2R=C_6H_3O_2\cdot NHR+C_6H_6O_2$.

E. C. SMITH.

Advances in the isolation of enzymes. R. WILLSTÄTTER (Ber., 1926, **59**, [*B*], 1—12).—A lecture delivered before the German Chemical Society. The author reaches the conclusion that the molecule of an enzyme is composed of a colloidal carrier and a purely chemically active group. The nature of the colloidal carrier appears to be variable, since each enzyme (as far as experiment allows judgment to be passed) can be separated from the chemically defined, colloidal companion without loss of its specific activity, and the affinity of the enzyme is not constant. A single, colloidal carrier does not, therefore, appear necessary if another suitable material is at the disposal of the enzyme. The latter is able to change its aggregates. Nevertheless, it is not yet possible to separate completely the chemically active groups (the enzyme molecule proper) from the protective colloid without loss of activity. H. WREN.

Influence of hydrogen-ion concentration on dextrinisation of starch by purified amylase. T. CHRZASZCZ, Z. BIDZINSKI, and A. KRAUSE (Rocz. Chem., 1925, **5**, 419—436).—See this vol., 93.

Enzymes of emulsin. I. Amylase action of emulsin preparations. K. JOSEPHSON (Ber., 1925, **58**, [*B*], 2726—2731).—The separation of the individual enzymes of emulsin has been partly effected by precipitation with alcohol, followed by fractional adsorption with aluminium hydroxide, elution of the adsorbate with disodium hydrogen phosphate, and dialysis; the use of aluminium hydroxide is less advantageous in this instance than in the case of yeast invertase. The behaviour of the purified enzyme mixtures has been examined towards starch and the β-glucoside, salicin. A parallelism between the power of hydrolysing starch and the β-glucosidase action is not observed. The former action must therefore be attributed to an amylase differing from β-glucosidase (cf. Kuhn, A., 1925, i, 636; Pringsheim and Leibowitz, A., 1925, i, 1043). H. WREN.

Milk-diastase. T. CHRZASZCZ and C. GORALOWNA (Biochem. Z., 1925, **166**, 172—189).—Milk shows very slight capacity for dissolving starch, but considerable saccharifying and dextrin-forming action. The optimum temperature and p_H vary with the diastase concentration. The former lies between 20° and 40°, for normal milk 30°, for colostrum between 35° and 45°. The optimum p_H lies between 5·8 and 6·2, but in the presence of bacteria containing diastase, between 5·0 and 5·5. One hundred c.c. of normal milk completely dextrinise 0·05—0·1 g. of soluble starch in 1 hr. at 30°; 0·3—0·8% sodium chloride and serum accelerate milk-diastase, indicating that the diastase is of animal, and not bacterial, origin. Diastase is inactivated in 1 hr. at 60—65°, in colostrum at 65—70°. This is applied to the determination of the temperature and duration of pasteurisation. The diastatic activity of cow's milk being denominated 100, those of sheep's, goat's, and mare's milks are 170, 50, and 130, respectively. Cream is more active than skimmed milk, and colostrum than normal milk, but colostrum becomes normal after the fourth day. The diastase content varies with the individual, and depends on its physiological condition. In diseases of the udder, the diastase content is increased. Diastase is precipitated with the caseinogen on coagulation, but a small quantity is left in the whey. The presence or absence of leucocytes has no effect on the diastase content. Milk contains no invertase.

E. C. SMITH.

Invertase. XI. Decrease of invertase in yeast. R. WILLSTÄTTER and C. D. LOWRY, jun. (Z. physiol. Chem., 1925, **150**, 287—305).—The invertase content of yeast is greatly decreased by a short digestion (¼—2 hrs.) with mineral acids (0·15—0·3*N*-sulphuric acid) or alkalis (0·05—0·1*N*-sodium hydroxide). The essential functions of the yeast-cells are not, however, impaired. The fermenting power in many cases is unaffected, but in others is reduced by 10—50%. During fermentation the invertase content returns fairly quickly. The study of fermentation and inversion of sucrose by yeasts very poor in invertase at a p_H of approximately 2 showed that fermentation takes place more quickly than the possible inversion. The authors suggest that ordinary yeasts ferment sucrose direct, *i.e.*, without previous inversion, and evidence of the direct fermentation of maltose will shortly be given.

H. I. COOMBS.

Invertase. XII. R. WILLSTÄTTER, K. SCHNEIDER, and E. WENZEL (Z. physiol. Chem., 1926, **151**, 1—30).—Preliminary separation of invertase from yeast is best carried out by plasmolysis with toluene, dilution, and neutralisation, followed by autolysis at 30° for a day, and final removal of protein by addition of acetic acid; the resulting water-clear solution contains about 85% of the invertase originally present. Purification of the invertase in such a solution may be effected by precipitation with alcohol or by adsorption on aluminium hydroxide (cf. A., 1924, i, 692). Addition of tannin to such a solution causes no precipitate at the ordinary temperature, but at 0° causes a precipitation of the enzyme, the completeness of the preci-

pitation being dependent on the concentration of tannin rather than on that of invertase; the enzyme can be recovered from the precipitate by dissolving the latter in water, followed by adsorption of the invertase on aluminium hydroxide; this process leads to an increase in the activity of the preparation, but to no change in its content of tryptophan. Fractional precipitation by lead phosphate of a partly inactivated preparation of invertase (equivalent amounts of diammonium hydrogen phosphate and lead acetate being added to its aqueous solution) leads to a separation of inactive material, which is contained in the first fraction, from active material contained in subsequent fractions; by this method a preparation of the enzyme was obtained which was completely free from tryptophan, the removal of tryptophan being favourably influenced by the addition of peptides (*e.g.*, leucylglycine) to the solution before fractional precipitation. Application of this fractional precipitation has led to the most active preparation yet obtained, having a sucrase value of 11·9; this preparation had 8·2% N, as compared with the much higher values for earlier preparations. It is thought that invertase is dependent for its stability on the presence of one or more protective colloids; the protective substance, however, is neither yeast gum nor a tryptophan- or tyrosine-containing peptide.

C. R. HARINGTON.

Enzyme action and ion antagonism. R. HÖBER and A. SCHÜRMEYER (J. Gen. Physiol., 1926, **8**, 265—269).—Invertase is sensitive to salts only in presence of colloids such as gelatin, albumin, globulin, lecithin, when its activity is reduced by salts. In the complexes, invertase–globulin and invertase–lecithin, an ionic equilibrium of the physiological cation-antagonism type can be shown; sodium and potassium on the one hand, and magnesium, calcium, strontium, barium, aluminium, and lanthanum on the other hand, oppose one another in certain concentrations, so that by maintenance of these proportions optimal action of the invertase is obtainable. The salt opposition and the cation antagonism are absent on the acid side of the isoelectric points of globulin and lecithin.

C. P. STEWART.

Maltase of barley malt, and the specificity of the disaccharases. J. LEIBOWITZ (Z. physiol. Chem., 1925, **149**, 184—194).—The maltose-hydrolysing enzyme of barley malt recently described by Pringsheim and Leibowitz (this vol., 202) has been further investigated and its marked differences from the maltase of yeast confirmed. It does not decompose α-methylglucoside, either at the optimum p_H for its own activity with maltose as substrate, or at the optimum p_H for the maltase of yeast, nor does it catalyse the synthesis of α-alkylglucosides from dextrose and the corresponding alcohol. It is also inactive in the hydrolysis of β-methylmaltoside, which is readily decomposed by yeast maltase. The new maltase is most stable at p_H about 6·0, increase in acidity leading to increased rate of destruction. Yeast maltase appears to attack the glucoside part of maltose, whereas malt maltase attacks the dextrose portion of the molecule. H. D. KAY.

Presence of a hitherto undescribed oxydase in certain fungi. J. WOLFF (Compt. rend., 1926, **182**, 343—344).—Ferrous salts in wines are oxidised (cf. B., 1926, 104) by an enzyme *ferrase*, which, unlike tyrosinase and laccase, is not inactivated by heating at 80° for 5 or 6 min. Ferrase occurs in *Russula fœtens* and *R. emetica*. L. F. HEWITT.

Phosphate metabolism. II. F. DEMUTH (Biochem. Z., 1925, **166**, 162—171).—The inorganic serum-phosphorus of a healthy dog was found to be 8·8 mg.%, of two rachitic dogs 5·3 and 6·0 mg.%, respectively. Dog's serum contains four times as much hexosediphosphatase as that of infants. The cartilage of healthy and rachitic infants contains very little hexosediphosphatase, formed bone somewhat more, and tissue from the region of ossification considerable quantities. In rachitic infants the latter tissue is four times as active as in healthy infants. The optimum p_H for hexosediphosphatase from healthy bone is 7·0, from rachitic bone is 7·9, as was found for rachitic serum (A., 1925, i, 1497), with a second optimum at 7·0. The bone marrow of rachitic animals and infants is only half as active as normal. Insulin, adrenaline, pituitary and thymus extracts, and choline chloride have no action *in vitro* on serum hexosediphosphatase. On a salt- and protein-free hexosephosphatase preparation from dialysed urine, $K^{\cdot}$, $Na^{\cdot}$, and $NH_4^{\cdot}$ have no action, $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$ shift the p_H optimum to the acid side; PO_4''', SO_4'', NO_3', and IO_3' inhibit; Cl', citrate, and acetate have no action. E. C. SMITH.

Comparative cell-free fermentation of hexosediphosphoric acid, dextrose, lævulose, sucrose, and invert-sugar. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **166**, 488—496).—When equimolecular ($M/4$) solutions of the above sugars are fermented at p_H 6·0—6·2 hexosediphosphate is most slowly attacked, and mixtures of equimolecular solutions of hexosediphosphate with dextrose, lævulose, sucrose, and invert-sugar, respectively, ferment more slowly than the equivalent concentration of hexose. On the other hand, concentrations of hexosediphosphate of $M/40$—$M/400$ caused considerable increase in the rate of fermentation of the other sugars. P. W. CLUTTERBUCK.

Preparation of standards for the colorimetric determination of pepsin. J. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1925, **149**, 173—178.—Fibrin is dyed, under standard conditions, with diphenylrosaniline in glycerol solution, and the amount of digestion after a given time determined by comparing the colour of the digest with that of standard glycerol solutions of the dye. The standards are stable for months. This method, unlike the old carmine–fibrin process, may be used for both α- and β-proteases. H. D. KAY.

Kinetics of the action of pepsin on fibrin. J. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1925, **149**, 179—183).—The amount of fibrin hydrolysed by a given quantity of dilute pepsin solution (gastric juice or extract of mucosa) is a linear function

of the time. Only with a concentrated pepsin preparation is the law of Schütz and Borissow obeyed. H. D. KAY.

Effect of radioactive radiations and *X*-rays on enzymes. V. Influence of variation of the thickness of the absorbing layer of solutions of pepsin on the rate of radiochemical inactivation of the enzyme. VI. Influence of variation of temperature on the rate of radiochemical inactivation of solutions of pepsin by β-radiation. R. G. HUSSEY and W. R. THOMPSON (J. Gen. Physiol., 1926, **9**, 309—313, 315—317; cf. this vol., 202).—V.—Under the experimental conditions employed, the effect of γ-radiation on dilute pepsin solutions is negligible in comparison with that of β-radiation. When the thickness of the absorbing layer of pepsin solution exceeds 0·661 cm., the available β-radiation appears to be completely absorbed, and in such circumstances (thicknesses up to 1·419 cm. have been studied) the mean reaction velocity coefficient for the inactivation of pepsin varies inversely with the volume of solution.

VI.—It is not yet possible to establish for k and its temperature coefficient values which will hold for any source of radiation of the type employed. The data indicate, however, that temperature has only a slight effect on the rate of inactivation of pepsin by β-radiation. C. P. STEWART.

Specificity of animal proteases. III. Trypsin and erepsin of the pancreas. IV. Spontaneous activation of trypsinogen. E. WALDSCHMIDT-LEITZ and A. HARTENECK (Z. physiol. Chem., 1925, **149**, 203—220, 221—230).—III.—By the methods of selective adsorption, the two proteolytic enzymes of the pancreatic juice may be separated into trypsin and an erepsin, the latter being identical with the erepsin of intestinal juice. The ability of pancreatic juice to hydrolyse simple synthetic peptides is due to its ereptic component; trypsin itself (either activated or otherwise) is inactive towards these compounds. Trypsin before activation will, however, hydrolyse certain peptones, protamines, and histones, but not caseinogen, fibrin, gelatin, gliadin, or zein. Only on activation by enterokinase will trypsin break down the latter group of proteins. Erepsin of pancreatic juice will not hydrolyse even the simple proteins. It is unstable in alkaline solution. The separation of the pancreatic proteolytic enzymes leads to a sharper division between the four types of proteolytic enzymes, (1) the peptidases (erepsin), (2) enzymes similar to inactivated trypsin, (3) activated trypsin, (4) pepsin. No one of these enzymes is capable of a complete hydrolysis of a protein of high mol. wt. Fractional hydrolysis by purified enzyme preparations should throw light on the inner structure of the proteins.

IV.—If a glycerol extract of the fresh dried pancreas is diluted with water, its activity towards caseinogen, which is zero at first, becomes marked after 3 or 4 days. The precursor of the activating agent may be separated from the extract by adsorption on colloidal alumina in faintly acid solution. The mother-liquor now remains inactivated; the trypsinogen in it is also far more stable than in the unpurified extract. On elution of the adsorbate with dilute ammonia, the activating agent is recovered, and may be used for the activation of the purified trypsinogen. It is probably identical with enterokinase. H. D. KAY.

Intestinal erepsin. E. WALDSCHMIDT-LEITZ and A. SCHÄFFNER (Z. physiol. Chem., 1926, **151**, 31—55).—Erepsin can be determined by alkalimetric titration (in 85% methyl alcohol) of the acidic groups liberated during its action on glycylglycine; the optimum p_H for the action of the enzyme is 7·8, and the hydrolysis follows the course of a unimolecular reaction. The enzyme is best extracted from the fresh intestinal mucous membrane by means of 87% glycerol; from the solution so obtained, after dilution with water, the enzyme may be precipitated by numerous reagents, but with much loss in all cases except that of dilute acetic acid, in which case 23% remains in solution and 65% is obtained in the precipitate; the enzyme is adsorbed from its aqueous solution by aluminium hydroxide to a high degree at p_H 4·7, progressively less at more alkaline reactions, and may be dissolved out from the adsorbate by means of alkaline phosphate solution; similarly it can be adsorbed on kaolin; neither treatment effects any concentration of the erepsin, but the aluminium hydroxide adsorption yields a product entirely free from trypsin. The trypsin-free intestinal erepsin so obtained is quantitatively and qualitatively similar to pancreatic erepsin (A., 1925, i, 1360) in the rate at which it hydrolyses various dipeptides and in its failure to hydrolyse proteins or their higher degradation products. C. R. HARINGTON.

Nomenclature of fermentation enzymes and oxydases. C. NEUBERG and C. OPPENHEIMER (Biochem. Z., 1926, **166**, 450—453).—Enzymes are divided into desmolases (including oxydo-reductases or dehydrases) and hydrolases. Peroxydase, phenolase, and tyrosinase are retained. Enzymes taking part in the breakdown of sugars are grouped together as zymases. P. W. CLUTTERBUCK.

Oxydo-reductases (dehydrogenases) of yeast. II. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **151**, 155—164).—Reducing power towards methylene-blue was restored to washed yeast by addition of biocatalyst-*Z* (cf. von Euler and Swartz, A., 1925, i, 209) or of boiled muscle extract, but not by various plant extracts; formaldehyde and acetaldehyde caused an inhibition of the residual reducing power of washed yeast; in presence of a co-reductase and with fresh yeast they had little effect. Warming fresh yeast at 40° for 30 min. increased markedly its reducing power, whether in presence or absence of aldehyde. The action of the biocatalyst-*Z* was not due to its inorganic constituents. Reduction of nitrate to nitrite by yeast could not be observed. C. R. HARINGTON.

Hydrolysis of polysaccharides by yeast. R. IWATSURU (Biochem Z., 1926, **166**, 409—413).—Hydrolysis of inulin by yeast preparations results in the formation of lævulose identified as the phenylmethylosazone, m. p. 151°. P. W. CLUTTERBUCK.

Action of alcoholic zymase. G. PARIS (Atti Congr. Naz. Chim. Ind., 1924, 446—449; from Chem. Zentr., 1925, II, 476).—Neuberg's theory is generally

confirmed. Glycerol is formed by reduction of glyceraldehyde, which is the first product of the degradation of dextrose. Acetic acid is formed only in the presence of alkali by the Cannizzaro reaction.
G. W. ROBINSON.

Relation between alcoholic fermentation and hydrogen-ion concentration. II. E. HÄGGLUND and A. M. AUGUSTSON (Biochem. Z., 1925, **166**, 234—241; cf. A., 1925, i, 476).—The rate of alteration of the optimum p_H for the fermentation of dextrose and maltose by yeast is dependent on, and may be made use of for determining, the rate of penetration of acid into the yeast-cell. Lactic acid penetrates relatively slowly, acetic acid more rapidly. The permeability of the cell wall is increased by drying.
E. C. SMITH.

Formation of acetylmethylcarbinol and βγ-butyleneglycol. A. LEBEDEV (Biochem. Z., 1926, **166**, 407—408).—The scheme of reactions involved in the conversion of methylglyoxal into alcohol suggested by Kluyver, Donker, and Hooft (this vol., 203) was previously published by the author (A., 1924, i, 464, 802). P. W. CLUTTERBUCK.

Synthesis of coproporphyrin by yeast. III. Coproporphyrin ester from pure cultures of *Saccharomyces anamensis*. H. FISCHER and H. FINK (Z. physiol. Chem., 1925, **150**, 243—260).—It was proved spectroscopically in the case of three moulds that coproporphyrin was synthesised when these were grown in a porphyrin-free medium. In the case of *Saccharomyces anamensis*, the coproporphyrin was isolated as the methyl ester, and this was identified crystallographically. Addition of blood to the medium did not increase the yield of coproporphyrin. Raising the temperature, however, seemed to increase the yield, the optimum being between 18° and 25° (cf. A., 1925, i, 866). H. I. COOMBS.

Biogens, inactive mother-substances of the two "bios." E. V. EASTCOTT (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 21—24; cf. Lucas, A., 1924, i, 1388).—Experiments with nearly 70 vegetable and animal products show that wherever addition of one of the "bios" increases the yeast crop, addition of the other leaves it unchanged. A filtered infusion of white barley flour contains more bios I after keeping for 24 hrs. at 25° than when it was first made, whereas the bios II content is unaltered. The increase in bios I can be prevented by first boiling the solution. Similarly, a filtered infusion of malt combings after keeping for 24 hrs. at 55° shows an increase in bios II. The names biogen I and II are suggested for the inactive substances from which the additional "bioses" are formed. In general, warming with alkali in solution converts biogens into "bios," whilst the action of alcohol, or of acids in solution or heating dry alone, converts bios II into biogen II. Both the biogens are precipitated by lime or baryta from alcoholic solutions. Bios II, instead of being a "delicate" substance, is found to be capable of resisting a large number of reagents. J. S. CARTER.

Reproduction of yeast in solutions to which no bios had been added. D. WHITEMAN (Trans. Roy. Soc. Canada, 1925, [iii], **19**, III, 24—25).—In order to determine whether or not the small crops obtained in solutions of sugars and salts are due to bios introduced as an impurity with the sugar, experiments were carried out with purified sucrose and dextrose, but the small crop obtained was proved to be due to the small amount of bios carried into the medium by the yeast used as seed. J. S. CARTER.

Influence of electrolytes on the electrophoretic migration of bacteria and of yeast cells. C.-E. A. WINSLOW and E. H. FLEESON (J. Gen. Physiol., 1926, **8**, 195—214).—The effect of electrolytes on electrophoretic charge in silica dust, bacteria, or yeast-cells varies only quantitatively. Low concentrations of electrolytes appear to increase the charge, especially in the case of yeast-cells; higher concentrations cause a decrease in charge, leading, sometimes, even to complete reversal with migration towards the cathode —an effect apparently due to the cation alone, and increasing with the valency of the cation. Sodium hydroxide behaves as an ordinary salt, and increased alkalinity does not further depress the charge already depressed by salts; increased acidity, however, owing to the special activity of the hydrogen ion (between that of bivalent and tervalent ions), does cause a further progressive decrease of charge. Certain electrolytes show individual peculiarities; thus potassium chloride is distinctly more effective than sodium chloride. The depressing effect of univalent and bivalent ions in moderately high concentrations is less with silica dust than with *Bacillus coli*, and greatest with yeast-cells. With aluminum chloride, however, silica dust shows the greatest effect. Very high concentrations of aluminium chloride ($>10^{-2}$ *M*) show a third effect, a decrease of the positive charge produced by lower concentrations. Organic substances—dextrose, glycerol, saponin—have no effect on electrophoretic migration velocity until the concentration reaches a point at which viscosity changes are involved. C. P. STEWART.

Behaviour of basic dyes to lipins. J. SCHUMACHER (Biochem. Z., 1925, **166**, 214—219).—The solubility of basic dyes of the rosaniline series in lipins has been investigated by determining the distribution of the dye between water and a 0·5% solution of lecithin in ether. The dyes most soluble in the ether layer are Victoria-blue, gentian-violet, rosaniline, and malachite-green. The solubility decreases in the order named. In the yeast-cell, previously freed of soluble acids by treatment with dilute mineral acid, combination occurs between the acidic part of the lipin and the basic dye. The solubility of rosaniline derivatives in lipins decreases with sulphonation and carboxylation. E. C. SMITH.

Acetic fermentation and the chemical processes carried out by acetic acid bacteria. C. NEUBERG and F. WINDISCH (Biochem. Z., 1926, **166**, 454—481).—The conversion of acetaldehyde into acetic acid by acetic acid bacteria is shown to be a process of dismutation, 2 mols. of aldehyde yielding 1 mol. each of ethyl alcohol and acetic acid, the alcohol being further attacked, and thus escaping detection. In the absence of air, the conversion of acetaldehyde into ethyl alcohol and acetic acid proceeds

almost quantitatively, and it is unnecessary to neutralise the acid as formed. The bacteria dismute also higher aldehydes, *e.g.*, *n*-butaldehyde and *iso*valeraldehyde. *Bacillus coli*, *B. lactis aerogenes*, and *B. propionicus* also dismute acetaldehyde. Acetic acid bacteria convert pyruvic and oxaloacetic acids quantitatively into ethyl alcohol and acetic acid, after decarboxylation. P. W. CLUTTERBUCK.

Mechanism of lactic acid formation by bacteria. II. C. NEUBERG and G. GORR (Biochem. Z., 1926, **166**, 482—487).—Lactic acid bacteria converted methylglyoxal quantitatively into lactic acid, and *Bacillus propionicus*, under the same conditions, gave a 90% yield. P. W. CLUTTERBUCK.

Fermentation of cellulose by thermophilic bacteria. J. A. VILJOEN, E. B. FRED, and W. H. PETERSON (J. Agric. Sci., 1926, **16**, 1—17).—A thermophilic organism has been isolated which destroys cellulose between 43° and 65°. The organism lives, but does not ferment at 38° and 72°. The spores can withstand a temperature of 115° for 35 min. The following carbohydrates, in addition to cellulose, are attacked by it: starch, raffinose, sucrose, maltose, lactose, mannose, galactose, dextrose, xylose, and arabinose. Organic nitrogen is necessary for the fermentation, and peptone is the best source. In a 1—5% suspension, from 70% to 95% of cellulose is destroyed, of which 50—55% is recovered as acetic acid, 5·25% as ethyl alcohol, and the rest as small quantities of butyric acid, carbon dioxide, hydrogen, and a fatty pigment soluble in ether. Fermentation begins 12—18 hrs. after inoculation, and in the absence of a supply of calcium carbonate is stopped by accumulation of acid. G. W. ROBINSON.

Tuberculin. Chemical composition of the active principle and the nature of the tuberculin reaction. E. R. LONG and F. B. SEIBERT (J. Amer. Med. Assoc., 1925, **85**, 650—652).—The active principle of tuberculin is non-dialysable, is not absorbed by animal charcoal, is destroyed by trypsin, is maximally but incompletely precipitated by acetic acid at p_H 4·0, and is completely precipitated by saturation with ammonium sulphate. The precipitate by ammonium sulphate can be separated into three protein fractions: (1) a water-soluble, heat-coagulable protein, (2) a non-coagulable, alkali-soluble, water-insoluble protein, and (3) a non-coagulable, water-soluble protein. Of these the first and third appear to be the most potent. The nature of the highly specific toxic action of this substance on the tissues of a tuberculous animal is not known. Preliminary experiments indicate that the tissues of the sensitised (tuberculous) animal do not act on tuberculin in such a manner as to render it toxic for normal animals, nor do they bind the active principle in appreciable quantity, so as to render a tuberculin preparation less toxic for another tuberculous animal.

CHEMICAL ABSTRACTS.

Assimilation of carbon dioxide. O. WARBURG (Biochem. Z., 1926, **166**, 386—406).—By investigation of the assimilation of carbon dioxide by *Chlorella* either under very faint or very strong irradiation, the effects of the photochemical and the Blackman reactions are separated. The specific photochemical action (ψ) for a given wave-length is greater the smaller the intensity, and with very low intensities the action (ψ_0) is proportional to the intensity. Measurement of ψ_0 in the red, yellow, green, and blue shows that ψ_0 is considerable in all regions, the percentage of irradiated energy obtained as chemical energy being, respectively, 59, 54, 44, 34%. The absorption coefficient, however, is largest in the blue, and no relationship appears to exist between the specific photochemical action and the degree of absorption. The amount of oxygen separated under the action of chlorophyll also decreases from the red to the blue. Both the photochemical and the Blackman reactions are powerfully inhibited by narcotics (*e.g.*, by $0{\cdot}5\times10^{-4}$ *M*-phenylurethane), but, whereas the photochemical reaction is not inhibited by hydrogen cyanide and sulphide, the Blackman reaction is inhibited. The percentage inhibitions with concentrations of sulphide of 10^{-6}, 10^{-5}, 10^{-4} *M* are 12, 72, 100%, respectively. Assuming that the Blackman reaction is the preliminary reaction, an attempt was made to decompose, with the development of oxygen, substances closely related to carbon dioxide by irradiation in presence of *Chlorella*. Oxygen was always obtained, but it originated from the nitrates in the medium. In the dark, the carbon of the cells reduces nitrate to ammonia and during irradiation, the complete reaction is as follows: $HNO_3+H_2O+2C=NH_3+2CO_2$ and $2CO_2=2C+O_2$. The reaction is completely inhibited by 0·0001*N*-hydrogen cyanide or sulphide, due to the inactivation of iron, which is supposed to assist the passage of oxygen from the nitrate to the carbon. The method was then used to test Willstätter's theory, according to which the photochemical reaction is the preliminary reaction. A given amount of *Chlorella* in a given time placed in *M*/300-hydrogen peroxide solution liberates about the same amount of oxygen as is obtained during irradiation in the Blackman reaction. For the latter reaction, the velocity between 0° and 30° is a linear function of the temperature, and the same is true of the formation of oxygen from peroxide by *Chlorella*. The Blackman reaction, also, is very sensitive to hydrogen cyanide, and, similarly, the percentage inhibitions of the peroxide reaction for concentrations of cyanide of $0{\cdot}5\times10^{-5}$, $1{\cdot}0\times10^{-4}$, $1{\cdot}0\times10^{-3}$ *M* are 32, 83, 93%, respectively. Both the Blackman and the peroxide reactions are very sensitive to narcotics (a variety of urethanes was used). The comparison favours Willstätter's theory. P. W. CLUTTERBUCK.

Biocatalysts concerned in carbohydrate metabolism. E. ABDERHALDEN (Z. physiol. Chem., 1926, **151**, 165—166).—Attention is directed to a misleading reference in a recent paper by Euler and Myrbäck (this vol., 205) to Abderhalden's work.

C. R. HARINGTON.

Application of enzyme laws to the oxidation of dextrose in healthy and diabetic animals. L. AMBARD, F. SCHMID, and M. ARNOVLYEVITCH (Presse méd., 1924, **32**, 721—723; from Chem. Zentr., 1925, II, 1291—1292).—It is suggested that the oxidation of dextrose is an enzymic process with insulin as co-enzyme. In normal animals, the oxid-

ation of carbohydrates accounts for 50% of the carbon dioxide produced. Intravenous injection of dextrose causes an increase of 48—66%. In diabetic animals, a dose of insulin insufficient to alter the blood-sugar level increases the output of carbon dioxide. Hyperglycæmia decreases the secretion of insulin. G. W. ROBINSON.

Effect of a protein-free acid–alcohol extract of the parathyroid glands on the calcium content of the blood and the electrical irritability of the nerves of parathyroidectomised and normal animals. L. BERMAN (Amer. J. Physiol., 1926, **75**, 358—365).—The extract raised the calcium content of the blood of normal dogs and of those in tetany and decreased the electrical excitability of the nerves. The latter effect seems to be dependent on the former (cf. Collip, A., 1925, i, 1017). R. K. CANNAN.

Placental hormone. E. GLIMM and F. WADEHN (Biochem. Z., 1925, **166**, 155—156).—By repeated fractional precipitation with lead acetate from alkaline solution of the placental extract obtained by Fränkel and Herrmann's method (A., 1923, i, 1257), a preparation has been obtained of which 10 mg. cause considerable hyperæmia of the rabbit's uterus in 4 days. E. C. SMITH.

Accessory growth factors. H. VON EULER and S. STEFFENBURG (Z. physiol. Chem., 1925, **149**, 195—202).—Bone marrow (calf) and blood (rat) both contain more of a fat-soluble growth factor and an anti-rachitic vitamin than the majority of other organs and body fluids. This suggests that the fat-soluble factor is intimately concerned in the life-history of the blood corpuscles. The parathyroid also contains both a growth-promoting and an antirachitic factor. Exposure to ultra-violet light promotes growth; for a given light source there is an optimum exposure period for maximal growth. If this period is exceeded, the rate of growth receives a definite check. H. D. KAY.

Vitamin-*B* and metabolism. R. H. A. PLIMMER and J. L. ROSEDALE (J. State Med., 1926, **34**, 117—121).—A balance must be maintained in the amount of vitamin-*B* in a diet and the amounts of fat, protein, and carbohydrate. Shortage of vitamin-*B* may lead to gastro-intestinal disturbance. H. J. CHANNON.

Metabolism in avitaminosis. A. BICKEL (Biochem. Z., 1926, **166**, 251—294).—During avitaminosis in dogs, the body-weight progressively decreases to about 48% in spite of the complete absorption of a mixed diet which is sufficient calorimetrically, body-fat almost completely disappearing. The difficultly oxidisable carbon, nitrogen, and the C : N ratio of the urine increase, the increase in carbon being probably due to the passage of fat into the urine. Towards the end, the ratio again diminishes. The slightly increased excretion of lactic acid is insufficient to explain the increased quotient. During avitaminosis, the total ash of the urine, and especially its phosphorus and calcium content, increases. Injection of insulin into dogs during avitaminosis decreases the excretion of difficultly oxidisable carbon. Calcium and phosphorus ions are essential to the action of insulin. P. W. CLUTTERBUCK.

Elasticity of cell membranes [of plants]. T. A. KRASNOSSELSKI-MAXIMOV (Ber. deut. bot. Ges., 1925, **43**, 527—537).—Direct measurements are recorded of the extent of contraction of the cell membranes of certain plant-tissues on plasmolysis. Cells were measured in a turgid condition in water, and afterwards in a hypertonic solution (usually 0·25—1·6*N*-potassium nitrate), so as to obtain complete plasmolysis and the greatest possible change in size. The palisade- and spongy-parenchyma cells of the leaves of typical sun-loving plants, such as the sunflower, showed a marked contraction on plasmolysis, whereas the same tissues of a shade-loving plant (*Impatiens parviflora*) showed a scarcely measurable contraction. The elasticity of the cell membranes is very much greater in the former than in the latter plant; and this difference explains earlier observations that sun-loving plants may lose 20—30% of their water content before loss of turgor of the cells induces wilting, whereas shade-loving plants may wilt before a measurable loss of water has taken place. C. T. GIMINGHAM.

Action of neutral salts on the penetration of plant plasma by hydrogen and hydroxyl ions. J. PORT (Biochem. Z., 1925, **166**, 105—115).—Salts to which the cell-wall is readily permeable assist the penetration into the plasma of hydrogen ions, and *vice versa*. The effect is brought about by the more rapid denaturation of the plasma proteins in acid+salt solution than in salt or acid solution alone. Salts increasing the rate of penetration of hydrogen ions are ammonium thiocyanate, nitrate, and chloride, sodium and potassium thiocyanates, and, in solutions of greater acidity than p_H 3·2, potassium acetate. Barium salts, and ammonium sulphate and calcium nitrate, which penetrate slowly, at first inhibit, and then accelerate penetration of hydrogen ions. Of the alkali salts not mentioned above, the inhibitory action increases in the order of anions: NO_3', Cl', (Br', I'), SO_4''; of cations: ($K^{\cdot}$, $Na^{\cdot}$), $Li^{\cdot}$, $Rb^{\cdot}$, $Cs^{\cdot}$. The salts of the alkaline earths, which themselves penetrate cells with difficulty, are strongly inhibitory. E. C. SMITH.

Diffusion of ions from living plant-tissues in relation to protein isoelectric points. W. H. PEARSALL and J. EWING (New Phyt., 1924, **23**, 193—206).—The rapid outward diffusion of chloride ions occurs when plant-tissue is brought to a hydrogen-ion concentration equal to or greater than that at which its chief protein (potato, carrot) or protoplasm (*Nitella*) is isoelectric. The method may be used to determine the isoelectric point of the protoplasm in tissues from which extraction of protein is difficult. In this manner, the isoelectric point of protoplasm of the beet was determined to be at or below p_H 4·3. CHEMICAL ABSTRACTS.

Swelling processes in hygroscopic movements. S. RYWOSCH (Biochem. Z., 1925, **166**, 24—46).—Observations on the curling of seed-pods and vegetable fibres in water and under varying conditions of humidity show that flexion depends, not only on the

difference between the rates of imbibition or desiccation of the hygroscopic organs on each side of the tissue, but also on the degree of swelling of the tissue as a whole. The rate of imbibition is dependent on the permeability of the epidermal layer and the humidity of the atmosphere, and the degree of flexion is also influenced by the pressure to which the layer of cells on the concave side of the tissue is subjected by the swelling of the cell-layer on the convex side.

E. C. SMITH.

Micro-determination of blood-sugar by Hagedorn and Jensen's method. E. KAUFMANN (Biochem. Z., 1925, **166**, 207—209).—A convenient form of pipette is described, and slight improvements in technique are suggested. E. C. SMITH.

Determination of lactic acid. Micro-determination in the blood. J. FREJKA and K. VŠETEČKA (Publ. Fac. Sci. Univ. Masaryk, 1925, **60**, 1—27).—The known methods for determination of lactic acid have been examined in an endeavour to elaborate a micro-method, and the following procedure has been found to give results within 96—101% for quantities of the order of 1 mg. present in 10 c.c. of blood. The blood is diluted with 10 c.c. of water and treated with freshly-prepared mercuric nitrate. The precipitate is removed, the excess of mercury precipitated, the liquid neutralised, again filtered, evaporated down, and treated with 1·5 c.c. of phosphoric acid and saturated with sodium sulphate; after admixture with sand, the lactic acid is removed with ether, the extract evaporated with ammonia, the residue dissolved in water, and excess of ammonia removed by distillation; the lactic acid in solution is determined by Bellet's method (A., 1913, ii, 636), using a modified apparatus. The polarimetric method gave 99—100% for urine, 91—94% for liver extract; this method is not generally suitable for physiological liquids. Meissner's method (A., 1915, ii, 187) gave high results. The colorimetric method of Polonovski gave 90—97% accuracy, and is recommended for rapid, approximate results. The degrees of accuracy obtained with other methods have been determined.

S. I. LEVY.

Determination of minute amounts of urea. J. T. WEARN and A. N. RICHARDS (J. Biol. Chem., 1925, **66**, 275—280).—The solution containing urea is heated at 150° in an autoclave with 10% hydrochloric acid for 1 hr. and the resulting ammonia determined colorimetrically with Nessler's reagent, using the apparatus of Dale and Evans (A., 1921, i, 142). Amounts of nitrogen of the order of 0·0005 mg. can be determined with a maximum error of ±8·5%.

C. R. HARINGTON.

Modifications of Folin's method for urea determination. J. ELLINGHAUS (Z. physiol. Chem., 1925, **150**, 211—214).—Methods are described for the determination of (*a*) ammonia, (*b*) urea, using permutite instead of aëration to separate the ammonia from the urine. The permutite is washed twice with water by decantation, and the ammonia liberated from it by the addition of sodium hydroxide. The resulting fluid is directly nesslerised. H. D. KAY.

Micro-determination of nitrogen. A. KULTJUGIN and E. GUBAREV (Biochem. Z., 1925, **164**, 437—441).—Acél's original method (A., 1922, ii, 225) is criticised on the ground that loss of nitrogen occurs either through insufficient combustion, or by overheating and volatilisation of ammonia. By the use of hydrogen peroxide, combustion is more rapid and complete, the results are more accurate, and ordinary glass may be used. 0·03 Mg. of urea, alanine, and asparagine are determined with an error of ±4%. E. C. SMITH.

Determination of dextrose, particularly in urine. L. ROSENTHALER (Arch. Pharm., 1925, **262**, 518—520; cf. B., 1925, 732).—Causse's method (J. Pharm. Chim., 1896, [vi], **3**, 433), in which an alkaline copper solution containing ferrocyanide is used, has been modified by Burmann and others (cf., *e.g.*, Schweiz. Apoth.-Ztg., 1917, **55**, 196) so that it can be applied to urine, but the end-point of the titration is not well defined. The difficulties can be overcome by using decolorised phenolphthalein solution, containing potassium cyanide, as an external indicator. Three solutions are required: (i) a standard solution of 5 g. of copper sulphate pentahydrate in 500 c.c. of water; (ii) a solution of 173 g. of Rochelle salt, 45 g. of sodium hydroxide, and 40 g. of potassium ferrocyanide in 500 c.c.; (iii) the indicator, prepared by dissolving 0·5 g. of phenolphthalein in 30 c.c. of ethyl alcohol, adding water until the mixture is opalescent, then 20 g. of sodium hydroxide followed by aluminium powder until the solution is decolorised; it is then made up to 150 c.c. and kept from contact with the air. For use, to each 10 g. 0·1 g. of potassium cyanide is added. The determination is carried out as follows: 10 c.c. of solution (i) and 10 c.c. of solution (ii) are mixed, diluted with 10 c.c. of water, and boiled. The dextrose solution is added until (beginning while the solution is still green) a drop gives a red colour on filter-paper moistened with the indicator (iii). The presence of urea, ammonium chloride, or uric acid in the dextrose solution is immaterial, but urine causes high results to be obtained. Nevertheless the method is applicable to the urine of diabetic patients. W. A. SILVESTER.

Determination of carbon in urine and dilute aqueous solutions. O. KAUFFMANN-COSLA and J. LEIBOVITZ (Biochem. Z., 1925, **163**, 230—232).—The determination is carried out by micro-combustion of 0·3—0·6 c.c. of the solution by the Liebig method. In this volume, 0·42% of carbon is determined with an error of ±5%. E. C. SMITH.

Determination of cystine by feeding experiments. H. C. SHERMAN and E. WOODS (J. Biol. Chem., 1925, **66**, 29—36).—Young rats were fed on a basal diet complete in every respect except for a deficiency of cystine. On adding cystine to the food of certain of these animals, a linear relationship could be observed, within certain limits, between the amount of cystine fed and the resultant additional gain in weight over that attained by the control animals. The experiments were repeated with the addition of caseinogen instead of pure cystine, the

results indicating that this protein contained 1·2—2·5% of cystine. C. R. HARINGTON.

Determination of total iodine in organs, blood, and urine. R. VON BODÓ (Biochem. Z., 1925, **161**, 401—405).—The material is fused with sodium hydroxide and a very small quantity of sodium nitrate in a nickel crucible. The mass is dissolved in water and, after filtering, the solution is carefully made slightly acid and boiled with chlorine water until excess of this is expelled. After cooling, potassium iodide and phosphoric acid are added and the iodine liberated is titrated with sodium thiosulphate. H. I. COOMBS.

Determination of phosphoric acid in small amounts of material. K. SAMSON (Biochem. Z., 1925, **164**, 288—294).—After precipitation of protein with trichloroacetic acid, inorganic phosphate is determined in the filtrate, and organic phosphate in the ashed precipitate, by the ammonium phosphomolybdate method. E. C. SMITH.

Detection of bismuth in organic material. P. W. DANCKWORTT and E. PFAU (Arch. Pharm., 1925, **263**, 502—506).—The organs are decomposed by soaking for 24 hrs. in nitric acid (*d* 1·44), the mixture being then evaporated on the water-bath, and eventually to dryness. The residue is redissolved in dilute nitric acid, cadmium sulphate is added, and hydrogen sulphide passed through the solution. The mixture of sulphides—the cadmium sulphide having taken down the bismuth sulphide, even if the latter is present in very small amount—is washed, redissolved in nitric acid, the solution is evaporated to dryness, and the residue again dissolved in nitric acid. This solution is tested with Aubry's quinine reagent (A., 1922, ii, 165) which is more stable when the quinine sulphate and the potassium iodide solutions are kept separate. One part of bismuth in 10,000 parts gives an orange precipitate, and a distinct turbidity is shown by 1 part in 1,000,000 parts. Of other metals that may be present, iron alone may interfere, and it can be detected by adding potassium ferrocyanide; the bismuth precipitate remains unchanged, and is recognisable under the microscope, particularly when a piece of blue glass is used as a support. W. A. SILVESTER.

Radiometric micro-analysis. R. EHRENBERG (Biochem. Z., 1925, **164**, 183—190).—Four methods are discussed whereby the radiometric method of Paneth and Hevesy may be adapted to the determination of the distribution of bismuth and lead in plants and animals. P. W. CLUTTERBUCK.

Toxicological investigation of mercury. KOHN-ABREST (Ann. Chim. analyt., 1925, [ii], 7, 353—355).—The finely divided organs (100—200 g.) are mixed with water, potassium chlorate and hydrochloric acid are added, and the mixture is carefully heated on a water-bath, any distillate being collected in a small amount of water. The residual fluid is filtered and washed with the distillate. Excess of chlorine is removed by sulphurous acid, and excess of the latter by boiling, after which hydrogen sulphide is passed into the liquid for 18 hrs. Half the precipitate is used for arsenic and antimony determinations, and half for mercury. In the case of mercury, the precipitate is treated with 5 c.c. of aqua regia, and the excess of acid evaporated in a vacuum in the cold. The dry residue is extracted with warm water, filtered, the filtrate made up to 20 c.c., 1 c.c. of hydrochloric acid is added, and a fine brass wire spiral put in to the solution, and left for 24 hrs. Mercury is deposited on the brass. After washing in water, alcohol, and ether, and drying, the wire is strongly heated in a test-tube, and the mercury collected in the cool part of the tube. On treating the mercury with iodine vapour, a crystalline ring forms. The mercuric iodide thus formed may be determined by dissolving it in 1 c.c. of a 1% solution of potassium iodide, and comparing the sulphide formed by treatment with hydrogen sulphide with standards. D. G. HEWER.

Electrolytic method of investigation of distribution of gold compounds in the organism. S. LOMHOLT (Compt. rend., 1925, **181**, 821—823).—Gold in tissues is determined by treatment with fuming nitric acid, evaporation to dryness, dissolving in aqua regia, making alkaline with ammonium hydroxide, addition of potassium cyanide, electrolysis, and weighing of the metal deposited. On injection of "sanocrysin" (sodium aurothiosulphate) into rabbits a considerable amount of gold is found in the kidney and large intestine; excretion of the gold by rabbits and man is slow and effected mainly by the kidneys. L. F. HEWITT.

[Pharmacological] determination of the ergotamine-ergotoxin titre of ergot. T. MASUDA (Biochem. Z., 1925, **163**, 27—35).—Two methods of evaluating ergot preparations by examining their inhibitory effect on adrenaline vasoconstriction in frogs are described. Considerable loss of activity of ergot infusions occurs on keeping for 8 days. E. C. SMITH.

Pharmacological determination of the ergotamine content of commercial ergot preparations. J. MAHN and M. REINERT (Biochem. Z., 1925, **163**, 36—40; cf. preceding abstract).—The therapeutic value of commercial ergot preparations cannot be judged solely on their ergotamine content, since other substances present (*e.g.*, histamine) have a considerable action on the uterus. E. C. SMITH.

Detection of bismuth in urine. D. GANASSINI (Boll. Chim. farm., 1926, **65**, 3—6).—The author criticises various suggested modifications of his method of detecting bismuth in urine (A., 1923, ii, 439). T. H. POPE.

Viscosimetric determination of amylase. W. C. DAVISON (Bull. Johns Hopkins Hosp., 1925, **37**, 281—282).—The method depends on a comparison of the viscosities of two similar Lintner starch solutions of suitable concentration, to one of which is added 0·1—0·4 c.c. of the amylase preparation, and to the other an equal amount of the boiled preparation. CHEMICAL ABSTRACTS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1926.

General, Physical, and Inorganic Chemistry.

Secondary spark spectrum of neon. L. Bloch, E. Bloch, and G. Déjardin (Compt. rend., 1926, **182**, 451—452).—A secondary spectrum of neon, situated entirely in the ultra-violet, has been obtained by the passage of an oscillating discharge through neon at various pressures in a silica tube without electrodes. The lines of greatest intensity are as follows: 2983·82, 2866·60, 2777·60, 2677·90, 2610·04, 2595·66, 2593·57, 2590·01 Å. F. G. Tryhorn.

Excitation of secondary spectrum of neon by electronic impact. G. Déjardin (Compt. rend., 1926, **182**, 452—454).—The excitation of the secondary spectrum of neon by electronic impact depends essentially on the intensity of the electron stream and the pressure of the gas. At pressures between 0·01 and 0·1 mm., an accelerating potential of 48—50 volts excites some lines in the secondary spectrum, notably the lines 3727·09, 3713·66, 3694·19, 3664·05, and 3334·89 Å. These lines are widened and reversed. At a slightly higher voltage (52—53), the lines 3574·65, 3568·47, 3232·38, and 3220·13 Å. appear. The complete spectrum is developed by a potential of 60 volts. When an especially intense stream of electrons is used, the secondary spectrum appears, at 1·6 mm. pressure, at a potential of 28—30 volts. The two excitation potentials of this secondary spectrum are taken as 28 and 49 volts, respectively, giving by difference the value 21 volts as the ionisation potential of neon. The ratio of these potentials for neon (2·28) agrees with that of the corresponding excitation potentials of the other inert gases. It is suggested that the two potentials correspond with the potentials of ionisation of the univalent ion, and of the double ionisation of the neutral atom. F. G. Tryhorn.

Infra-red spectrum of the calcium arc in a vacuum. O. Sandvik and B. J. Spence (Astrophys. J., 1925, **62**, 265—269).—The wave-lengths of 30 lines, 17 of which are new, in the range 8500—20,000 Å. have been measured and tabulated with their intensities. Other lines were also observed, but were too weak to permit of wave-length determinations. A. A. Eldridge.

X-Ray spectra of the lower elements. R. Thorœus (Phil. Mag., 1926, [vii], **1**, 312—321).—An extension of previous work by Siegbahn and Thorœus (Arkiv Mat. Astr. Fys., 1924, **18**, No. 24; 1925, **19A**, No. 12) on extending the range of wave-lengths within the K and L series. The X-ray tube has been modified to screen the anticathode surface from deposits of metal from the filament. Crystals of palmitic and lauric acids have been employed as reflecting crystals for the longer wave-lengths. Measurements of the lines Ll, $L\eta$, and $L\beta$, and the doublet $L\alpha_1\alpha_2$ have been made for the elements rubidium, bromine, selenium, arsenic, zinc, copper, nickel, cobalt, iron, manganese, and chromium, and of the doublet $K\alpha_1\alpha_2$ for fluorine. The wave-lengths given are based on that of the $K\alpha$ line of sodium. A. E. Mitchell.

Fundamental level of the iron atom. N. K. Sur (Nature, 1926, **117**, 380).—A criticism of Laporte's statement (A., 1924, ii, 364; this vol., 215) that astrophysical data and the almost complete classification of the lines of iron support the view that the chief lines proceed from five fundamental levels, constituting a quintuplet d-group. A. A. Eldridge.

Polarised emission of mercury lines. H. W. B. Skinner (Nature, 1926, **117**, 418).—The mercury spectrum has been excited by a directed stream of electrons from an oxide-coated filament, and the polarisation of the lines examined. The results appear consistent with the view that the polarisation occurs in the case of combinations of the p or P levels with the D_1, d_2, and d_3 levels. Visual investigation is possible with the lines 5770 and 5791 Å. The degree of polarisation decreases with increase in the speed of the electrons, and the effect is believed to be caused by the directed character of the electron stream. The polarisation of the yellow lines is reduced to zero by a magnetic field of about 20 gauss at right angles to the stream and in the direction of observation. The results may be interpreted theoretically. A. A. Eldridge.

Intensity distribution in the fine structure (satellites) of the mercury triplets $2p_1$–$2s$. J. L. Snoek, jun. (Z. Physik, 1926, **35**, 883—887).—The best results were obtained by using a narrow capillary Geissler tube, ordinary mercury vapour lamps producing self-reversal of the strong lines. The ratio of intensities of the satellites was found to be quite independent of the strength of the current. E. B. Ludlam.

Quantum theory of the doublet spectra and their anomalous Zeeman effects. J. Kudar (Z. Physik, 1926, **35**, 888—893).—Theoretical. The

magnetic interaction of the radiating electron and the core and the relativity energy of the electron are discussed. E. B. LUDLAM.

Stark effect for H_β and He 4686 Å. J. S. FOSTER (Astrophys. J., 1925, **62**, 229—237).—The results of fine analysis of the components of H_β, measured in fields up to 47 kilovolts/cm., indicated that spurious components are sometimes obtained which may be ascribed to confusion of the source, the applied field not possessing the same direction for all atoms, leading to incomplete separation of the p and s components. It is suggested that Stark's results (Ann. Physik, 1915, [iv], **48**, 193) may be explained by similar effects. Three fine-analysis components of the ionised helium line 4686 Å. have separations of 0·39 and 0·37 Å. at the maximum field (46 kilovolts/cm.), the theoretical value being 0·33 Å. A. A. ELDRIDGE.

X-Ray spectroscopy of the Compton effect and of the Clark-Duane pseudo-lines. H. SEEMAN (Z. Physik, 1926, **35**, 732—742).—The difficulty of obtaining the secondary spectrum sufficiently free from the primary spectrum is discussed and a method suggested. The relative intensities of the Compton and the primary radiation will be dependent on the distances of the crystal and the source of scattered radiation from the anticathode. Resonance reflexion excited in the crystal cannot be detected, as it would be concealed by the greater effect of reflexion from the crystal layers. E. B. LUDLAM.

Polarisation of X-rays by reflexion from crystals. H. MARK and L. SZILARD (Z. Physik, 1926, **35**, 743—747).—When X-rays falling on a crystal are reflected at 90°, as in Bragg's method, the radiation is completely polarised. If the incident rays are polarised, then there is no reflexion at all when the plane of the reflected rays would lie in the plane of vibration of the incident rays. In this manner, a crystal can act as a polariser and an analyser. Simultaneously there is spectral dispersion. Using iron as the scatterer, it was found that the fluorescent radiation at an angle of 90° to the incident rays was not polarised, in contrast to the reflected rays. E. B. LUDLAM.

Fluorescent screen for use with X-rays. R. JAHODA and L. LILIENFELD.—See B., 1926, 220.

Electric discharge in gases and the accompanying radiations. A. DAUVILLIER (Compt. rend., 1926, **182**, 575—577; cf. A., 1925, ii, 1116).—Previous work led to the prediction of variations in gaseous density in different parts of the discharge. A narrow transverse beam of soft X-rays has been used to explore the different regions by means of variations in opacity which accompany localised variations in pressure. At the cathodic edge of the negative glow a thin region (less than 0·5 mm.) is invariably observed to contain a considerably increased number of positive ions. A similar but less marked effect is found at the sharp cathodic edge of the positive glow. No region of rarefaction was observed. The radiation generally proceeds from the visible glows except in the Crookes dark space. Schumann rays varying in intensity with current strength originate in the positive glow. The radiation from the negative glow depends on the pressure if the voltage is maintained constant. At pressures of the order of 1 mm. Schumann rays are emitted; at 1/10 mm. intense, characteristic, relatively short wave X-rays (*e.g.*, the L-series of argon) appear. The radiation from the Crookes space is very soft in front of the cathode, becoming more and more penetrating as the edge of the negative glow is approached, until it undergoes a sudden discontinuous increase. It is thus entirely due to cathodic electrons. The soft X-rays consist almost entirely of characteristic radiations, depending on the nature of the anticathode. The intensity–voltage curves exhibit discontinuities in accordance with accepted diagrams of levels. R. A. MORTON.

So-called positive photo-electric emission (inverse effect), and the reality of the sub-electron. E. J. LORENZ (Phil. Mag., 1926, [vii], **1**, 499—509).—The work of Hake (Z. Physik, 1923, **15**, 110) and of Wasser (A., 1925, ii, 80) on the inverse photo-electric effect has been repeated with drops of oil, glycerol, and mercury in different gases. It is shown that the inverse effect reported by Hake and Wasser as indicating a discharge of positive electricity has no real existence, but is a spurious effect produced by stray or scattered ultra-violet light striking the condenser plates and liberating photo-electrons which are caught by the drops in the electron apparatus. Work with mercury drops has shown that the smallest charge taken up by any drop is $4{\cdot}77 \times 10^{-10}$ e.s.u., and that this is independent of both the size of the drops and the method of charging. The results are in agreement with those of Wasser in that only those mercury drops which do not satisfy Millikan's $e_1^{2/3}-1/pa$ relationship yield values of less than $4{\cdot}77\times10^{-10}$ e.s.u. for the electronic charge. Such drops are not solid spheres of mercury. For pure mercury drops, the correction constant A, in Stokes' law, is 0·695. A. E. MITCHELL.

Photo-electric fatigue. A. PREDVODITELEV and A. WITT (Z. Physik, 1926, **35**, 783—791).—The photo-electric fatigue is attributed to the adsorption of a layer of gas on the surface of the metal. The rate of adsorption is given by the formula $dc/dt = q(C_\infty - C)^2$, where C is the amount adsorbed, C_∞ the adsorption capacity, and q the adsorption coefficient, which was not affected by the treatment to which the metal had been subjected. E. B. LUDLAM.

Principles of the thermionic effect. N. VON RASCHEVSKY (Z. Physik, 1926, **35**, 905—919).—The hypotheses underlying the various methods of deducing the formulæ for thermionic emission are considered. E. B. LUDLAM.

Estimation of the duration of the emission of light by hydrogen positive rays from their behaviour on passing out of an electric field into free space. B. M. BLOCH (Z. Physik, 1926, **35**, 894—904).—Photographs are obtained of the light emitted as the hydrogen passes out of the electric field, and from the length of the part which shows

broadening due to Stark effect it is concluded that the duration of emission is at most 10^{-10} sec.

E. B. LUDLAM.

Excitation of the *O*-energy levels in tungsten by electron bombardment. O. STUHLMAN, jun. (J. Elisha Mitchell Sci. Soc., 1925, **41**, 20).—Measurements of the number of secondary electrons emitted from a tungsten grid on which accelerated thermo-electrons from a tungsten filament are allowed to impinge lead to the following values of n/R for *O*-energy levels: O_2—O_1 0·608; O_4—O_3 2·96; O_5 5·20.

CHEMICAL ABSTRACTS.

Excitation of spectrum lines by collisions of electrons. G. HERTZ (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 767—774).—Experiments have been made on the excitation of spectral lines of mercury, helium, neon, zinc, and thallium by impact of accelerated electrons, under conditions which minimise errors due to potential differences between different points of the source of the electrons, disturbances through space charges in the observation region as a result of the use of high current densities, and the tendency of the electron discharge to change into an arc discharge. With mercury vapour at 0·03 mm. pressure, only lines with an excitation potential less than 8·0 volts appear when the potential accelerating the electrons is 8·7 volts. When the latter is raised to 9·7 volts, a strong line at 3650 Å. (excitation potential 8·8 volts) appears, which is entirely lacking at the lower potential. With helium at 0·8 mm. pressure, at small current densities the individual lines may be made to appear successively in the order of their excitation potentials. The same effect was shown with neon between pressures of 0·5 and 1·0 mm., development of the red lines, between potentials of 18·9 and 20·0 volts, being especially striking. The calculated value of the excitation potential of the yellow neon line at 5852 Å. is 0·4 volt higher than that of the lines at 6143, 6402, and 6506 Å., and although the former line is absent at the lowest tension required to excite the latter lines, yet when its appearance is brought about by an increase of some tenths of a volt in the accelerating potential, its intensity exceeds that of the other lines. With zinc, a spectrum consisting only of the triplet 5680, 4722, and 4811 Å. was obtained by a suitable potential, an increase of 1 volt being necessary to produce the strong red line at 6362 Å. The excitation potential of the green thallium line was determined as 3·5 volts, confirming the $2p_2$ state as the normal condition in thallium. F. G. TRYHORN.

Motion of an electron in the field of a solid centre with regard to change of mass by radiation. M. BRONSTEIN (Z. Physik, 1926, **35**, 863—882).—Theoretical. The electron moves in an ellipse of which the perihelion is displaced a little after each revolution, but in the opposite direction from the Sommerfeld displacement.

E. B. LUDLAM.

Investigation into the theory of the "three point gap." C. E. WYNN-WILLIAMS (Phil. Mag., 1926, [vii], **1**, 353—378).—From experiments with various forms of three-point gaps, it is suggested that the three-point effect is caused by the ionisation of the gas in the main gap by a radiation of wave-length limits between 1000 and 13 Å. emitted by the pilot discharge. Disturbances of the field, passage of ions into the gap, or photo-electric effects produced by the radiation or by ultra-violet light possibly assist, but are not essential for, the production of the three-point effect. A. E. MITCHELL.

Body of high electron and light emission. C. A. LAISE.—See B., 1926, 198.

Constancy of atomic weights. H. V. A. BRISCOE and P. L. ROBINSON (Nature, 1926, **117**, 377—378).—The atomic weight of silicon derived from measurements of the densities of samples of silicon tetrachloride of different origin show a maximum variation of 1 in 6000, the extreme values being 28·058 and 28·063. Although the results do not afford conclusive proof of the invariability of the atomic weight of silicon, they confirm those of Jäger and Dijkstra (A., 1925, ii, 83), which, on re-computation, show a difference of 1 in 1477.

A. A. ELDRIDGE.

Direct determination of the relative proportions of the isotopes of lithium. M. MORAND (Compt. rend., 1926, **182**, 460—462).—By measuring the current carried by the positive rays of the isotopes of lithium, the relative proportions of Li^6 and Li^7 were found to be 1 : 14 or 1 : 15, corresponding with an atomic weight of 6·93—6·94 for ordinary lithium. The current corresponding with the rays of Li^7 in these conditions was a few microamperes. When this current was increased, the proportion of Li^6 appeared to become greater, the ratio Li^6 : Li^7 rising to 1 : 2 or 1 : 3. This is attributed to a broadening of the line due to Li^7 and its encroachment on the electrode collecting the current carried by the rays of Li^6. When correction was made for the dispersion of the Li^7 rays, the ratio 1 : 14 was found.

F. G. TRYHORN.

Extraction and determination of uranium-*X*. R. DE (J. Chim. phys., 1926, **23**, 197—204).—See this vol., 220.

Mesothorium-2. D. K. YOVANOVITCH (J. Chim. phys., 1926, **23**, 1—37).—A rapid method for the separation of mesothorium-2 from mixtures with salts of barium, mesothorium-1, radiothorium, thorium-*X*, radium, its active deposit, and the active deposit of thorium is described. The addition of traces of oxides of metals of the cerium group serves to entrain the mesothorium-2 which is obtained along with these metals in solution and is precipitated as oxalate. The purity of the product thus obtained was shown by the determination of its half-value period. Fractional precipitation of the rare-earth metals of the cerium group in the presence of mesothorium-2 causes an accumulation of the mesothorium-2 in the last fraction, *i.e.*, with the lanthanum. The magnetic spectrum of the β-particles from mesothorium-2 shows 43 lines of energies between 8×10^6 and $3{\cdot}89\times10^4$ volts. Of these, twelve have not been recorded previously. The origin of the high-speed β-particles is discussed and

it is suggested that the energy is transmitted to the electrons by high-frequency γ-rays originating in the disintegration of the nucleus. A. E. MITCHELL.

Chemical properties of mesothorium-2 and actinium. (MLLES.) E. GLEDITSCH and C. CHAMIE (Compt. rend., 1926, **182**, 380—381).—Mesothorium-2 and its isotope actinium resemble the cerium earths, and particularly lanthanum. Neutral solutions of rare earths (containing in some cases additions of magnesium or aluminium salts) were subjected to ordinary separations in the presence of mesothorium-2 in amounts equivalent to 5 mg. of radium. The resulting products were tested for radioactivity. Magnesium and aluminium precipitates were quite inactive. Potassium sulphate was added to a neutral solution of rare-earth sulphates until the absorption spectrum of neodymium was no longer visible; only 1·4% of the mesothorium-2 then remained in solution. When the cerium earths were oxidised by means of potassium permanganate and potassium carbonate, the precipitate of hydrated ceric oxide was inactive. Repetition of the experiment in the presence of both radiothorium and mesothorium-2 resulted in a quantitative separation, the former element accompanying the cerium, the latter the lanthanum–neodymium fraction. Addition of bromine to an alkaline suspension of rare-earth hydroxides resulted in a neodymium–praseodymium-free solution containing lanthanum and 87·4% of the mesothorium-2. R. A. MORTON.

Photographic method of determining mobility of recoil atoms. G. H. BRIGGS (Proc. Camb. Phil. Soc., 1926, **23**, 73—77).—The experiments are of a preliminary character. A current of air was allowed to travel across a line of mesothorium bromide above which was placed a charged plate. A record of the points at which the recoil atoms from the mesothorium reached the plate was obtained by placing the latter face downwards on a photographic plate. Comparison of the blackened bands produced with and without an air current indicates a spreading of the deflected band corresponding with an average range of mobilities between 1·84 and 1·24 cm./sec. per volt/cm., with a peak value of 1·59. No peak corresponding with a mobility of 4·35, as found by Erikson (this vol., 4), was observed. A comparison of the experimental conditions appears to indicate that recoil atoms of so high a mobility can only exist in a strong electric field, or in the absence of a high degree of ionisation in the exposure apparatus.

M. S. BURR.

Highly emanating radium preparations. O. HAHN and J. HEIDENHAIN (Ber., 1926, **59**, [*B*], 284—294).—Attempts are described to obtain radium preparations which, in the air-dried condition, evolve emanation and thus are characterised by high emanating power. Direct attempts to obtain radium salts in a form exposing large surfaces are only partly successful, for although radium sulphate can readily be prepared in the colloidal state and is then highly emanating, it very easily passes into the crystalline condition, with consequent loss of emanating power. Better results are obtained by depositing the radium salt on a disperse carrier. For this purpose, solutions of lanthanum salts containing radium–barium compounds are precipitated with hydrofluoric acid, whereby the radium passes quantitatively into the precipitate. The products are hard, friable masses in the air-dried condition and exhibit high emanating power. After 3 months, the mean value is 68—69%, but the products age distinctly, so that after 6 months the mean value is 59—60%, and after 12 months 56%. For the production of high emanating power, it is necessary that the weight of lanthanum should be great in comparison with that of radium, since the coalition of radium barium fluoride to larger crystals is thereby impeded; the emanating power diminishes continuously as the proportion of barium in the product increases. The preparations suffer from the disadvantage that the emanating power is insufficiently high for practical purpose, and, further, that the regeneration of radium from the aged specimens is tedious. More satisfactory results are obtained with iron hydroxide as carrier. If ferric chloride solution containing radium sulphate is precipitated by a slight excess of ammonia at the atmospheric temperature, the radium passes quantitatively into the precipitate, the emanating power of which is 98—99%; the preparations age much less rapidly than when lanthanum fluoride is used. Radium may be precipitated as carbonate instead of as sulphate. Preparations containing higher proportions of radium appear to age less rapidly than those containing a lower proportion, but this observation may be due to insufficient washing of the latter. Rejuvenation of an aged specimen is effected simply by dissolving in dilute hydrochloric acid, followed by precipitation with ammonia containing ammonium carbonate. The preparations are conveniently preserved in air containing 70—90% of moisture. If the specimens become dry, their emanating power may be restored by exposure to moist air. The use of the preparations in the preparation of concentrated radon, of radium-*D*, and polonium is described, together with the appropriate apparatus.

The emanating power is determined by enclosing the preparation in a capacious U-tube and, after a definite interval, transferring the emanation to an emanation-electroscope. The total emanation is determined by dissolving the specimen and preservation of the solution in a closed vessel for a definite period, followed by transference to the electroscope. The method has the advantage of requiring only minimal amounts of radium. Alternatively, the specimen is enclosed in a weighing bottle and the γ-ray activity of the active precipitate is measured immediately and after a definite interval.

H. WREN.

Retardation of β-particles. J. D'ESPINE (Compt. rend., 1926, **182**, 458—460; cf. A., 1925, ii, 622).—An investigation of the retardation of β-particles from thorium-*B*, radium-*B*, and radium-*C*, by screens of copper, aluminium, silver, and gold, indicates that the retardation is independent of the nature of the screen, but depends, up to 20 mg./cm.^{2}, on its mass per cm.^{2}

F. G. TRYHORN.

γ-Ray spectrography. Secondary β-spectra and crystalline diffraction. J. THIBAUD (Ann. Physique, 1926, [x], **5**, 73—152).—The characteristic γ-ray spectra of radium and thorium have been examined by the method previously described (A., 1924, ii, 515; 1925, ii, 10). Einstein's numerical relation between the energy of a γ-ray and that of the corpuscle which it excites is completely verified, the effect of any "recoil" accompanying the expulsion of an electron being shown to be negligible. It appears to be generally true that the natural β-ray spectra of all elements which, on disintegration, emit γ-rays at the same time as β-rays is a secondary photo-electric effect of the γ-radiation. Further experiments on the diffraction of γ-rays by crystals (A., 1925, ii, 176) give results for the wave-length and energy which are in good agreement with those obtained by the first method, if the variation of mass with velocity according to the Lorentz–Einstein expression be taken into account. No evidence of the existence of the *J*-electron level of Barkla has been obtained. R. CUTHILL.

Moment of momentum of the electrons of rotating molecules. H. LESSHEIM (Z. Physik, 1926, **35**, 831—849).—The behaviour of rotating molecules in an electric field is considered, in particular, the deflexion of a molecule in a non-homogeneous field. An attempt is made to account for the low specific heat of rotation of hydrogen, but none of the nine curves obtained is satisfactory.

E. B. LUDLAM.

Law of inertia for radiating masses. [SIR] J. LARMOR (Nature, 1926, **117**, 300).

Conservation of momentum and the Döppler principle. G. E. M. JAUNCEY (Nature, 1926, **117**, 343—344).—The relation between mass and energy based on the relativity theory is employed in the derivation of a formula for the Döppler principle, which is thus apparently deduced without recourse to a wave theory. For light of about 4000 Å. emitted by the hydrogen atom, the change of mass on emission of a quantum $h\nu$ is computed as 5×10^{-33} g.

A. A. ELDRIDGE.

Quantised motion of a diatomic molecule in the Kramers model. E. HALLÉN (Z. Physik, 1926, **35**, 642—651).—The author shows that it is not justifiable to disregard all the motions of a diatomic molecule except rotation about a fixed axis. In certain circumstances, rotation of the plane through the angular momentum of the electron and the axis of the molecule about the latter may take place. The energy in this case associated with the quantum numbers is calculated and shows a more complicated course than in the simpler case considered by Kramers (*ibid.*, 1923, **13**, 343) and by Kramers and Pauli (A., 1923, ii, 445).

E. B. LUDLAM.

Coupling possibilities of the quantum vectors in the atom. S. GOUDSMIT and G. E. UHLENBECK (Z. Physik, 1926, **35**, 618—625).—The possibilities of coupling the two quantum vectors of the atomic ion and the two vectors of an electron are considered and illustrated by the case of terms of the spectra of the alkaline earths and of neon. E. B. LUDLAM.

Structure of iodine. H. COLLINS (Chem. News, 1926, **132**, 165—170).—Speculative.

Atomic dimensions. R. G. LUNNON (Proc. Physical Soc., 1926, **38**, 93—108).—The estimated diameters of the atoms of the elements obtained by different methods are compared. The data considered were obtained from atomic volumes, *X*-ray analysis, van der Waals' equation, compressibility, viscosity of liquids, solutions, and gases, diffusion of ions, latent heat of solution, scattering of *X*-rays, ionisation potentials, band spectra, chemical constants, optical rotation, molecular films, impacts of electrons on gases, density changes, m. p., Bohr's theory of the hydrogen atom, and Langevin's theory of diamagnetism, and an extensive bibliography is given. The results, which are fairly concordant, show that the addition of an inner electron shell gives an increase in diameter of about 0·5 Å. in all cases.

C. J. SMITHELLS.

Structure of the hydrogen molecule ion. H. C. UREY (Physical Rev., 1926, [ii], **27**, 216—237). —A fuller account of work already published (A., 1925, ii, 1105).

Production of some spectra of carbon, oxygen, and nitrogen in the presence of neon. W. H. B. CAMERON (Phil. Mag., 1926, [vii], **1**, 405—417).—In the presence of neon, the Swan bands of the carbon spectrum are developed more than the Ångström bands. This result is similar to those obtained by Merton and Pilley (A., 1925, ii, 737, 1024) with helium and by Johnson and Cameron (A., 1924, ii, 639) with argon. With a pressure of 25 mm. of neon, a system of comet-tail bands, similar to those obtained with helium, is developed. The carbon line spectrum persists faintly. Only the carbon arc line at 2478 Å. could be obtained. Some of the doublets of C_{II} were present. The negative carbon bands are developed as with helium. With small traces of carbon, a strong development of the CH band at 4315 Å. and associated heads and a moderate development of the OH bands was obtained. As with argon, tubes filled with high-pressure neon and containing a trace of sulphur showed Martin's CS bands when the amount of carbon was sufficiently small to show the CH bands. A new system of bands of greater intensity than those obtained with helium or argon, comprising thirteen heads extending from 2257·7 to 2582·2 Å., has been obtained. These are of the usual type degraded towards the red. In neon–oxygen mixtures at all pressures of neon, a condensed discharge revealed all the elementary lines of oxygen as well as the series spectrum. No trace of the green aurora line was obtained. With neon–nitrogen mixtures, results similar to those of Merton and Pilley for helium–nitrogen mixtures were obtained. In addition, a number of lines, possibly belonging to the nitrogen arc spectrum, were found. The results are discussed in conjunction with those of Merton and Pilley and of Johnson and Cameron, and it is suggested that the inert gas used plays a part in the development of spectra requiring the ionisation

or complete disruption of a molecule by limiting the energy available for breaking down the molecule, by conserving the products of disruption, and by limiting the energy available for exciting these products. It is also suggested that the energy is imparted to the gas rather through the medium of excited atoms of the inert gas than by direct electron impact. A. E. MITCHELL.

Spectra of the neutral carbon monoxide molecule. R. C. JOHNSON (Nature, 1926, **117**, 376—377).—A quantum analysis is given of a new band spectrum associated with carbon, observed by Cameron between 2100 and 2160 Å. in the presence of neon; the system is represented by $\nu = K + (1728{\cdot}2n' - 14{\cdot}6n'^2) - (2151{\cdot}7n'' - 12{\cdot}7n''^2)$, where n' and n'' are initial and final quantum numbers, and K has the values 48534·3, 48496·5, 48478·2, 48461·0, and 48431·2. Comparison with the formula for Birge's fourth positive carbon bands shows that they have the same final electronic state, the normal state of the carbon monoxide molecule. Birge has shown that the final state of the Ångström band emitter coincides with the initial state of the fourth positive carbon emitter; an analogous coincidence exists between the final state of the third positive band emitter and the initial state of the emitter of Cameron's bands, but the weight of the available evidence is against identification of the initial energy levels of the third positive system and the Ångström bands. All four systems must be attributed to carbon monoxide, and it is doubtful whether any spectra can be attributed to a carbon dioxide molecule. Similarly, the silicon oxide and titanium oxide band spectra are probably due to SiO and TiO, and not to the dioxides. A. A. ELDRIDGE.

Structure of the negative oxygen bands. R. FRERICHS (Z. Physik, 1926, **35**, 683—688).—A special form of discharge tube was employed, the cathode consisting of a block of aluminium in which a channel was cut 2 mm. wide and the pressure so regulated that the whole of the discharge took place in the channel, producing an intense source of light. Five groups of bands, in the red, yellow, and green, were photographed in a grating spectrograph; the wave-lengths are given and characterised as Q branches. The photographs did not give satisfactory material for the fainter P and R branches. The negative oxygen bands possess no common term with the other oxygen band systems. E. B. LUDLAM.

Band spectra of aluminium. G. ERIKSSON and E. HULTHÉN (Z. Physik, 1926, **35**, 722).—Corrections in the data of their paper (this vol., 107). The moment of inertia of the hydride AlH should have been given as $4{\cdot}62 \times 10^{-40}$ g. cm.^{2} instead of $1{\cdot}54 \times 10^{-40}$. E. B. LUDLAM.

Absorption spectra of aluminium and cobalt. N. K. SUR and K. MAJUMDAR (Phil. Mag., 1926, [vii], **1**, 451—462).—The $2p_1 - 2s$ and $2p_2 - 2s$ lines of aluminium do not appear in absorption below 1520°. The higher members of the $2p - md$ are reversed at 1650°, whilst at 1725° the second pair of the series, $2p - ms$, also appear in absorption. In all the plates, the lines at 2874·24 and 2450·10 Å. of the $2p - md$ series of gallium and the line at 4172·06 Å. of the $2p - ms$ series of gallium were reversed. The absorption spectrum of cobalt has been examined between 4500 and 3000 Å. at 2000°. These lines have been classified according to the classification of Catalán and Bechert (A., 1925, ii, 611), and it is shown that many lines belonging to the three largest terms f^1, f^2, and F^1 are reversed. The line at 4190·709 Å. was reversed. This line belongs to the group suggested by Catalán and Bechert as being resonance lines, but is the only one of the group obtained in absorption. A. E. MITCHELL.

Water-spark absorption spectrum of iron. N. K. SUR (Phil. Mag., 1926, [vii], **1**, 433—450).—The absorption spectrum of iron has been obtained by spectroscopic analysis of the high-frequency spark produced between two iron electrodes immersed in water. The results are compared with the work of Laporte (A., 1924, ii, 364) on the classification of iron lines. All multiplets having the three highest groups of terms d^1, f^1, and occasionally F^1 as initial orbits are obtained in absorption. Some weak lines are also obtained in absorption and are shown to correspond with an increase of two in the azimuthal quantum number. This is not in accord with Sommerfeld's selection principle. This method of obtaining the absorption spectrum is as useful as the usual furnace method. It is suggested as probable that the iron spectrum should show a term higher than the d term. A. E. MITCHELL.

Extinction of the mercury resonance radiation in mercury vapour at high pressure. W. ORTHMANN and P. PRINGSHEIM (Z. Physik, 1926, **35**, 626—632).—A quartz tube was so arranged that one end of it which contained mercury could be heated to a desired temperature and the remainder of the tube kept at a different temperature. Thallium was contained in a side tube. Radiation with the mercury resonance line 2536·7 Å. produced the thallium fluorescence by collision with excited mercury atoms even when the pressure of the mercury was so high that the mercury fluorescence was itself extinguished. Even when the pressure of mercury was greater than one atmosphere, several of the thallium lines preserved their full intensity, although the pressure of thallium vapour was only about 0·01 mm. Consequently, the metastable mercury atoms must have retained their state of excitation after suffering 10,000 collisions. E. B. LUDLAM.

Intensity of the resonance radiation of mercury vapour. F. Goos and H. MEYER (Z. Physik, 1926, **35**, 803—811).—The resonance radiation from different depths in mercury vapour at various pressures was photographed and the intensities were measured in a Koch photometer. The curves showing relation of intensity to depth of layer do not show a simple exponential law. E. B. LUDLAM.

Quenching of resonance radiation and the breadth of absorption lines. R. W. DITCHBURN (Proc. Camb. Phil. Soc., 1926, **23**, 78—84).—Theoretical. Slater's theory of radiation (A., 1925, ii, 478) is discussed with reference to recent experimental work. M. S. BURR.

Absorption of ultra-violet light by organic compounds. L. MARCHLEWSKI and (MLLE.) A. NOWOTÓWNA (Bull. Soc. chim., 1926, [iv], **39**, 159—167).—See this vol., 222.

Rate of decay of fluorescence of solutions of dyes. E. GAVIOLA (Z. Physik, 1926, **35**, 748—756).—The extremely short interval of time is determined by utilising the Kerr effect; the values obtained ranged from 1·3 to $4·7\times10^{-9}$ sec., and are decidedly smaller than those obtained by previous workers.

E. B. LUDLAM.

Fluorescence of fluorescein in acid solutions. B. BATSCHA (Ber., 1926, **59**, [*B*], 311—315).—Addition of 0·1*N*-aqueous solutions of hydrochloric, hydrobromic, nitric, sulphuric, oxalic, tartaric, and citric acids to an alcoholic solution of fluorescein causes, in the case of the first four acids, a rapid increase of the intensity of fluorescence to a maximum; with oxalic acid, the increase is less rapid, whereas it is slowest with tartaric and citric acid. A relationship is thus established between fluorescence and hydrogen-ion concentration if it be assumed that the acids are dissociated in the alcoholic solution to the same relative extent as in water. Similar results are obtained in aqueous-alcoholic (4 : 1) solution, but the phenomena are more obscured. The same difference in the action of strong and weak acids is observed when their *N*-solutions are employed; hydrochloric and hydrobromic acids, however, exhibit an exceptional effect, since addition of them in quantity greater than that required to develop maximum fluorescence causes an unusually rapid decline of the effect. The luminescence phenomena of solid (cf. Batscha, A., 1925, ii, 181) and acid solutions of fluorescein is attributed to union of the substance by means of its free valencies with compounds forming hydrogen ions to unstable, complex molecules which absorb light during or after their formation and emit light during their decomposition. Luminescence depends mainly on concentration and temperature. The weakening of luminescence when the concentration of fluorescein or hydrogen ions is increased beyond that required for the maximum effect is ascribed to the more rapid formation and decomposition of the complexes, which involves the absorption and emission of smaller quantities of light. Increase of temperature causes a diminution in the fluorescence of fluorescein in acid solution. The transition from fluorescence to phosphorescence occurs naturally when the rate of reaction is sufficiently reduced; this is the case in the solid fluorescein solutions (*loc. cit.*), in which the molecules can only vibrate less rapidly than in liquid solution, so that it is possible for a greater quantity of light to be absorbed under otherwise identical conditions and for the subsequent emission to be spread over a longer period. H. WREN.

Relations between fluorescence and phosphorescence in solid and liquid media. S. J. VAVILOV and W. L. LEVSCHIN (Z. Physik, 1926, **35**, 920—936).—For intervals down to 10^{-6} sec. a spark and rotating mirror were employed; for longer intervals, 10^{-3} sec., a perforated rotating disc was used. Fluorescence and phosphorescence in solids appear to be different processes from those in viscous liquids. Uranium glass gives phosphorescence but no fluorescence; the light begins after the exciting light is cut off, and reaches a maximum. When the illumination is very intense, the absorption is less, as the excited molecules do not recover their unexcited state rapidly enough. A method of estimating the mean duration of the excited state is based on this conception. The spectra of the fluorescence and phosphorescence of rhodulin-orange-*N* in solid sugar are the same and the phosphorescence remains polarised for one or two seconds. E. B. LUDLAM.

Luminescence on heating the oxides of chromium, iron, zirconium, and titanium and magnesium pyrophosphate. L. WÖHLER (Kolloid-Z., 1926, **38**, 97—111).—Luminescence of chromium oxide is hindered by precipitation with ammonia from solutions containing sulphate and favoured by low concentration of the chromium solution. The atmosphere in which the luminescence occurs and the water content have no influence on the phenomenon. Iron oxide is strongly luminescent only if precipitated from boiling solution; if precipitated in the cold, it must be well washed with hot water. Zirconium oxide which contains impurities, such as filter fibres, does not show the phenomenon. Titanic acid is luminescent, whether precipitated from hot or cold solution, and "meta"-zirconic acid is also luminescent. The luminescence temperature is lowered with increasing quantity. For 0·8 g. of chromic oxide, the temperature in dry hydrogen is 530—550°, although in air or oxygen it begins at 425° on account of the exothermal decomposition of the chromic dioxide formed; for ferric oxide, the temperature is 538°; for 0·08 g. of zirconium dioxide it is 590°, for 0·25 g., 435°; for titanium dioxide about 500°; for magnesium pyrophosphate about 700°. The rise of temperature on luminescence depends on the previous treatment and experimental conditions, on the quantity and the specific heat. It may be as much as 50—100° for 0·1 g. of substance. The phenomenon occurs only with rapid rise of temperature, and with the substance in the anhydrous (or almost anhydrous) state. An analogy is traced between the luminescence phenomena of the oxides and their adsorption of organic acids. In the case of adsorption of methyl-violet by magnesium pyrophosphate, no difference is observed before and after luminescence. The hypothesis is advanced that the cause of the luminescence phenomenon is due to a type of surface fusion or sintering.

L. L. BIRCUMSHAW.

Calorimetric determination of surface luminescence. L. WÖHLER and M. RABINOWITSCH (Kolloid-Z., 1926, **38**, 111—114).—The thermal value of the luminescence of chromium oxide was determined in an ice calorimeter, using an electrical method of heating, and found to be about 8—11 cal./g., according as the oxide was precipitated from concentrated or dilute solution. The change to sintered oxide by luminescence is never quite complete. Measurements of the adsorption of *m*-nitrobenzoic acid showed that the oxide with the greatest heat development

also had the greatest adsorptive effect, indicating this to be a surface phenomenon. The sintered oxide showed only a very small adsorptive capacity. The values for the surface area calculated from the above data agreed in order of magnitude with the surfaces found for similar substances. L. L. BIRCUMSHAW.

Nature of active nitrogen. (LORD) RAYLEIGH (Nature, 1926, **117**, 381).

[Nature of active nitrogen.] E. J. B. WILLEY (Nature, 1926, **117**, 381).—The heat of formation of active nitrogen is about −43,000 cal./g.-mol., a result not reconcilable with the hypothesis that active nitrogen is atomic. Active nitrogen apparently represents a metastable molecule at a not very high energy level. A. A. ELDRIDGE.

Nature of active nitrogen. M. DUFFIEUX (Nature, 1926, **117**, 302—303).—It has already been shown that if the first positive group of nitrogen bands is ascribed to a diatomic molecule of mass 28, the second positive group (which predominates in the discharge on activation of nitrogen) and the negative group are due to the atom of mass 14 (cf. A., 1924, ii, 134, 711) rather than to a metastable diatomic molecule. In the conditions attending the emission of the two groups of bands, nitrogen atoms are present which are more likely to emit a band spectrum than none at all; the line spectrum universally attributed to the nitrogen atom is probably due to an ionised atom. The atomic view of the phenomenon is also supported by Angerer's results (A., 1921, ii, 257). A. A. ELDRIDGE.

Theory of the breakdown of liquid dielectrics. A. GYEMANT (Wiss. Veröff. Siemens-Konzern, 1925, **4**, 68—74).—See A., 1925, ii, 1028.

Molecular volume of water in crystalline hydrates. E. MOLES (Anal. Fís. Quím., 1925, **23**, 557—585).—A consideration of the molecular volume of water in crystalline hydrates confirms the existence of cationic and anionic hydrates. The molecular volume of water in cationic hydrates is, as a rule, 14·6, a value which coincides with that calculated for water at absolute zero. The corresponding value in anionic hydrates is 10·0, and is found also when water forms acids with anhydrides or hydroxides with oxides. In monohydrates, water is generally united with the anion. Hydrogen in acids behaves as a normal cation. These rules hold for sulphates, chlorides, nitrates, and nitrites, with the exception of rare-earth salts. It is confirmed that in the "vitriols" six of the water molecules belong to the cation and the seventh to the anion. There is a parallel relationship between thermal and volume data for hydrates. G. W. ROBINSON.

Influence of optical properties on the measurement of the thickness of tarnish films [on metals]. G. JUNG (Z. physikal. Chem., 1926, **119**, 111—122).—Apparent anomalies in the rate of increase of thickness of films (oxides, halides, etc.; cf. Tammann and Marais, A., 1924, ii, 485) on metals, as deduced from interference colours, can be explained as due to incorrect interpretation of the optical phenomena. The influence of the various factors to which the colours are due is discussed. L. F. GILBERT.

Optical studies on lactic acid and its anhydride. R. DIETZEL and R. KRUG (Arch. Pharm., 1926, **264**, 117—131).—See A., 1925, i, 1036.

Optical anisotropy of some simple inorganic gaseous compounds. K. R. RAMANATHAN and N. G. SRINIVASAN (Phil. Mag., 1926, [vii], **1**, 491—496).—The depolarisation of the light scattered by gaseous hydrogen chloride, hydrogen sulphide, and ammonia has been measured. In all cases, the depolarisation in a direction normal to the incident beam is 0·008. The results are discussed in connexion with the results of Rayleigh (A., 1920, ii, 574) on the anisotropy of argon and of Cabannes and Lepape (A., 1924, ii, 644) on xenon and krypton. It is suggested that the small degree of asymmetry of the molecules is due in hydrogen chloride and in hydrogen sulphide to the electrons belonging to the hydrogen atoms being transferred to the outermost orbits of the chlorine and sulphur atoms, respectively, and thus tending to the symmetrical argon configuration. In ammonia, it is considered that the electrons belonging to the three hydrogen atoms have transferred themselves to the nitrogen to complete the neon configuration. Visual measurements of the depolarisation with carbon monoxide give the same value as that calculated for nitrogen from similar measurements of Raman and Rao (Phil. Mag., 1923, [vi], **46**, 427) on air and oxygen, thus supporting the view that the configurations of the outer orbits of these are similar. A. E. MITCHELL.

Properties of chromatic emulsions. C. M. SOGANI (Phil. Mag., 1926, [vii], **1**, 321—333).—A practical and theoretical examination of the optical properties of homogeneous and non-homogeneous chromatic emulsions. Expressions have been deduced for the intensity of the transmitted light and the angular scattering, and are in accord with the experiments. A. E. MITCHELL.

Explanation in terms of atoms of the refractive data of organic compounds. K. FAJANS and C. A. KNORR (Ber., 1926, **59**, [*B*], 249—265).—On the basis of the Lewis–Langmuir theory of the distribution of electrons in the molecule, the molecular refraction of organic compounds is divided into linking and octet refraction. The relationships are particularly simple in the case of the saturated hydrocarbons. By reason of the equivalence of the four carbon valencies in methane, the eight valency electrons are regarded as uniformly distributed between the four C:H linkings (the dots indicate electrons, not bonds in the usual sense), so that one-fourth of the molecular refraction of methane represents the refraction of the simple C:H linking. The value for the C:C group is deduced by subtracting the value for six C:H linkings from the molecular refraction of ethane. Since all the valency electrons in these hydrocarbons are concerned in the union of the atoms, the division of molecular refraction among the electron groups is identical with the division into linking refractions (cf. Steiger, A., 1921, ii, 473). With substituted hydrocarbons, a different case

arises. In methyl chloride, for example, after subtracting the refraction for three C:H linkings from the molecular refraction of the compound, there remains a residue representing the refraction of the eight electrons of the chlorine atom, two of which are shared with the carbon atom, whereas the remaining six oscillate round the chlorine nucleus. The refraction of the chlorine octet united to carbon is deduced in the usual manner from the molecular refraction of propyl chloride, amyl chloride, and carbon tetrachloride, whereby a value constant to a first approximation is obtained. This value is lower than the refraction of the free chlorine ion and of the same order of magnitude as that of the chlorine octet united to hydrogen. Similar considerations are extended to a large number of groups. Relationships are established between the refraction values of an octet united to various groups which may be explained on the basis of the deformation theory. The deforming (stabilising) action of a hydrocarbon residue attached to a carbon, oxygen, nitrogen, sulphur, fluorine, or chlorine octet is greater than the corresponding action of a hydrogen nucleus, whereas the converse is the case with the large octet of bromine or iodine. The additivity of the molecular refraction of saturated aliphatic hydrocarbons when a single refraction equivalent is used for the carbon and hydrogen atom (or, as is preferable from a theoretical point of view, a single linking refractive value is used for the C:C and C:H linking) is explained by the assumption that the alteration of one of the four equivalent pairs of electrons of the carbon octet attached to four similar groups does not cause measurable refractive change in the remaining pairs. Previous failure to resolve the molecular refraction of alcohols and ethers or of the three types of aliphatic amines without the use of more than three equivalents for the atomic refraction is due to the fact that successive similar substitutions in the oxygen or nitrogen octet cause dissimilar changes of refraction and that these changes differ from those produced by similar substitutions in the carbon octet. The differing optical effect of successive similar substitutions in the oxygen or nitrogen octet is ascribed to the impossibility of grouping the electrons into four equivalent pairs (cf. Stoner, A., 1925, ii, 85).

H. WREN.

Influence of boric acid on the rotatory power of malic acid and tartaric acid. I. Boric-malic complexes. E. DARMOIS (J. Chim. phys., 1926, **23**, 130—156).—Examination of the optical rotatory power of mixtures of boric and malic acids has shown the existence of two series of complexes. One series is lævorotatory, corresponding probably with the acid $H_3BO_3,3C_4H_6O_5$ and gives well-crystallised *salts* of sodium, ammonium, and aniline of the form $H_3BO_3,3C_4H_5O_5M$. The other series, $4H_2B_4O_7,C_4H_4O_5M_2$, has not been isolated. The complexes are dextrorotatory and are stable only in dilute solutilons.

A. E. MITCHELL.

Rotatory power of camphor. R. LUCAS (Compt. rend., 1926, **182**, 378—379).—The rotatory power of camphor in formic acid solution is distinctly smaller than in benzene solution, whilst in concentrated nitric acid *d*-camphor shows feeble lævorotation. This inversion of optical activity is strongly marked in concentrated sulphuric acid solutions. Evidence is given that the change is not due to chemical action. The results support the view (A., 1925, ii, 742) that camphor exists in solution as a mixture of α-(dextrorotatory) and β-(lævorotatory) forms, the ratio α/β varying in different solvents. In the two-term Drude expressions advanced by Lowry and Cutter (*ibid.*, 357), the terms correspond with these two forms. The α-form is probably identical with the form in which camphor exists in the crystalline state. The values for the dispersion of camphor in acetone solution calculated from the first term agree with the values of Seherr-Toss for the dispersion of the crystal form. The absorption spectrum of the β-camphor is under investigation.

R. A. MORTON.

Determination of Kerr constants in optically active substances. W. ILBERG (Physikal. Z., 1925, **26**, 901—908; cf. de Mallemann, Ann. Physique, 1924, [x], **3**, 5—239).—Transparent isotropic substances exhibit double refraction under the influence of an electric field (Kerr effect). Measurement of the birefringence constant of an optically active liquid is difficult, since the ellipticity of the emergent vibration depends on the rotatory power as well as on the true birefringence. The Kerr constant of carbon disulphide has been used to confirm the validity of the Goüy–Wiener formulæ applied to the case when a strong magnetic field is used to confer an artificial rotation (Faraday effect) with simultaneous production of electric birefringence under definite experimental conditions. The figures obtained for B: $3{\cdot}58\times10^{-7}$ for λ 539, t 18°; $4{\cdot}25\times10^{-7}$ for λ 490, t 19°, compare well with the data of Lyon (Ann. Physik, 1915, [iv], **46**, 764). For certain optically active liquids, the natural rotatory power is nullified by a superimposed Faraday effect and the electric double refraction is then measured in the ordinary way. *l*-Pinene has a vanishingly small Kerr effect. For amyl bromide $B=6{\cdot}23\times10^{-7}$ (λ 537, t 17°); $6{\cdot}03\times10^{-7}$ (λ 539, t 23°). Amyl acetate and camphor oil failed to yield results owing to deficient insulating properties. The Kerr constant for the former is probably of the same order as that for carbon disulphide; for camphor oil, it is exceedingly small.

R. A. MORTON.

Structure of molecules. R. T. BIRGE (Nature, 1926, **117**, 300—302).—Recent work appears to indicate a comprehensive analogy between the electronic energy levels of molecules and of atoms. Since in all molecules where data are available, series of energy levels are known fitting approximately into the customary formulæ of line spectra, it is considered (on the basis of data for certain diatomic molecules) that the energy levels associated with the valency electrons of molecules agree in all essential respects with those associated with the valency electrons of atoms. The spacing in the multiple levels is often approximately the same as for the corresponding atom, *e.g.*, for CO^+, Mg^+, NO, Al, but not for CN, BO. It follows that the electronic structure of the two systems must be similar, and it

appears that the valency electron has the special characteristic of movement in a path projecting beyond those of other electrons, but also of penetrating the region between the two nuclei, so playing a definite part in determining the strength of a chemical linking. A. A. ELDRIDGE.

Asymmetric nitrogen atoms in natural products. T. M. LOWRY (Nature, 1926, **117**, 417).—Whatever opinion is held as to the asymmetry of the trisubstituted ammonia from which it is derived, the nitrogen atom of the pyrrolidine ring of the nicotinium ion must be regarded as asymmetric, a deduction which receives support from the fact that nicotine acetate has $[\alpha]_D$+18·85°, whilst nicotine has $[\alpha]_D$−169°. The anomaly is not observed in cases where the formation of a salt is unaccompanied by fundamental change in the character of the asymmetric system. Further, the rotatory dispersion of nicotine acetate is "complex," whilst that of nicotine is "simple." A. A. ELDRIDGE.

Molecular mechanics. R. CASARES (Anal. Fis. Quim., 1925, **23**, 551—556).—Starting from the inverse square law for intramolecular attraction and the thermal vibration of molecules, the author deduces a hyperbolic relationship between molecular distance and the temperature of equilibrium between a liquid and its vapour. This relationship is followed approximately, provided a distinct temperature origin is taken for each substance, namely the temperature at which molecular motion ceases. This temperature is termed by the author "tension zero." Only with permanent gases, such as hydrogen, helium, and neon, does the tension zero coincide with absolute zero. G. W. ROBINSON.

Physical system of the elements. C. G. BEDREAG (Ann. sci. Univ. Jassy, 1926, **13**, 315—345; **14**, 47—59).—See A., 1925, ii, 363; this vol., 7.

Co-ordination and co-valency. J. A. V. BUTLER (Trans. Faraday Soc., 1925, **21**, 349—359).—See this vol., 111.

Thermal agitation in solids and liquids. J. FRENKEL (Z. Physik, 1926, **35**, 652—669).—Crystals are regarded as partly dissociated, some of the ions remaining outside the equilibrium positions of the crystal lattice. The motions of the atoms are characterised by probabilities relative to the dissociation of the atoms, their displacement in the interstices of the lattice, and their acquisition of an empty point in the lattice. The dependence of these magnitudes on temperature is determined and the variation of electrical conductivity of binary salts with temperature calculated. Liquids are regarded as much more closely resembling solids than gases; the motion of the ions is not at all like "worms creeping"; their displacement takes place in a series of single steps from one position of equilibrium to another. The viscosity coefficient calculated for mercury is found to be of the right order of magnitude. E. B. LUDLAM.

Dvi-manganese and eka-cæsium. F. H. LORING (Chem. News, 1926, **132**, 101—102).—The films previously obtained (A., 1925, ii, 1124; this vol., 12) have been intensified and the wave-lengths of the lines re-measured. The lines ascribed to the $L\alpha_2$ and $L\beta_1$ radiations of element 75 and to the $L\alpha_1$ radiations of element 87 have wave-lengths of 1·434, 1·234, and 1·029 Å., respectively, compared with the theoretical values, 1·4298, 1·2358, and 1·0276, respectively. A film taken from manganese phosphate showed two very faint lines of wave-lengths 1·433 and 1·233. A. R. POWELL.

Non-existence of the amorphous state. P. P. VON WEIMARN and T. HAGIWARA (Kolloid-Z., 1926, **38**, 129—136).—A *résumé* is given of the views on the crystalline nature of matter developed by the first author since 1907, and fresh evidence is produced in support of these views. *X*-Ray examination by the Debye-Scherrer-Hull method of highly-dispersed barium sulphate precipitates, prepared by precipitation from aqueous solutions of 0·1*N*-, *N*-, and 7*N*-concentration, showed that all barium sulphate precipitates, even the gelatinous, are crystalline, and that the structure of the crystal is identical with that of barytes. Experiments with fine powders of iron and aluminium hydroxides and oxides, prepared by mechanical disintegration, confirmed the authors' view that gœthite can be transformed into hæmatite by extreme mechanical disintegration. Under the same conditions, a complete, or almost complete, disappearance occurs of the interference bands in the *X*-ray photographs of diaspore, hydrargillite, gœthite, and corundum. It is maintained that even when *X*-ray examination appears to show that the material is amorphous, this must not be taken as a proof that it is so. L. L. BIRCUMSHAW.

Symmetry of the ions in the crystal lattice. W. EHRENBERG (Z. Physik, 1926, **35**, 616—617).—Linear polarised *X*-rays were reflected from a rock-salt crystal so arranged that the electric vector was parallel to the edge of the cube; on rotating the crystal through 45°, the intensity of the reflected radiation was the same as before. The actual symmetry is greater than the minimum required by crystallographic theory. E. B. LUDLAM.

Bending of rock-salt in air and water. M. LEWITSKY (Z. Physik, 1926, **35**, 850—862).—The bending was examined by means of the deflexion of a beam of light from mirrors attached to the crystal and also by *X*-rays. The latter method shows no change of structure when the elastic limit is reached, but the Laue spots enlarge when the crystal flows. In water and in salt solution, the elastic limit and modulus remain the same as in air, and so does the limit found by *X*-rays. In water, the crystal begins to flow immediately after passing the elastic limit, and there is much greater permanent deformation as well as increased strength. The deformation produced after passing the elastic limit and before flow sets in is attributed to pure translation. For the specimen used (Bachmut rock-salt), the elastic limit is 720 g./mm.^{2}, and the modulus 419·7 kg./mm.^{2} at the ordinary temperature, and 400 g./mm.^{2} and 3380 kg./mm.^{2}, respectively, at 350°. E. B. LUDLAM.

Structure of carborundum (SiC). H. Ott (Z. Krist., 1925, **61**, 515—531).—Carborundum (type II) can be considered as having a zinc blende structure twinned along a trigonal axis. The compound is non-polar. CHEMICAL ABSTRACTS.

Crystal structure of germanium tetraiodide. F. M. Jaeger, P. Terpstra, and H. G. K. Westenbrink (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 747—766).—An X-ray examination of germanium tetraiodide has been made by the Hull, Debye, Bragg, and Laue methods. A cubic space lattice is indicated, with an edge of 11·89 Å. The unit cell contains 8 molecules. Goniometric measurements of the crystals indicated symmetry of either the tetrahedral pentagonaldodecahedral or the dyacisdodecahedral type. A correlation of the radiograms obtained by the above methods suggests that the symmetry is of the latter type, corresponding with the space group T_h^4. In the structure proposed, each germanium atom is surrounded by four iodine atoms situated at the corners of a regular tetrahedron. Of the 32 iodine atoms in a unit cell, 24 have equivalent positions in the structure. Two germanium tetraiodide molecules on each cube diagonal are to be regarded as grouped in pairs, and in such pairs six iodine atoms are always in equivalent positions to one another. The two other iodine atoms are directed outwards from the molecular pair. The iodine atoms of such a pair are placed at the corners of an acute rhombohedron, the axis of which is a diagonal of the cubic cell. Adjacent germanium atoms are situated at the corners of an obtuse rhombohedron, coaxial with that of the iodine atoms. In the combined molecular pairs, both germanium atoms are placed at the centres of two diametrically opposed tetrahedra, the corners of which are occupied by iodine atoms. The intensities of the X-ray reflexions calculated from this structure are in good qualitative agreement with the observed intensities. F. G. Tryhorn.

Structure of aragonite. S. Tomkeieff (Proc. Durham Phil. Soc., 1924—1925, **7**, 103).—See A., 1925, ii, 1035.

X-Ray examination of *i*-erythritol. W. G. Burgers (Phil. Mag., 1926, [vii], **1**, 289—303).—X-Ray examination has shown that the space group of *i*-erythritol, which crystallises in the tetragonal-bipyramidal class, is C_{4h}^6. The spacing of the planes on the a-axis is 12·76 Å. and on the c-axis 6·83 Å. The body-centred unit cell contains 8 molecules and all the evidence points to centro-symmetry of the crystal molecule. The stereochemical configuration assigned to *i*-erythritol is thus confirmed crystallographically. A. E. Mitchell.

Growth of crystals. P. Terpstra (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 794—796).—The factor R in Valeton's formula $G = R(c_1 - c_2)$ (Z. Krist., 1923—1924, **59**, 135) for the rate of growth of a small crystal at the centre of a sphere of slightly supersaturated solution assumes the form $R = (kD/S)/(k+D/S)$ (where D is the diffusion coefficient of the solution, k a constant, and S the thickness of the layer of solution at rest in contact with the face of the crystal) if the lines of diffusion are parallel to one another. A graphical method is suggested to illustrate the effect of changes of value in k, D, and S on the factor R. If one of the quantities k or D/S is large compared with the other, the value of R approaches that of the smaller. The possibility arises that although k may differ considerably for different faces, the velocities of growth may differ but little, causing convexly curved parts in the surface of the crystal. Near the margin of a crystal face, the diffusion lines are convergent, and an analysis of Valeton's formula in these circumstances indicates that a slowly growing face will be most likely to remain plane to the margin. F. G. Tryhorn.

Limiting states in the crystal phase. L. Grenet (Compt. rend., 1926, **182**, 318—320).—In the temperature–composition diagrams of the systems iron–silicon, iron–nickel, and iron–cobalt, opposite branches of the curve approach one another in a manner analogous to the mutual solubility curves of partly miscible liquids. An actual meeting of the branches has not hitherto been observed. The possibility of such a meeting is suggested, the two crystalline phases at that point having identical properties, but differing only in their lattices. W. A. Caspari.

Non-parallel growth of one crystal on another. L. Royer (Compt. rend., 1926, **182**, 326—328).—The condition for oriented growth of two non-isomorphous crystals in contact is that the two-dimensional reticular lattices of the contiguous faces should be similar, whatever be the shapes and dimensions of the space-lattices. Face-centred sodium chloride and body-centred ammonium bromide cannot grow on one another in parallel orientation, but non-parallel growths are possible on certain faces because the spacing of the former (5·63 Å.) stands to that of the latter (3·99 Å.) in the ratio $\sqrt{2}:1$. Thus on cubes of sodium chloride, alcoholic ammonium bromide deposits cubes turned through 45°; on (110) faces it deposits crystals the (110) faces of which are turned through 90°. On (111) and (210) faces no oriented growth could be obtained. W. A. Caspari.

Magnetisation and thermo-magnetic phenomenon of nickel. P. Weiss and R. Forrer (Ann. Physique, 1926, [x], **5**, 153—213).—The magnetisation of nickel in varying fields has been measured at temperatures from 20° to 630°. From the thermo-magnetic effect (evolution of heat accompanying magnetisation), the "spontaneous magnetisation," *i.e.*, that due to the molecular fields in absence of any external field, can be calculated. In this way, isotherms of true magnetisation can be constructed. The specific heat calculated from the thermo-magnetic effect at different temperatures agrees with that determined directly. From the fact that the lines of equal magnetisation are not rectilinear above the Curie point, it is concluded, in order to derive a satisfactory magnetic equation of state, that the law of the molecular magnetic field must be modified so as to take into account variation in the atomic moment with temperature. R. Cuthill.

Correlation of remanent magnetism and specific resistance of some pure iron-carbon alloys. E. D. CAMPBELL (Trans. Faraday Soc., 1925, **21**, 338—348).—See this vol., 17.

Effect of rolling on the crystal structure of aluminium. E. A. OWEN and G. D. PRESTON (Proc. Physical Soc., 1926, **38**, 132—147).—Sheets of aluminium were examined by the ionisation spectrometer and by photographic methods to discriminate between the contradictory results obtained by previous observers using the two methods, as to the final orientation of the crystals in the rolled material. The results show that when a cast specimen of aluminium containing a number of large crystals with random orientation is rolled, the crystals break up into a large number of small crystals. These tend to take up a definite orientation, each crystal having a cube diagonal in the direction of rolling and a (211) plane in the plane of rolling. Two sets of crystals exist in the rolled material, one set being the optical image of the other in the plane of rolling. These results confirm those of Wever (Z. Physik, 1924, **28**, 69). The type of space lattice remains unaltered and no change greater than 0·5% could be detected in the lattice parameter. C. J. SMITHELLS.

Fatty acids and smectic substances. G. FRIEDEL (Compt. rend., 1926, **182**, 425—427; cf. A., 1923, ii, 223, 224; 1925, ii, 1129).—The length of the carbon chain and hence the distance apart of the crystal planes of palmitic acid make *X*-ray spectrographs of the acid similar to those of substances in the smectic state, but since smectic substances are in the form of a pile of parallel lamellæ, whereas crystals contain parallel planes in three dimensions, the radiograms may be distinguished by the absence of any but first-order annulæ in those of smectic substances. L. F. HEWITT.

Chemistry of solids. C. H. DESCH (Brit. Assoc. Rep., 1925, 30—54).

Determination of the molecular weight of proteins. T. SVEDBERG and R. FÅHRAEUS (J. Amer. Chem. Soc., 1926, **48**, 430—438; cf. A., 1925, ii, 528).—When a solution is centrifuged until equilibrium is attained between the diffusion and the sedimentation due to centrifugal force, the mol. wt. of the solute is given by the expression $M=2RT \log (C_1/C_2)/\omega^2(1-V\rho)(x_1-x_2)(x_1+x_2)$, where C is the concentration of the solution at distance x from the centre of rotation (positive towards the centre), V the partial specific volume of the solute, ρ the density of solvent, and ω the angular velocity of the centrifuge. The mol. wt. of the solute is therefore determinable by measuring the relation between the concentration of the solution at two points at known distances from the centre of rotation, the other variables in the above expression being known. The ultracentrifuge of Svedberg and Rinde (A., 1925, ii, 233) with specially constructed cells and a recording photomicrometer, have been used for the determination of the mol. wt. of carbon monoxide-hæmoglobin and of methæmoglobin and the results obtained indicate that hæmoglobin solutions are built up of molecules containing four groups of the minimum mol. wt. of 16,700 (computed from the iron content), whilst the absence of any systematic variation of mol. wt. with distance from the centre of rotation indicates that in one and the same solution all the molecules have probably the same mass. F. G. WILLSON.

Specific heats, heats of vaporisation, and critical temperatures of California petroleum oils. E. H. ZEITFUCHS.—See B., 1926, 181.

Heats of formation and densities of hydrides. A. SIEVERTS and A. GOTTA (Z. Elektrochem., 1926, **32**, 105—109).—The heat of formation of the solid hydride of a metallic mixture rich in lanthanum was calculated by means of Hess' law, from the difference between the heats of solution of metal and hydride in aqueous hydrochloric acid, the hydride being prepared by direct union of hydrogen and the heated metal. A linear relationship between heat of formation and volume of hydrogen absorbed is found, and this is interpreted as showing that a mixture of metal and saturated solid solution of hydride and metal is formed. The heat of formation of saturated solid solution per molecule of absorbed hydrogen is found to be +40,620 cal. If the temperature of hydride formation is sufficiently raised, homogeneous solutions are formed, and it is found that the dilution of the saturated solution with solid is a further exothermic process. The densities of metal and of saturated solid solution of hydride in metal were found to be 6·69 and 5·85, respectively, at 20°. C. H. D. CLARK.

Physico-chemical properties of hydrogen iodide. R. MIRAVALLES and E. MOLES (Anal. Fis. Quím., 1925, **23**, 509—523).—Hydrogen iodide has m. p. −50·0°, and normal b. p. −36°. The vapour pressure between −56° and −35° has also been determined. From the experimental data thus obtained, it is deduced that $\log p=7{\cdot}20833-1025{\cdot}71/T$ and that the molecular heat of evaporation is 4916 cal. Trouton's constant is 20·74, or (by the Nernst formula) 20·90. Hydrogen iodide is thus a normal gas. The critical temperatures, calculated from the normal b. p. by the Guye-Guldberg rule, is 420. The higher figures for the b. p. and the lower figures for the m. p. obtained by earlier workers may be attributed to the presence of impurities. G. W. ROBINSON.

Melting points of barium, strontium, and calcium oxides. E. E. SCHUMACHER (J. Amer. Chem. Soc., 1926, **48**, 396—405).—A new method of determining the m. p. of certain oxides is described. The m. p. of the oxides of barium, strontium, and calcium were found to be 2196°, 2703°, and 2849° Abs., respectively. W. THOMAS.

Constitution of aromatic compounds and their physical and chemical properties. III. IV. V. I. A. PASTAK (J. Chim. phys., 1926, **23**, 61—77).—The m. p. and solubilities of disubstituted benzenes and the m. p. of polysubstituted naphthalenes are discussed. A. E. MITCHELL.

Variation of the thermal conductivity of gases with pressure. H. GREGORY and C. T. ARCHER (Phil. Mag., 1926, [vii], **1**, 593—606).—The hot-wire method, in which the temperature of the wire was maintained constant to a high degree of accuracy, and

all precautions were taken to eliminate convective losses, has been used to study the variation of the thermal conductivity of air with pressure, from atmospheric pressure down to 1—3 mm. A thin platinum wire passing centrally down a vertical glass tube of 0·5 cm. diameter was kept at a constant temperature (within the range 4—18°) by passing a current through it, the tube being immersed in a thermostat at 0°, and the changes in the current necessary to maintain constancy as the pressure of the air in the tube was decreased, were determined. The current required was from 0·1 to 0·2 amp. and could be measured to 0·0001 amp. In the range 76—20 cm., the conductivity was constant to the order of accuracy of the method. On further decreasing the pressure, a decrease in conductivity became apparent, but did not amount to more than a few per cent. until the pressure fell below 1 cm., when the conductivity began to fall off rapidly. Assuming convective losses to be absent, the results confirm Maxwell's theory. A. B. MANNING.

Thermochemical examination of existence of metastable alkali halides. E. LANGE and F. DÜRR (Z. Elektrochem., 1926, **32**, 85—87).—The observation of Berthelot and Ilosvay (A., 1884, 704) that the heats of solution of alkali halides are different according as the salts have been previously melted or not has not been confirmed. The differences obtained by the present authors using sodium and potassium chlorides never exceed 2 cal. per molecule, which is within the experimental error. If a very small quantity of the cube-centred variety of sodium chloride is present after melting and cooling, there is a rapid change to the stable modification, so that the conclusion must not be reached that the alkali halides consist of a mixture of more than one modification at the ordinary temperature. The results of Berthelot and Ilosvay may possibly be partly attributed to a small quantity of moist air entering during the melting and leading to hydrolysis.

C. H. D. CLARK.

Dilatometric investigation of [hydrates of] sodium carbonate. M. USSANOVITSCH (Z. physikal. Chem., 1926, **119**, 139—140).—Petroleum appears to be a suitable liquid for use in dilatometric measurements in the neighbourhood of 30°, as with the employment of this liquid the transition point of the system $Na_2CO_3,10H_2O \rightleftharpoons Na_2CO_3,7H_2O + 3H_2O$ was found to be 31·85°, in complete agreement with Ketner (A., 1902, ii, 308). L. F. GILBERT.

Velocity of sound in liquids and its relation to the heat of vaporisation. T. V. IONESCO (Ann. sci. Univ. Jassy, 1926, **13**, 278—314; cf. A., 1925, ii, 644).—The formula $V=\sqrt{Lv/(v-b)}$, derived from van der Waals equation, is applicable to all normal liquids, as is Lewis' formula $V=\sqrt{L/\alpha T}$. The van der Waals constant b can be deduced from a determination of the velocity of sound.

Critical temperatures and pressures of alkali halides; molecular surface tension and its temperature coefficient. J. J. VAN LAAR (Z. anorg. Chem., 1925, **149**, 324—352; cf. A., 1925, ii, 950, 1141).—The critical temperature and pressure may be calculated from the equations $T_c=A/7$, and $p_c=RT_c/16b_0$, which are deduced from the simplified vapour-pressure equation $\log p=-A/T+C$, and the equation of state, assuming that $b_c=2b_0$ and $a_c=a_0$ instead of $1{\cdot}6\,a_c=a_0$ as for normal substances. For alkali halides A is approximately 19,000, and hence $T_c=2750°$ Abs. Sodium salts have maximum and bromides minimum values. The values of p_c calculated from the above equation do not agree with those calculated from the simplified vapour-pressure equation; the latter are too low, indicating that this equation does not hold at high temperatures. If in van der Waals' equation $\log p_c/p=f(T_c/T-1)\,f$ is assumed to increase linearly with the temperature, a more correct expression for p_c is obtained, namely, $\log p_c=(C-f_0)+\phi T_c$, where C and ϕ are constants. A second method of calculating the critical temperature is from the m. p., the ratio for alkali halides being approximately 1·7, except for lithium and sodium fluorides. A third method of calculation is from the temperature coefficient (Θ) of the molecular surface energy, and the values thus obtained agree with those found by the first method except for lithium, sodium, and rubidium chlorides, and sodium bromide. For alkali halides, Θ has an abnormally low value and it is calculated that, if r' is the apparent molecular or ionic radius for cubic packing and r the actual radius, then $r'/r=2{\cdot}7$. The actual radii of the alkali ions may then be calculated from the densities of the halides. The values thus obtained are 0·51, 0·62, 0·78, 0·83, and $0{\cdot}89\times10^{-8}$, which are in good agreement with those of Born and Lorenz. The low values of Θ are not due to association. By a fourth method, the critical temperature is calculated from the coefficient of expansion (α). For limiting substances, $\alpha T_c=0{\cdot}5$, but for the alkali halides the mean value is 0·78. It is shown that the value of αT_c is proportional to a_c/a, and hence when this is 1·6 times too small, as for the alkali halides, αT_c is 1·6 times too great. Molten electrolytes are thus regarded as ordinary limiting substances ($\gamma=1$), so that, for example, $b_c/b=2\gamma=2$; but a_0/a_c is 1·0 instead of 1·6, because r'/r is 2·7 instead of 1·0. The values of the critical temperatures and pressures, of the temperature coefficients of the molecular surface tension, and of the coefficients of expansion are thus accounted for. The law of corresponding states can only be applied to molten electrolytes with these restrictions. A. GEAKE.

Pressures developed on explosion of gaseous mixtures at high densities. W. T. DAVID (Phil. Mag., 1926, [vii], **1**, 334—337).—The explanation given by Bone, Newitt, and Townend (A., 1925, ii, 800), that the increase in the ratio of the maximum pressure, developed during the explosion of inflammable gases in a closed vessel, to the initial pressure with increasing initial pressure, is due to the increasing opacity of the gaseous medium with pressure to the radiation emitted during the explosion, is inadequate. The author has shown (A., 1911, ii, 1046) that the radiation emitted per radiating molecule, when the gaseous mixture is at any given temperature, decreases as the density of the mixture increases, and that, therefore, at any given temperature

the vibratory energy contained by these molecules decreases as the density of the system increases. It follows, then, that the specific heat of gases like carbon dioxide and steam will decrease as the density increases at temperatures at which they emit infrared radiation. It is suggested that this decrease in specific heat is the largest factor in the effect described by Bone, Newitt, and Townend.

A. E. MITCHELL.

Vapour pressures of solid and liquid hydrogen cyanide. J. H. PERRY and F. PORTER (J. Amer. Chem. Soc., 1926, **48**, 299—302).—Vapour pressures of hydrogen cyanide were measured from −30·4° to the triple point for the solid, and from the triple point to 27·32° for the liquid. The derived equations for the pressures in mm. are for the solid and liquid, respectively, $\log P=9\cdot33902-(1864\cdot8/T)$ and $\log P=7\cdot744603-(1453\cdot063/T)$. The triple point of hydrogen cyanide was calculated to be −14·86° at a vapour pressure of 131·16 mm. The normal b. p. is 25·65°. The latent heats of sublimation, fusion, and evaporation are 316·13, 69·29, and 246·84 cal./g., respectively. The method and apparatus employed were the same as in the previous investigation (cf. this vol., 117). W. THOMAS.

Vapour pressure of phosphoric oxide. (MISS) J. M. A. HOEFLAKE and F. E. C. SCHEFFER (Rec. trav. chim., 1926, **45**, 191—200; cf. Smits and Rutgers, A., 1925, ii, 268).—Phosphoric oxide exists in at least two crystalline forms and also as an amorphous solid. The vapour-pressure curves corresponding with these three forms have been investigated. The usual volatile crystalline variety has a sublimation point in the region of 360°. At temperatures between 400° and 500° the metastable sublimate changes into the amorphous form, the pressure falling nearly to zero. Further heating converts the amorphous powder into a very viscid liquid, the change proceeding without any apparent discontinuity in the vapour-pressure curve. Prolonged heating at 500° results in the transformation of the viscid liquid into a modification consisting of microscopic needles melting at 569°. Some evidence was obtained for the existence of a third crystalline form (plates) stable above 570° and metastable in presence of the needles.

J. S. CARTER.

Adjusted vapour pressures of zinc and cadmium. C. G. MAIER (J. Amer. Chem. Soc., 1926, **48**, 356—364).—Recorded data referring to the vapour pressures of zinc and cadmium have been critically recalculated in order to express the experimental values consistently for thermodynamic calculations. On the assumption that zinc and cadmium are perfect monatomic gases, standard free energy equations have been derived for volatilisation, sublimation, and fusion. The expressions for the vapour pressure for zinc, liquid and solid, and cadmium, liquid and solid, are $\log P=12\cdot0013-(6670/T)-1\cdot1265\log T$, $\log P=9\cdot4181-(6883\cdot0/T)-0\cdot05029\log T-3\cdot277\times10^{-4}T$, $\log P=12\cdot2870-(5819\cdot4/T)-1\cdot2572\log T$, and $\log P=9\cdot7170-(5907\cdot8/T)-0\cdot4323\log T-2\cdot840\times10^{-4}T$, respectively. W. THOMAS.

Vapour pressure of arsenic trioxide. E. R. RUSHTON and F. DANIELS (J. Amer. Chem. Soc., 1926, **48**, 384—389).—The vapour pressures of octahedral and liquid arsenic trioxide have been measured and the following equations derived: octahedral, $\log P=-(6670/T)+13\cdot728$; liquid, $\log P=-(2722/T)+6\cdot513$. The octahedral form melts at 275° and the monoclinic at 315°. The transition temperature of octahedral to monoclinic is 250°, but the change is very slow. The vitreous form, although less stable than the monoclinic, may be formed by condensing the vapour between 275° and 315°. The heats of vaporisation found by the Clausius-Clapeyron equation are: liquid, 31·5; octahedral, 77·1; monoclinic, 71 (estimated). W. THOMAS.

Vapour pressure of bromine. F. E. C. SCHEFFER and M. VOOGD (Rec. trav. chim., 1926, **45**, 214—223).—The vapour-pressure curve of bromine has been investigated over the temperature range −20° to 300°. F. p. is −7·6° and b. p. 58·4°/760 mm. The equation $\log p=-2087/T-3\cdot449\log T+17\cdot871$, where p is the pressure in mm. of mercury and T the absolute temperature, represents very satisfactorily the vapour pressures of bromine up to about 3 atm. The critical temperature is 311° and the corresponding pressure 102 atm. J. S. CARTER.

Limits of validity of gas equations. II. W. HERZ (Z. Elektrochem., 1926, **32**, 31—33).—The equations of state of Berthelot ("Sur les Thermomètres à Gaz," Paris, 1903) and Wohl (A., 1914, ii, 430) have been applied to the following substances in the gaseous state and at the saturation pressure, over wide ranges of temperature: hexane, di*iso*butyl, benzene, fluorobenzene, methyl formate, ethyl alcohol, carbon tetrachloride, stannic chloride, ammonia, chlorine, argon, oxygen, and hydrogen. Both equations give a satisfactory reproduction of the relation between p, v, and T. There is little to choose between them, but possibly Wohl's equation has a slight advantage. With increasing temperature the value of pv passes through a maximum, and the temperature at which this occurs bears for most substances approximately the same ratio to the critical temperature, viz., about 0·8 (absolute unit). N. H. HARTSHORNE.

Theory of the state of matter. III. Relation between surface tension and the constants in the equation of state. F. SCHUSTER (Z. Elektrochem., 1926, **32**, 46—47).—The equation $b_k=c_1\cdot T_s/\gamma_s$ (where b_k is van der Waals' constant, c_1 is a constant, and T_s and γ_s are the b. p. and surface tension, respectively) is deduced. The value of c_1 for the normal liquids benzene, chlorobenzene, bromobenzene, iodobenzene, chloroform, carbon tetrachloride, toluene, hexane, octane, naphthalene, ethyl ether, ethyl acetate, ethyl propionate, propyl acetate, carbon disulphide, and stannic chloride is approximately constant, the mean being $3\cdot11\times10^{-4}$, but with the associated substances water, methyl alcohol, ethyl alcohol, propyl alcohol, methyl formate, acetone, hydrogen sulphide, hydrogen bromide, and hydrogen iodide considerable divergences are recorded. Van der Waals' second constant a_k is given by the expression $a_k=c_2\cdot T_s^2/\gamma_s$, where c_2 is a constant which for the

above normal liquids has the mean value $6{\cdot}1\times10^{-6}$, but, like c_1, varies considerably with the associated substances. N. H. HARTSHORNE.

Relation of the internal latent heat of evaporation to the molecular surface energy, in connexion with the modified law of corresponding states. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 781—793).—The value 4 deduced by van Urk (*ibid.*, 356) for the ratio of the internal latent heat of evaporation of a substance to its molecular surface energy is not a universal constant, but depends on the type of substance, and on the value of the reduced coefficient of direction of the straight line between $\frac{1}{2}d_0$ and d_c, where d_0 and d_c represent the reduced liquid densities at $T=0$ and $T=T_c$. A general formula for the above ratio is deduced, from which it is found that the ratio approximates, for $T=\frac{1}{2}T_c$, to the value of the coefficient f in the vapour-pressure formula $\log(p_c/p)=f(T_c/T-1)$. The ratio approaches $\frac{1}{2}f_0$ for $T=0$, where f_0 is the extrapolated limiting value of f at $T=0$. For "ordinary" substances (*e.g.*, benzene, chloroform, ether, carbon tetrachloride) the value of the ratio, at $T=0$, is 5·3; at $T=\frac{1}{2}T_c$, 7. The corresponding values for argon, nitrogen, and oxygen are 3·9 and 5·3, and for hydrogen, 2·8 and about 4·4. At temperatures near T_c the ratio becomes much greater (10—50). A preliminary account is given of further considerations which result in a value 14 for the above ratio in the case of molten alkali halides.

F. G. TRYHORN.

Corresponding states and surface phenomena. G. BOITARD (J. Chim. phys., 1926, **23**, 205—208).—An application of the author's theory (A., 1925, ii, 865) to surface phenomena. The reduced surface energy and reduced surface tension are defined, respectively, in terms of the molecular surface energy and surface tension in relation to the critical pressure and critical volume. The results are discussed in connexion with the equation of Eötvös.

A. E. MITCHELL.

Compressibility and decomposition of nitric oxide. E. BRINER, H. BIEDERMANN, and A. ROTHEN (J. Chim. phys., 1926, **23**, 157—175).—See this vol., 16.

Viscosity measurements of pure liquids. A new viscosimeter. J. DUCLAUX and J. ERRERA (Kolloid-Z., 1926, **38**, 138—141).—The disadvantages of the usual type of viscosimeter are summarised, and an improved form of apparatus is described which is claimed to give accurate results for viscosities between 1 and 30, and for times of flow of 20—200 sec. The apparatus is a modification of the Ostwald viscosimeter, the glass tube being cemented at its lower end to a short, wide, porous clay tube. The time of flow of the liquid past two marks on either side of the bulb is measured in the usual way. The tube is contained in a wider glass tube, with a bulb sealed into the side, which also contains the experimental liquid maintained at constant level. Figures are given for ethyl ether and amyl alcohol to prove that the product of pressure and time of outflow is constant, at least for pressures between 96 and 165 mm.

L. L. BIRCUMSHAW.

Equal viscosities. O. FAUST (Z. anorg. Chem., 1926, **150**, 175—176; cf. Herz, A., 1925, ii, 1049).—The ratio of the temperature at which a liquid has the viscosity 0·0040 to the critical temperature is somewhat higher for associated than for normal substances. This was to be expected, since the association will be less at the critical temperature, and this temperature therefore lower than would correspond with the degree of association for a viscosity of 0·0040. Substances with low molecular volumes, *e.g.*, chloroform, ethyl iodide, and benzene, frequently have higher viscosities at a given vapour pressure than have other substances, and they have correspondingly high values for the temperature ratio above. A. GEAKE.

Isomeric chromic chloride hexahydrates. J. R. PARTINGTON and S. K. TWEEDY (Nature, 1926, **117**, 415).—Violet solutions of chromic chloride hexahydrate have a higher viscosity than the analogous green solutions, as would be anticipated from Werner's formulation, whereas Britton's view (A., 1925, ii, 1204) requires the reverse to be the case. It is presumed (cf. Birk and Biltz, this vol., 110) that the viscosity of the bluish-green salt,

$$[CrCl(H_2O)_5]Cl_2,H_2O,$$

would be greater than that of the violet salt,

$$[Cr(H_2O)_6]Cl_3.$$

A. A. ELDRIDGE.

Air bubble viscosimeter. G. BARR (Phil. Mag., 1926, [vii], **1**, 395—405).—An examination and theoretical discussion of the air bubble viscosimeter has shown that if there is a close concordance between the surface tensions of the liquids compared, and if the diameter of the tube is such that the bubble moves slowly, the time required for the bubble to travel a given distance is proportional, within 5—10%, to the viscosity. The instrument may thus be used for the approximate comparison of the viscosities of materials of the same class.

A. E. MITCHELL.

Viscosity of alloys at high temperature. J. COURNOT and K. SASAGAWA.—See B., 1926, 161.

Deviations from Dalton's law of partial pressures. M. TRAUTZ and O. EMERT (Z. anorg. Chem., 1926, **150**, 277—303).—Fuchs (A., 1918, ii, 298), using an interferometer method, found deviations as great as 3% from a linear relationship between the refractive index and the composition of mixtures of gases. This is due to an error in calculation, and when corrected the linear relation holds within his experimental error. The change in pressure when gases are mixed without change of volume has now been measured for binary mixtures of sulphur dioxide and carbon dioxide with hydrogen, nitrogen, oxygen, and air, of hydrogen with oxygen and nitrogen, and of oxygen with nitrogen. The gases were contained in two 100-c.c. pipettes, and were forced simultaneously into a mixing vessel by siphoning mercury from this vessel into the bottoms of the pipettes. The mixing vessel was connected through a toluene gauge

with a 1400-c.c. globe of air, and the change in pressure was determined by measuring the volume of mercury required to be run into the globe to restore the gauge to zero. The pressure measurements were accurate to 0·01 mm. of mercury. The pressure changes were calculated from van der Waals' equation, taking $a_{1,2}=\sqrt{a_1 a_2}$ (Berthelot); $b_{12}=[\frac{1}{2}(\sqrt[3]{b_1}+\sqrt[3]{b_2})]^3$; $A=x^2a_1+2x(1-x)a_{1,2}+(1-x)^2a_2$; $B=x^2b_1+2x(1-x)b_{1,2}+(1-x)^2b_2$, where a and b are van der Waals' constants and x and $(1-x)$ are the mol. fractions of gases 1 and 2. Changes of a and b with temperature were allowed for by van Laar's equations for their temperature coefficients, $a_T=a_c \cdot e^{\alpha(1/RT-1/RT_c)}$ and $b_T=b_c \cdot e^{\alpha(1/RT-1/RT_c)}$, where a_c and b_c are values at the critical temperature T_c. The results thus calculated agree with the experimental results to within 0·1 mm. of mercury and are thus sufficiently accurate for all ordinary gas analyses. Expressed to the nearest 0·01 mm., the calculated results indicate correctly the effect of temperature and pressure (which was always about atmospheric) on the change of pressure, but the absolute values are not exact. In general, calculation gives too high pressures, the error varying from $+0{\cdot}32\times10^{-3}$ atm. for oxygen and sulphur dioxide to $-0{\cdot}26\times10^{-3}$ atm. for hydrogen and sulphur dioxide. A. GEAKE.

Constitution of alloys of aluminium, copper, and zinc. D. HANSON and M. L. V. GAYLER (J. Inst. Metals, 1925, **34**, 125—170).—See A., 1925, ii, 974.

β-Transformation in copper–zinc alloys. J. L. HAUGHTON and W. T. GRIFFITHS (J. Inst. Metals, 1925, **34**, 245—260).—See A., 1925, ii, 973.

α-Phase boundary in the copper–tin system. D. STOCKDALE (J. Inst. Metals, 1925, **34**, 111—124).—See A., 1925, ii, 973.

Colloidal separations in alloys. J. H. ANDREW and R. HAY (J. Inst. Metals, 1925, **34**, 185—192).—See A., 1925, ii, 954.

Gold–nickel alloys. W. FRAENKEL and A. STERN (Z. anorg. Chem., 1926, **151**, 105—108).—The crystallisation temperatures of alloys of gold and nickel lie on a continuous curve having a minimum of 950° for alloys containing 15—20% of nickel. A continuous series of mixed crystals is thus formed, and microscopical observation showed that 20% and 40% alloys are homogeneous, the former corresponding with the supposed eutectic mixture of Levin (A., 1905, ii, 532) and of de Cesaris (A., 1914, ii, 57). A. GEAKE.

Metal-pairs forming a continuous series of mixed crystals. J. A. M. VAN LIEMPT (Rec. trav. chim., 1926, **45**, 203—206).—It is probable that the number of metal-pairs which form a continuous series of mixed crystals is much smaller than that suggested by the results of thermal analysis. The following binary systems constitute this class of metal pairs: Ag–Au; Ag–Pd; Au–Pd; Co–Ni; Ni–Pd; W–Mo; Fe–V; K–Rb; Pd–Pt; Cu–Ni; (Co–Mn). Cuy's rule (A., 1923, ii, 831) connecting the maximum deviation of the liquidus curve with the relative difference of the two lattice parameters is not applicable to binary metal systems. Metals forming a continuous series of mixed crystals have the same type of space lattice and almost the same parameter. The converse, however, does not hold. J. S. CARTER.

Systems formed by certain inorganic compounds with liquid sulphur dioxide. P. A. BOND and H. T. BEACH (J. Amer. Chem. Soc., 1926, **48**, 348—356).—Sulphur dioxide and liquid tetrahalides are only partly miscible at lower temperatures. The critical solution temperatures recorded are: stannic bromide 48·6° (two liquid phases possible down to 16·3°); carbon tetrachloride −29·3° (two liquid phases possible down to −45°). With stannic chloride, no stable conjugate liquids are formed, but a metastable two-phase liquid system lying completely below the solid–liquid solubility curve may be realised. There was no evidence of the formation of compounds at temperatures above the m. p. of sulphur dioxide. W. THOMAS.

Influence of temperature on the reciprocal solubility of the monoalkyl ethers of ethylene glycol and water. H. L. COX and L. H. CRETCHER (J. Amer. Chem. Soc., 1926, **48**, 451—453).—Binary mixtures of water and bis(β-alkoxy)ethyl ethers, ethylene glycol monoalkyl ethers, and ethylene glycol dialkyl ethers, give closed solubility curves similar to that obtained for nicotine and water (cf. Hudson, A., 1904, i, 446). Complete solubility data for the systems water–ethylene glycol mono-*n*-butyl ether and water–ethylene glycol mono*iso*butyl ether, determined by the method of Alexejew (A., 1886, 847), are detailed. F. G. WILLSON.

Solubility of hydrogen in tin and aluminium at high temperatures. L. L BIRCUMSHAW (Phil. Mag., 1926, [vii], **1**, 510—522).—Hydrogen is only slightly soluble in tin at 306°. At 800°, the solution rate follows the equation $w=3{\cdot}38-2{\cdot}86e^{-0{\cdot}0074t}-0{\cdot}52e^{-0{\cdot}0666t}$, where w is the amount dissolved at time t, indicating that the rate of solution is governed by the rate of diffusion of the gas through the bulk of the metal. Hydrogen is soluble to a considerable extent in aluminium at 670°. Both these results contravene the statement of Sieverts and Krumbhaar (A., 1910, ii, 410) that hydrogen is quite insoluble in tin and aluminium, and that where solution in a metal does take place the equilibrium is attained almost instantaneously. It is difficult to remove all the gas from the metals in a vacuum. The reasons for this are discussed. A. E. MITCHELL.

Solubility and grain size. II. D. BALAREV (Z. anorg. Chem., 1926, **151**, 68—70; cf. A., 1925, ii, 853).—It is probable that when a substance such as calcium sulphate is powdered, some particles are formed which are too small to be visible, and the solubility will thus not correspond with the size of the visible particles. Thus when crystals of ammonium magnesium phosphate are crushed under concentrated ammonium hydroxide with a glass rod, an opalescent liquid is obtained which will pass through a filter unchanged. A. GEAKE.

Solubility of double nitrates of praseodymium and neodymium with bivalent metals. W. PRANDTL and H. DUCRUE (Z. anorg. Chem., 1926, **150**, 105—116).—The authors have determined the solubilities in water of the double nitrates $2M^{III}(NO_3)_3,3M^{II}(NO_3)_2,24H_2O$, where M^{III} is praseodymium or neodymium and M^{II} is magnesium, zinc, nickel, cobalt, or manganese. Measurements were made at temperatures from 15° up to the m. p. In general, the solubilities are about ten times those in concentrated nitric acid, and the praseodymium salts are more soluble than the corresponding neodymium salts. The differences are greatest at temperatures between 15° and 60°, and less at higher temperatures. The most suitable double nitrates for separating praseodymium and neodymium by fractional crystallisation are those of magnesium.

A. GEAKE.

Solubility of amino-acids at various hydrogen-ion concentrations. K. SANO (Biochem. Z., 1926, **168**, 14—33).—The solubilities of tyrosine, cystine, and leucine at various hydrogen-ion concentrations conform to the theory of Michaelis. The dissociation constants, calculated from the solubility data, are: leucine, $K_a=3\cdot16\times10^{-10}$, $K_b=2\cdot8\times10^{-12}$; tyrosine, $K_{a_1}=7\cdot94\times10^{-10}$, $K_{a_2}=7\cdot94\times10^{-11}$, $K_b=1\cdot6\times10^{-12}$; cystine, $K_{a_1}=1\cdot4\times10^{-8}$, $K_{a_2}=1\cdot4\times10^{-10}$, $K_{b_1}=1\cdot8\times10^{-12}$, $K_{b_2}=4\cdot5\times10^{-13}$. R. K. CANNAN.

Influence of citrates on the precipitation of barium sulphate. M. L. NICHOLS and O. J. THIES, jun. (J. Amer. Chem. Soc., 1926, **48**, 302—309).—The conditions under which apparently true solutions of barium sulphate of various concentrations can be prepared were determined. In such solutions, the barium sulphate is present in the form of very finely-divided negatively charged particles. They are precipitated by positive colloids and also by certain electrolytes; the precipitated sulphate is flocculent and readily passes through filter-paper. A slight motion of the particles is observed in an endosmose apparatus. Determinations involving the precipitation of barium sulphate in the presence of citrates can be made satisfactorily, provided that slightly more than enough acid to convert the citrates into citric acid is previously added to the solution. W. THOMAS.

Fractional precipitation. III. Induced precipitation. Apparent contradictions to theoretical requirements. Feigl's hypothesis of the formation of sulphides. O. RUFF and B. HIRSCH (Z. anorg. Chem., 1926, **151**, 81—95; cf. A., 1925, ii, 992; this vol., 126).—The apparent contradictions of the law of mass action enumerated by Feigl (A., 1925, ii, 70) are due to incorrect data. Feigl's mixed sulphides, containing two metals in stoicheiometric proportions, are not reproducible. Abnormal, so-called induced, precipitation is generally due either to combination in some form between the primary sulphide and hydrogen sulphide, or to the formation of an impervious layer of the less soluble sulphide around particles of the more soluble sulphide. A. GEAKE.

Distribution of a substance between two solvents, and its solubility. W. PERSCHKE (Z. anorg. Chem., 1926, **151**, 239—252).—It is shown thermodynamically that the distribution-ratio of a substance between two immiscible solvents must be equal to the ratio of its solubilities in the solvents provided that it has the same mol. wt. in each, and that its presence does not affect the miscibilities of the solvents. Observed deviations from this relation are probably due to non-fulfilment of the latter condition. It is found that the distribution ratio of azobenzene between hexane and methyl alcohol or of succinic acid between water and ethyl ether at the ordinary temperature is, for a particular concentration of distribute, equal to the ratio of its solubilities in the two liquid phases formed by this concentration. To account for the fact that the distribution ratio of a liquid between two liquids with which it is completely miscible is not always unity, it is suggested that a mixture of completely miscible liquids consists of a pair of completely miscible conjugates the composition of which is altered by addition of a third substance. R. CUTHILL.

Partition of a mixture between two immiscible solvents. W. PERSCHKE and TSCHUFAROV (Z. anorg. Chem., 1926, **151**, 121—126).—The partition coefficient of acetic acid between amyl alcohol and water is alcohol : water=0·920, and that of hydrogen peroxide is 0·142. When both solutes are present, the coefficients are 0·944 and 0·130, and within the experimental error identical with the values obtained singly. The partition coefficients of these solutes between ethyl ether and water are also unaffected by the presence of each other.

A. GEAKE.

Adsorption of gases by activated charcoal at very low pressures. I. At air temperature. H. ROWE (Phil. Mag., 1926, [vii], **1**, 109—131).—The adsorption of carbon dioxide, nitrogen, oxygen, and carbon monoxide by activated coconut charcoal has been measured at the ordinary temperature over the pressure range 10^{-4}—10^{-1} mm. Before making a measurement, the charcoal was completely freed from gases by heating at 450°, the apparatus being exhausted to a pressure less than 10^{-5} mm. The amount of carbon dioxide adsorbed per g. of charcoal varied from 5·165 c.c. (measured at 1 mm. and 15°) at a pressure of $0\cdot326\times10^{-3}$ mm. to 150·5 c.c. at $73\cdot02\times10^{-3}$ mm. Below $1\cdot5\times10^{-3}$ mm., the relation between amount adsorbed and pressure is linear, whilst above $1\cdot75\times10^{-3}$ mm. the relation is best expressed by the formula $\log \alpha/P=A_0-A_1\alpha$, where α is the amount adsorbed, P is the pressure, and A_0 and A_1 are constants. Above $2\cdot5\times10^{-3}$ mm., the relation may also be expressed by the Freundlich equation $\alpha=kP^{1/n}$, the value of $1/n$ being 0·358. The amount of nitrogen adsorbed per g. varied from 0·1313 c.c. at $3\cdot231\times10^{-3}$ mm. to 6·642 c.c. at $117\cdot0\times10^{-3}$ mm. The adsorption isotherm is linear below 30×10^{-3} mm. Above this pressure, the equation $\log \alpha/P=A_0-A_1\alpha$ holds. The value of $1/n$ in the Freundlich equation increases with rise in pressure. This is the reverse of the variation shown by carbon dioxide, and differs also from the results of Claude and Titov. For oxygen, the attainment of equilibrium at the higher pressures used was relatively slow, and it was found impossible to remove all the adsorbed oxygen by the method

employed (cf. Lowry and Hulett, A., 1920, ii, 536). The amount adsorbed per g. varied from 2·299 c.c. at $0{\cdot}136\times10^{-3}$ mm. to 670·1 c.c. at $74{\cdot}49\times10^{-3}$ mm. The adsorption isotherm is similar to that for carbon dioxide. The adsorption of carbon monoxide was intermediate in amount between that of nitrogen and that of carbon dioxide. For all four gases, the adsorption isotherm is better represented by $\log \alpha/P=A_0-A_1\alpha$ than by the more usual Freundlich equation. At very low pressures the value of $A_1\alpha$ is negligible compared with that of A_0, and the relationship between α and P is linear.

A. B. Manning.

Adsorption. VII. Adsorption of mixtures of carbon dioxide and hydrogen by wood charcoal. A. Magnus and H. Roth (Z. anorg. Chem., 1926, **150**, 311—325).—At 123° and 148·7°, from a mixture of carbon dioxide and hydrogen, the volume of carbon dioxide adsorbed is proportional to its partial pressure, but at lower temperatures this is the case only at low partial pressures, thus at 0° only up to 7%. The adsorption of hydrogen is proportional to its partial pressure over the whole range at 0°, but at higher temperatures the adsorption passes through a maximum and then decreases with increasing partial pressure. This maximum occurs at progressively lower pressures as the temperature increases, and at 148·7° is at 70%. The influence of temperature is not in close agreement with the adsorption equations of Lorenz and Landé or of Eucken. At lower temperatures, the constant derived from each equation drifts with the temperature; at the higher temperatures, there is no drift, but there are still considerable variations.

A. Geake.

Adsorption. VIII. Heat effect of the absorption of carbon dioxide by wood charcoal. A. Magnus and M. Brauer (Z. anorg. Chem., 1926, **151**, 140—152).—The heat evolved when carbon dioxide is absorbed by wood charcoal has been measured at temperatures of 16—40° and at various pressures. At constant temperature, it diminishes with increasing pressure, and at constant pressure with rising temperature. The maximum variation was from 6250 cal./mol. when the pressure during absorption rose from 678 to 757 mm. (at 19·9°) to 10,030 cal. when the pressure range was 0—9 mm. (at 22·2°). The temperature coefficient rises from 3·9 cal./mol. per degree at 194 mm. pressure to 5·55 at 444 mm. The index $1/n$ in Freundlich's formula $v=v'p^{1/n}$, where v' and v are the volumes adsorbed when the pressure is unity and p, rises slightly with the temperature. The results agree better with the Lorenz–Landé theory than with that of Eucken.

A. Geake.

Active carbon. VI. Theory of adsorption by carbon. O. Ruff (Kolloid-Z., 1926, **38**, 174—177; cf. A., 1925, ii, 1125).—The author's views on the structure of active carbon are developed. The centres of adsorption are the unsaturated, unoriented atoms or atomic complexes which are present in all amorphous carbons together with saturated atoms and mineral residue. Whenever these unsaturated groups are present on the surface, the carbon is active. Such unsaturated atoms may be covered by a thin skin of saturated carbon, in which case the observed adsorption is explained on the basis of Eucken's and Pólányi's theory, whilst adsorption in the former case (directly on the unsaturated groups) is interpreted in accordance with Langmuir's theory. A mechanism is suggested for the formation of the skin of saturated carbon by carbonisation. Various properties of active and inactive carbon are discussed and considered to be in agreement with the above hypotheses.

L. L. Bircumshaw.

Adsorption. I. Adsorption by coconut charcoal from alcohol–benzene and acetone–benzene mixtures. F. G. Tryhorn and W. F. Wyatt (Trans. Faraday Soc., 1925, **21**, 399—405).—See this vol., 19.

Adsorption by coconut charcoal of saturated vapours of pure liquids. II. F. G. Tryhorn and W. F. Wyatt (Trans. Faraday Soc., Feb., 1926, advance proof).—The adsorption of a number of organic substances by coconut charcoal has been studied by direct weighing of the charcoal suspended in air saturated with the vapour of the pure liquid. Adsorption is at first rapid and depends on the rate of diffusion of the vapour determined by $p/\sqrt{M}$, where p and M are the vapour pressure and mol. wt. of the liquid, respectively. After a time interval which increases as p diminishes, no further increase of weight with time is observed. The rates of adsorption, plotted against time, show, in general, a sharp discontinuity at a certain point, and this cannot be attributed to any of the usual factors which influence adsorption. The explanation adopted is that adsorption leads to an increase of density in the surface layers of charcoal, which at saturation gives rise to a liquid film. The formation of liquid accounts for the observed discontinuity, and leads to a sudden decrease in the rate of adsorption. The theory is upheld by microscopical observation of the adsorption of benzene by a piece of charcoal, and by the observation that the velocities of adsorption at the break points are in the same order as the corresponding values of $p/\sqrt{M}$.

C. H. D. Clark.

Stages in adsorption by coconut charcoal from mixed vapours. III. F. G. Tryhorn and W. F. Wyatt (Trans. Faraday Soc., Feb., 1926, advance proof).—The adsorption of alcohol–benzene and acetone–benzene mixtures has been studied by placing various liquid mixtures of known composition in a small test-tube in sealed tubes together with charcoal at 20°, examining the composition of the adsorbed phase at different intervals. The curves which represent the number of mols. of each liquid adsorbed as a function of the total number of mols. adsorbed consist of three distinct portions. In the first and last stages, the liquids are adsorbed in constant ratio, and the adsorption is represented in each case by two approximately straight lines. The intermediate stage, marked at both ends by sharp breaks, shows no increase in the total number of mols. adsorbed, but benzene is found to displace alcohol or acetone.

During the first stage, adsorption of each liquid occurs at a rate which depends on the value of $p/\sqrt{M}$.

The first break is attributed to the appearance of liquid the composition of which is different from that of the liquid in bulk, so that during the second stage adjustment occurs to establish equilibrium. It is actually found that the ultimate composition differs from that of the liquid in bulk, but this is explained by selective adsorption by the charcoal. During the third stage, isothermal distillation of liquid occurs into the internal spaces of the charcoal. This behaviour is due to the curvature of the liquid surfaces exposed on and between the grains, the vapour pressure over a concave surface being less than that over a flat surface. C. H. D. CLARK.

Sorption of vapours by alumina. L. A. MUNRO and F. M. G. JOHNSON (J. Physical Chem., 1926, **30**, 172—188; cf. Pearce and Alvarado, A., 1925, ii, 381; Perry, this vol., 19; Munro and Johnson, A., 1925, ii, 191).—The adsorption of water vapour by alumina has been studied, at various concentrations and temperatures, by a dynamic method more accurate than that previously used. The alumina gel was obtained from an aqueous solution of the nitrate by precipitation with concentrated ammonia, dried at 100°, and heated to 300°. Results are better expressed per g. of active Al_2O_3 than per g. of sorbent (Al_2O_3,xH_2O). Data for temperatures of 80°, 60°, 50°, and 40° with partial pressures of vapour from 72·7 to 23·5 mm. are given. The sorption curves for 80°, 60°, and 50° (lower portion) resemble those obtained in gas–charcoal and gas–silica gel systems. The isotherm for 40° changes direction and flattens as the partial pressure of the vapour approaches the vapour pressure of the liquid at the temperature of the alumina. The equations of both Freundlich and Patrick apply to the isotherms for 80° and 60°; Trouton's sorption rule (A., 1906, ii, 333) also holds approximately. The curves showing the relative rates of sorption of water by alumina at 50° for different concentrations resemble those obtained by Harned (A., 1920, ii, 292) for the adsorption of gases by charcoal. The efficiency of the alumina as sorbent is also discussed. L. S. THEOBALD.

Absorption of gases by colloidal solutions. A. GATTERER (J.C.S., 1926, 299—316).—The solubilities of carbon dioxide and acetylene in ferric ferrocyanide and ferric hydroxide sols are recorded between 5° and 25°. Carbon dioxide is more soluble in these sols than in water; the reverse holds for acetylene (cf. Findlay and Howell, A., 1915, ii, 258; Geffcken, A., 1904, ii, 708). The temperature coefficient of absorption at a given temperature varies, with increasing concentration, as the absorptive power of the colloidal solution for the gas. The results indicate that some factor other than absorption is involved. Dispersion has a slight influence; the absorptive power of less highly-dispersed systems is depressed at higher temperatures by an amount which depends on the specific surface of the colloid and the quantity of peptising agent present. The high solubility of carbon dioxide in colloidal ferric hydroxide may be explained by the formation of the complex $\{[x\mathrm{Fe(OH)_3}]y\mathrm{Fe}\}_2(y\mathrm{CO_3})_3$. The sols used were characterised by the measurement of certain physical properties. S. K. TWEEDY.

Mechanism of the adsorption of ions. R. AUDUBERT and (MLLE.) M. QUINTIN (J. Chim. phys., 1926, **23**, 176—196).—A fuller account of work already published (cf. A., 1925, ii, 384).

Influence of the electric field on the adsorption of neutral molecules. A. FRUMKIN (Z. Physik, 1926, **35**, 792—802).—Curves are given showing the surface tension of mercury plotted against the corresponding potentials between the mercury and the solution, and the effect on the shape of the curves produced by the addition of substances such as amyl alcohol. A quantitative theory is developed for the influence of the electric field on the adsorption of the neutral molecule. E. B. LUDLAM.

Determination of the adsorption of ions on colloidal particles by means of Donnan's membrane equilibrium theory. H. RINDE (Phil. Mag., 1926, [vii], **1**, 32—50).—An attempt has been made to determine the values of the hydrogen-ion activity on opposite sides of a collodion membrane separating a sulphur sol in dilute hydrochloric acid solution from dilute hydrochloric acid alone, for sols of different particle size, and for concentrations of acid up to 0·5*N*. From the results the concentration of the anions adsorbed by the sulphur sol has been calculated on the basis of Donnan's theory. Measurements of the osmotic pressure of the system at equilibrium and of the corresponding membrane potential were made. The sulphur sols, containing 8—34 g. per litre, were prepared by Raffo's method (A., 1908, ii, 683), purified by coagulation and resolution, and graded by fractional coagulation. The hydrogen-ion activity was determined by Biilmann's quinhydrone electrode, other methods, *e.g.*, the ordinary hydrogen electrode and the use of indicators, failing in the presence of the sulphur sol. The membrane potential has its highest value when the acidity of the colloid is small, decreasing when the acidity rises and approaching zero. The curve for osmotic pressure against acidity has the same shape as the membrane potential curve, but approaches a certain positive value instead of zero. This should correspond with the osmotic pressure of the colloid particles themselves, but the values are actually in the reverse order to that expected from an ultramicroscopic examination of the sols. All the calculated osmotic pressures are many times larger than the observed. It thus appears impossible to calculate either the size of the particles or the membrane equilibrium from the osmotic pressure. The adsorption of the chlorine ions by the sulphur particles varies with the concentration of unadsorbed ions in accordance with Langmuir's theory. The same theory is shown to be applicable to Loeb's results on the osmotic behaviour of proteins. Attention is directed to a number of errors in a recent paper by Bjerrum (A., 1925, ii, 111) on the osmotic pressure and membrane potential of colloidal chromium hydroxide.
A. B. MANNING.

Quantitative adsorption analysis by Wislicenus' method. R. LORENZ (Kolloid-Z., 1926, **38**, 124—126).—The shaking and filtering methods for studying adsorption are compared, and it is shown that

the filtering method is better adapted for the investigation of many natural processes. Wislicenus' automatic apparatus is described. Fibrous alumina is recommended as adsorbent, and the solution under investigation should be used in concentrations of 0·1—0·4%. The use of the apparatus in the domain of plant physiology is discussed.

L. L. BIRCUMSHAW.

Adsorption. XII. Explanation of positive and negative acclimatisation; influence of hydrolysis and of precipitating electrolytes on the coagulation of arsenious sulphide sols. S. GHOSH, A. K. BHATTACHARYA, and N. R. DHAR (Kolloid-Z., 1926, **38**, 141—151; cf. Ghosh and Dhar, A., 1925, ii, 386, 511, 778).—The fact that the actual amount of univalent electrolyte (potassium chloride or nitrate etc.) required to coagulate Prussian-blue and arsenious sulphide sols in presence of strong acids, is less than the calculated amount, has been ascribed to the diminution of hydrolysis in presence of these acids, with consequent decrease of peptisation (*loc. cit.*). Further experiments on the coagulation of arsenious sulphide sols by mixtures of electrolytes support this explanation. It was observed that the hydrolysis of the coagulating electrolyte has a pronounced influence on the coagulation of the sol, and that in presence of sodium benzoate, sodium nitrite, etc., more than the calculated quantity of potassium or barium chloride is required for precipitation. Smaller quantities of crystal-violet, strychnine, or quinine hydrochloride are required to coagulate arsenious sulphide sol if the electrolyte is added slowly than if it is added rapidly. This phenomenon depends on the adsorption of ions carrying the same charge as the sol, and may be termed "negative" acclimatisation, in contrast to the "positive" acclimatisation obtained with strong electrolytes. It is maintained that abnormal behaviour on dilution and towards electrolytes, increase of velocity of the colloid particles in an electric field by addition of small quantities of certain electrolytes, and the phenomenon of marked positive acclimatisation are mainly to be traced to the stabilisation of the sol by adsorption of ions carrying the same charge. L. L. BIRCUMSHAW.

Nature of the interfacial layer between an aqueous and a non-aqueous phase. F. L. USHER (Trans. Faraday Soc., 1925, **21**, 406—424). —See this vol., 20.

Structure of thin films. VII. Critical evaporation phenomena at low compressions. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1926, **A**, **110**, 423—441; cf. A., 1925, ii, 32).—The apparatus and technique for measuring the pressure exerted by films on a water surface with an accuracy of 0·01—0·02 dyne/cm. are described. The pressure on a copper foil float 11 cm. long is balanced by the torsion of a fine wire with an accurately graduated divided head, the calibration of which in absolute measure is effected by hanging weights on a small balance mounted on the wire. To prevent leakage past the float, the ends of the latter are attached by very thin strips of gold ribbon to brass pieces pressed tightly against the walls of the trough. The substance to be investigated (dissolved in light petroleum) was placed on a clean water surface by means of a very fine dropping pipette, and as soon as the solvent had evaporated and a steady pressure was attained, the latter was read. The surface pressure of a unimolecular film has been determined as a function of the surface concentration for a number of fatty acids, esters, alcohols, and nitriles at the ordinary temperature. For areas greater than 5000 Å.^{2} per molecule, the pressures (F) tend to a value within 25% of that given by $Fa=RT$, R having the same value as for a perfect gas. Between 100 and 5000 Å.^{2}, the pressure–area isothermals closely resemble the ordinary pressure–volume isothermals for a liquid and its vapour. With longer chains in the molecule there is a horizontal "vapour-pressure" region, terminating on the one hand in an imperfect gaseous film and on the other in either the condensed or the expanded type of film. When the chains are shorter, a condition which corresponds with a higher temperature, the "vapour-pressure" region disappears, and the films are above their "critical point." Expanded films are analogous to liquids, and there is considerable cohesion between the molecules in them.

A. B. MANNING.

Spreading of solids on water surfaces. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1926, **A**, **110**, 441—443; cf. preceding abstract).—Cary and Rideal's observations on the spreading of myristic acid on water (A., 1925, ii, 1046) have been continued down to very low compressions. A small pressure, that of the "gaseous" state of the films, is set up within a few seconds after the crystal touches the surface, and the "two-dimensional vapour pressure" very soon afterwards. After remaining constant at this value for some minutes, the pressure finally rises very rapidly.

A. B. MANNING.

Spreading of one liquid on the surface of another. R. S. BURDON (Proc. Physical Soc., 1926, **38**, 148—160).—The spreading of water and solutions of inorganic salts on mercury has been examined. Purest "conductivity" water spreads very slowly on clean mercury, but spreading is accelerated by traces of acid and totally inhibited by traces of alkali in solution. Solutions of neutral salts and acids spread rapidly, and in consequence of absorption of carbon dioxide, alkaline solutions are found to spread after some time. Electrostatic fields up to 4000 volts/cm. applied perpendicular to the surface produce no results, but small potentials applied to electrodes in contact with the mercury and the drop cause spreading when the mercury is positive, and inhibit it when the mercury is negative. The method of photographing films on mercury surfaces is described. C. J. SMITHELLS.

Foaming power and surface tension. O. BARTSCH (Kolloid-Z., 1926, **38**, 177—179; cf. Koll.-Chem. Beihefte, 1925, **20**, 1; A., 1924, ii, 832).—The view expressed by Ostwald and Steiner (A., 1925, ii, 771) that there is no necessary relationship between foaming power and lowering of surface tension is disputed. A determination of the surface tension–concentration curves and foam stability–concentration

curves for a number of alcohols and fatty acids in water shows that the foam stability increases up to the point where the surface tension lowering is practically a maximum, and then decreases rapidly. Thus foaming power is lost if the surface-active substance is added in excess. This behaviour is explained by the heterogeneity theory, which postulates a maximum of foaming power when equal numbers of solvent and solute molecules are present in the surface layer. The essential condition for the formation of foam is a surface film in which the concentration of the dissolved substance is different from that in the body of the solution. The behaviour of lyophilic colloids, and the influence of solid particles on foam stability, are briefly discussed.

L. L. BIRCUMSHAW.

Growth and dissolution of crystals. M. VOLMER and G. ADIKARI (Z. Physik, 1925, **35**, 170—176).—The growth of crystals has been examined by means of a micro-kinematograph. Crystals from supercooled benzophenone were found to be projected outside the surface of the liquid. The observations suggest the existence of an adsorption layer of molecules on the face of the crystal; these molecules are in a state which is intermediate between those which are characteristic of solutions and crystal lattices. The molecules are displaced along the surface in directions which are determined by the direction of crystal growth. E. B. LUDLAM.

Permeability of membranes. K. C. SEN (J. Indian Chem. Soc., 1925, **2**, 289—292).—Colloidal copper ferrocyanide is precipitated by alcohols in the presence of small quantities of electrolytes. The purer and more dilute the sol, the greater is its stability towards alcohols. The concentration of alcohol necessary for coagulation is considerable: in the case of 60% ethyl alcohol, coagulation occurred in an hour (cf. A., 1925, ii, 664). The higher the mol. wt. of the alcohol the greater is its precipitating power. It is suggested that this coagulation explains why a copper ferrocyanide membrane is rendered permeable to sugar by the presence of alcohol. R. W. WEST.

Permeability of nickel to hydrogen. Influence of pressure. V. LOMBARD (Compt. rend., 1926, **182**, 463—465; cf. A., 1923, ii, 570).—The rate of passage of hydrogen, under 770 mm. pressure, through nickel discs of various thicknesses (from about 0·2 to 1·0 mm.) has been determined. The permeability, d, is related to the thickness, h, by an expression of the type $d=K/a^h$, where K and a are constants.

F. G. TRYHORN.

Ionic permeability of membranes. VII. Permeability of the collodion membrane to multivalent cations. L. MICHAELIS and A. FUJITA (Biochem. Z., 1925, **164**, 23—30).—The permeability of a collodion membrane is by far the greatest for hydrogen ions, then after large intervals come the ions of rubidium and potassium, then sodium, and finally lithium. It is practically impermeable to all bi-, ter-, and quadri-valent cations and even univalent anions. It is probable that it is more permeable to the hydroxyl ions than to the other anions.

P. W. CLUTTERBUCK.

Separation of crystalloids from one another by dialysis. L. KAHLENBERG (Phil. Mag., 1926, [vii], **1**, 385—394).—A number of mixtures of crystalloids have been separated by dialysis in pyridine solution with a rubber membrane. In every case, the substances chosen were such that one was soluble in both pyridine and hydrocarbons, whilst the other was soluble only in pyridine. The one soluble in hydrocarbons passed through the rubber. Mixtures of carbamide with sucrose, maltose, lactose, galactose, dextrose, and lævulose, respectively, in aqueous solution have been separated by dialysis with a copper ferrocyanide membrane. In all cases, the carbamide passed through the membrane. Membranes composed of "lanoline" impregnated on silk have been employed successfully for the separation of various pairs of substances in aqueous solution. The results are attributed to the selective absorption by the cholesterol present in "lanoline," and it has been shown also that phytosterol possesses the same selective adsorptive properties. Animal oils containing cholesterol and plant oils containing phytosterol have been shown to possess selective osmotic properties. It is suggested that living cells owe their selective osmotic properties to extremely delicate films of these sterols. Of all the substances tested carbamide passes most rapidly through these membranes.

A. E. MITCHELL.

Silver chromate rings in silicic acid gel. E. HATSCHEK (Kolloid-Z., 1926, **38**, 151—154).—Well-defined rings are formed on addition of 20—25% silver nitrate solution to a gel obtained by adding 10 c.c. of sodium silicate solution (d 1·555) to 100 c.c. of a 4% sodium dichromate solution. This is inconsistent with the view held by Dhar and Chatterji (A., 1925, ii, 959) that silver chromate rings cannot be obtained in silicic acid gel. Microscopical examination shows that the rings consist of two modifications of silver chromate: red or yellow needles, and larger crystals, bluish-violet in colour. The remarkable fact is observed that many rings lie in the still yellow-coloured gel, and therefore the complete exhaustion of the reacting component in the gel under the last ring is not a necessary condition for the formation of another ring. This is in disagreement with Bradford's theory (Biochem. J., 1916, **10**, 169), and with theories which postulate a "membrane" formation, such as that of Fischer and McLaughlin (A., 1922, ii, 206), and of Traube and Takehara (A., 1924, ii, 834), but not with Ostwald's theory (cf. A., 1925, ii, 530).

L. L. BIRCUMSHAW.

Microcryoscopy: molecular weight determination in trinitrotoluene. I. PASTAK (Bull. Soc. chim., 1926, [iv], **39**, 82—83).—Trinitrotoluene may be used in place of camphor for microcryoscopic mol. wt. determinations by the method of Rast (A., 1923, ii, 57, 312), but Rast's experimental methods require modifying as follows. Known weights of the given substance and of trinitrotoluene are melted together and then ground, the process being repeated several times to give a homogeneous mixture. Capillary tubes are filled with the mixture and with pure trinitrotoluene, respectively, and the

difference in m. p. determined by slow uniform heating in the usual apparatus. By this method, the lag of the thermometer is constant and does not affect the lowering of f. p. from which the mol. wt. is calculated. Trinitrotoluene is specially suitable for polynitro-compounds. W. HUME-ROTHERY.

Theory of molecular weight determinations in mixed solvents. C. WAGNER (Z. physikal. Chem., 1926, **119**, 53—58).—Theoretical (cf. Drucker and Weissbach, A., 1925, ii, 953). L. F. GILBERT.

Internal friction and density of mixed aqueous solutions of salts and acids. W. GRUNERT (Z. anorg. Chem., 1926, **151**, 309—312; cf. A., 1925, ii, 859).—The density and internal friction of solutions of hydrochloric and nitric acids at 20° are increased by addition of sodium chloride and potassium nitrate, respectively, by amounts proportional to the amount of salt added over the whole concentration range examined. Mixtures of sulphuric acid and ammonium sulphate at 20°, 40°, 60°, and 80° behave in this way in respect to density, but the rate of increase of internal friction increases slowly with the sulphuric acid concentration until this corresponds with complete conversion of the sulphate into hydrogen sulphate, after which it remains constant. These mixtures show the greatest rate of increase of internal friction, and the hydrochloric acid–chloride mixtures the least. R. CUTHILL.

Dielectric constants of solutions of electrolytes. R. T. LATTEY (Z. physikal. Chem., 1926, **119**, 104—106).—A reply to incidental criticism by Walden, Ulich, and Werner (A., 1925, ii, 512). Attention is directed to an apparent error in one of their calculations. L. F. GILBERT.

[Dielectric constants of solutions of electrolytes.] P. WALDEN, H. ULICH, and O. WERNER (Z. physikal. Chem., 1926, **119**, 107—110; cf. preceding abstract).—The validity of Lattey's calculation is acknowledged, but the authors' values for the dielectric constants of solutions of electrolytes (A., 1925, ii, 773) are only very slightly affected by the application of the corrections entailed.
L. F. GILBERT.

Molten salts as solvents for strong electrolytes. P. GROSS (Z. anorg. Chem., 1926, **150**, 339—342).—The anomalous behaviour of electrolytes in solvents of low dielectric constant is probably due to the correspondingly large force between the ions. The assumption that highly dissociated molten salts have high dielectric constants is improbable, because concentrated aqueous solutions of strong electrolytes such as lithium chloride have lower dielectric constants than water. The activity of ions in aqueous solution depends on the total ion concentration; in a dilute solution with a molten salt as solvent this will be practically constant, and the activity will therefore be independent of the concentration of the solute.
A. GEAKE.

Nickel sulphide sols. I. P. C. L. THORNE and E. W. PATES (Kolloid-Z., 1926, **38**, 155—158).—The investigation was undertaken with a view to establish the conditions for the stability of the brown nickel sulphide sol which is frequently obtained during analysis. By addition of nickel sulphate solution to excess of ammonium sulphide solution in sealed vessels, a stable sol is formed if the nickel concentration lies between 0·08 and 0·01 g. per litre. The colloidal nature of the brown liquid may be proved by ultrafiltration by means of collodion membranes. The sol is also formed by passing excess of hydrogen sulphide through a solution of nickel hydroxide in ammonia. The sol varies in colour from black to light brown, according to the proportion of nickel sulphide, and is characterised by marked stability. The action of atmospheric oxygen causes slow coagulation. Cataphoresis shows that the particles are negatively charged. The slow development of the brown colour is considered to be due to the slow growth of the particles, and may also be connected with the fact that nickel sulphide occurs in three modifications (cf. Thiel and Gessner, A., 1914, ii, 277).
L. L. BIRCUMSHAW.

Physico-chemical properties of solutions of germanium dioxide [and arsenic trioxide]. W. A. ROTH and O. SCHWARTZ (Ber., 1926, **59**, [*B*], 338—348).—Germanium dioxide gives colloidal solutions with negatively charged particles in water and also very faintly acidic, true solutions; it is the only solid dioxide of the group which exhibits the latter property. For solutions prepared as far as possible out of contact with glass and containing 4·0—0·23 g. of germanium dioxide in 1000 g. of solution, the constant increment of d_{18}^{18} is $(80{\cdot}6\pm0{\cdot}3)\times10^{-5}$ per g. of germanium dioxide in 1000 g. of solution. The molecular volume of dissolved germanium dioxide is calculated to be 20·2 c.c., whereas the corresponding figure for the solid state is 22·24 c.c. The atomic refraction of germanium is found to be about 8·9 from observations on the densities of its solutions and their refractive index determined by the aid of Löwe's interferometer. This value agrees with that derived from observations with germanium bromide or germanium tetraethyl, but differs widely from that (about 1·6) derived from the tetrachloride. In comparison with the refractive indices of the tetrachlorides of carbon, silicon, and tin, that of germanium tetrachloride appears low. The specific conductance of solutions of germanium dioxide saturated at low temperatures leads to the value $1{\cdot}2\times10^{-7}$ for the dissociation constant; constant values are not obtained with solutions which have been saturated at a higher temperature, but their conductivity is greater than that of cold saturated solutions. The most concentrated aqueous solution of germanium dioxide is about $N/35$ at 18° and $N/50$ at 0°. The molecular depression of the f. p. is 1·83—1·85° over the whole range of concentration. Even in the most dilute solutions which can be examined cryoscopically, arsenious oxide, which in many respects resembles germanium dioxide, is weakly associated and, in addition, converted almost completely into $HAsO_2$ or H_3AsO_3. H. WREN.

Colloid chemistry of bismuth. A. GUTBIER (Z. anorg. Chem., 1926, **151**, 153—156).—Colloidal solutions of bismuth may be obtained by reducing

bismuth nitrate–glycerol solutions with sodium hyposulphite or with sodium hydroxide and formaldehyde. Such solutions are dark brown by transmitted light; they are re-oxidised by air, but may be dialysed under liquid paraffin. If reduced with sodium hyposulphite, the solution is rapidly, completely, and irreversibly coagulated when heated or when concentrated in a vacuum. If reduced with formaldehyde, the dialysed solution may be concentrated on a water-bath to a viscous mass containing 5·4% of bismuth. A. GEAKE.

Preparation of colloidal silver by electrolysis. A. LOTTERMOSER and S. BAUSCH (Z. Elektrochem., 1926, **32**, 87—92).—An investigation of the conditions affecting the formation of silver and silver oxide sols by electrolysis, with special reference to the influence of protective colloids. The sol formed at the cathode when silver nitrate is electrolysed between platinum electrodes in a U-tube (cf. Billitzer, A., 1902, ii, 454) is found to consist of silver oxide. Billitzer stated that the sol was stabilised by adding gelatin, but the action is found to consist in a partial reduction of silver oxide to silver by the gelatin in presence of light. The presence of silver in the sols formed by the electrolysis of silver salts is always due to some secondary process. With alternating current and silver electrodes it is found that the electrolyte plays no essential part in the silver sol formation. In further experiments in which sodium hydroxide solutions were electrolysed between silver electrodes, by the use of both direct and alternating current, it was found that the initial degree of dispersion of the sols formed is greater in presence of a protective colloid. Colloid formation is promoted by the heat liberated by the current and by the evolution of gas from the electrodes. The dark brown sols obtained under these conditions consist of silver and silver oxide, and may be stabilised by previous addition of sodium silicate, the action of which is attributed to the silicic acid formed by hydrolysis. Using direct current, a layer of oxide is formed on the anode, and a disperse system containing silver oxide with a little silver is formed. The presence of the latter is due to reduction by cathodic hydrogen, the process being assisted by stirring the electrolyte. C. H. D. CLARK.

Apparent viscosity of colloidal solutions and a theory of neutral colloids as solvated micelles capable of aggregation. J. W. MCBAIN (J. Physical Chem., 1926, **30**, 239—247; cf. Trans. Faraday Soc., 1924, **20**, 22—24).—Mechanical explanations of the high viscosity of colloidal solutions are discussed. The order of magnitude of the apparent viscosity of dilute "nitrocotton" solutions is such that it cannot be ascribed to simple massive particles according to the views of Einstein (Ann. Physik, 1906, [iv], **19**, 289) and Hatschek (A., 1913, ii, 559). Neither solvation nor the assumption of a film of solvent enveloping each particle is adequate as an explanation, and the impossible assumption that the whole volume of the solution is to be ascribed to the particles also fails to explain the viscosities observed. The high viscosities are attributed to the increased shear which is imposed on the solvent when the small rigid colloidal particles or micelles cohere to form open or loose aggregates suspended in the solvent. These structures practically immobilise the solvent which they embrace, and this involves interference between the particles and deformation when the solution is made to flow. The highest viscosity slopes do not reflect high solvation, but rather insufficient solvation to disintegrate the particles. Viscous sols such as "nitrocotton" do not exhibit true viscous flow. The flow is dependent, in such cases, on the type of viscosimeter, and the apparent viscosity is influenced by the rate of shear. Experiments with "nitrocotton" in benzylformanilide at 25°, in ethylformanilide at 55°, and in a mixture of phenylbenzylurethane and phenylurethane at 55° show that strict proportionality between efflux and shearing stress is not obtained.

In the author's theory of neutral colloids as solvated micelles capable of aggregation, the linking up of the micelles to form larger structures is accomplished by forces which are as local and specific as those operative in adsorption or in residual affinity. Substitution in the particles by various substances, particularly by mixed solvents, loosens these linkings. Solvation becomes the essential factor in gelatinising and dissolving "nitrocotton" and in explaining the apparent viscosity of the resulting systems. The efficiency of a solvent will depend on the dismemberment brought about, and in the poorer solvents this dismemberment is less complete, with a resulting higher viscosity.

L. S. THEOBALD.

Influence of hydrogen-ion concentration on the viscosity and elasticity of gelatin solutions. H. FREUNDLICH and H. NEUKIRCHER (Kolloid-Z., 1926, **38**, 180—181; cf. Freundlich and Schalek, A., 1925, ii, 112).—An investigation has been made by Hess' method of the behaviour of 0·5% gelatin solutions of varying acidity. The p_H of the solutions, varied by addition of 0·001*N*- to 0·5*N*-hydrochloric acid, was measured by means of a quinhydrone electrode. From the curves obtained, which show deviation from Poiseuille's law, the viscosity and elasticity of the solutions were derived. Both quantities show a minimum in the neighbourhood of the isoelectric point (p_H 4·7) and a maximum on the acid side. L. L. BIRCUMSHAW.

Method for rendering visible molecular aggregates of albumin and other submicroscopic structures. H. BECHHOLD and L. VILLA (Biochem. Z., 1925, **165**, 250—260).—The system *Bacillus coli*–egg-albumin in solution is treated with excess of gold chloride and potassium carbonate solutions, the excess being removed by washing on an ultrafilter. The gold fixed by the protein or micro-organism remains as a nucleus after burning on a slide, and this is intensified until visible in the ultramicroscope by treatment with gold chloride, potassium carbonate, and ferricyanide solution followed by formaldehyde. It is computed that each albumin particle consists of about 50 albumin molecules and that each particle, before intensification, had a minimal diameter >4 but <10 μμ. P. W. CLUTTERBUCK.

Colloid charge. R. KELLER (Kolloid-Z., 1926, **138**, 158—165).—It is emphasised that the charge on

a colloid particle results from the difference in the dielectric constant of the disperse phase and the dispersion medium, and is an intrinsic property of the particular system considered, the influence of adsorbed ions being greatly exaggerated. The colloid charge is supposed to reside in the dispersion medium. The definition of the p_H of colloidal solutions in terms of the ionic product of pure water is erroneous, since the dielectric constant of the solution differs from that of water. The state of the system is described more accurately by the determination of its hydrogen-ion concentration by electrometric methods.

L. L. BIRCUMSHAW.

Electric charge of colloid particles. W. REINDERS (Chem. Weekblad, 1926, **23**, 130—134).—A summary and discussion of recent work.

S. I. LEVY.

Variation of the charge of colloidal particles with concentration of electrolytes. I. Arsenious sulphide sol and acids. J. N. MUKHERJEE and S. G. CHAUDHURY (J. Indian Chem. Soc., 1925, **2**, 296—309).—Migration velocity measurements show that the variation of the charge of colloidal arsenious sulphide with different concentrations of acid depends on the nature and method of preparation of the sols. Simple behaviour is exhibited only by sols which contain excess of arsenious acid; the irregularities observed in other cases are attributed to interaction between polythionic acids and hydrogen ions present in the sols (cf. Murphy and Mathews, A., 1923, ii, 156). Acetic and formic acids lower the charge to a greater extent than oxalic and hydrochloric acids. The smaller dielectric constants of acetic and formic acids cause an increase in the electrical adsorbability with a corresponding decrease in the charge. It is found that the order of the coagulating power of these acids is the reverse of the capacity to diminish the charge. This is attributed to the diminution of the dielectric constant. R. W. WEST.

Equilibrium in colloid systems. O. K. RICE (J. Physical Chem., 1926, **30**, 189—204; see Tolman, A., 1913, ii, 488).—A theoretical paper in which the phase rule is deduced in a form applicable to colloid systems. By its use it is inferred that with both charged and uncharged particles equilibrium exists only if the particles are of one size, or of a few definite sizes. In an examination of the stability of the equilibria, two types, temporary and permanent, have been found. The relation between these and the conditions of stability are considered in detail. Coagulation is also discussed. L. S. THEOBALD.

Relation between properties and chemical composition of soil colloids. M. S. ANDERSON and S. E. MATTSON (Science, 1925, **62**, 114—115).—The various properties of the colloidal material from different soils are more or less related; they also appear to be related to the chemical composition. Data suggesting a correlation between the molecular ratio $SiO_2 : (Al_2O_3+Fe_2O_3)$, the heat of wetting, and the adsorption of ammonia are tabulated.

A. A. ELDRIDGE.

Optical behaviour of fibrous alumina. W. KRAUSZE (Koll. Chem. Beihefte, 1926, **21**, 282—304; cf. Wislicenus, A., 1908, ii, 261).—The double refraction of fibrous alumina shows a minimum value when the fibres are filled with a liquid of refractive index about 1·53. This residual double refraction is positive with reference to the direction of growth of the crystals. This may be due either to difference in dispersive power of the fibres and the liquid or to the fibres themselves. Fibres in the interstices of which various substances have been allowed to crystallise have also been examined. Colouring the crystals with methylene-blue, iodine, gold, silver, and mercury produces dichromatism, and, except in the case of methylene-blue, affects the double refraction.

R. CUTHILL.

Colloid chemistry of urine: an example of a clinical dispersoid analysis. F.-V. VON HAHN (Kolloid-Z., 1926, **38**, 136—138).—A linear relationship exists between the surface activity and density of normal urine. Defining 1 Graham (*Gh*) as the surface activity due to a reduction of the surface tension of the solvent by 1%, it is found that $Gh = 0{\cdot}69(d-1{\cdot}004)$. There is also a clear connexion between surface tension and colour intensity in normal urine, between viscosity and density, between viscosity and optical activity, and between surface activity and optical activity. No evidence is available for the existence of a connexion between surface activity and viscosity, and the relationship found by Lichtwitz between colloid content, surface tension, and viscosity is shown to be erroneous, since it rests on the assumption that the whole of the surface active constituents of urine are in the dispersoid condition, which is not the case. L. L. BIRCUMSHAW.

Combination of salts and proteins. II. Determination of the concentration of combined ions from membrane potential measurements. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1926, **9**, 351—360).—A method is described for the measurement of membrane potentials of gelatin–salt solutions, from which, together with analysis of the solutions, the concentration of ions combined with the protein may be calculated. The values so obtained for the chlorides of hydrogen, lithium, potassium, and zinc are in good agreement with those obtained by direct concentration cell measurements.

C. P. STEWART.

Electrolytic concentration of protein solutions and hydrophile colloids. J. REITSTÖTTER and G. LASCH (Biochem. Z., 1925, **165**, 90—95).—Using a three-chambered cell, it is possible to achieve a ten-fold concentration of the colloid with the elimination of electrolytes. C. RIMINGTON.

Alteration of albumin by heat. M. SPIEGEL-ADOLF (Kolloid-Z., 1926, **38**, 127—129; cf. A., 1925, ii, 199).—Earlier work on the globulins has been extended to serum-albumin. It is found that pure serum-albumin coagulates completely on heating. By the action of dilute alkali or acid, this coagulate regains its solubility in water, partly or completely, according to the proportion of acid or alkali to albumin, and the water-soluble albumin thus obtained cannot be

distinguished from ordinary albumin, either by physico-chemical or by biological means. When albumin is heated in presence of acid or alkali, it retains its solubility in water; whether this is partial or complete, depends on the proportion of acid or alkali to albumin. The effect of addition of neutral salts on the behaviour of acid- or alkali-albumin when heated can be observed only when the salt is added before heating, independently of whether the albumin is denatured or still water-soluble. The results obtained appear to support the "ring-formation" theory advanced by Hofmeister, Pauli, and others. L. L. BIRCUMSHAW.

Physical chemistry of globulins. VII. Effect of addition of salts to acid- and alkali-globulin. M. ADOLF (Koll. Chem. Beihefte, 1926, **21**, 241—281; cf. A., 1925, ii, 199).—*E.M.F.* measurements show that addition of salt always reduces the hydrogen-ion activity in an acid-globulin solution by an amount which increases with increasing valency of the salt anion, but decreases with increasing valency of the salt cation. The acid reaction never disappears, however. Addition of salts to an alkali-globulin solution reduces the hydroxyl-ion activity, and the solution may ultimately become acid. The conductivities of mixed solutions of salts with acid- and alkali-globulins is less than the sum of the conductivities of the components to an extent which appears to depend on the valencies of the salt ions. Addition of a salt to solutions of either globulin reduces and may destroy the mobility of the protein ion. In the case of acid-globulins, this effect increases with increasing valency of the salt anion, and decreases with decreasing valency of the salt cation; alkali-globulins show the opposite behaviour. Measurements of chloride-ion activity show that mercurous chloride combines with the anion of sodium globulinate with simultaneous dissociation of chloride ions. Neutral salts reduce the viscosity of acid-globulin solutions, the value ultimately reaching a minimum with increasing salt concentration. R. CUTHILL.

I. New methods in micro-physico-chemistry. II. Cataphoresis of substances under physiological conditions. III. Cataphoresis of oxygen and carbon dioxide. Positive oxygen? IV. Cataphoresis of sugars. R. KELLER (Biochem. Z., 1926, **168**, 88—93, 94—97, 98—105, 106—109).—I. An introduction to the following papers, with a *résumé* of the principles involved in the methods developed for the study of the electrical condition of cells.

II. The behaviour of dyes in the histological micro-cataphoresis apparatus of Fürth (A., 1925, ii, 1057) is similar to that observed in cataphoresis experiments *in vitro* between non-metallic electrodes under high potential gradients.

III. [With J. GICKLHORN.]—Nascent oxygen (or hydrogen peroxide) is attracted to the cathode; carbon dioxide is repelled. The respiring organs of the higher and lower animals are negative to surrounding tissues, due to an abundance of reducing centres and a slightly greater alkalinity. The positive centres are concentrated in granules.

IV. [With J. GICKLHORN.]—Dextrose migrates to the anode in alkaline or neutral solution. In acid solution, all sugars pass to the cathode. Insulin goes to the anode. R. K. CANNAN.

Elasticity of jellies of cellulose acetate in relation to physical structure and chemical equilibria. H. J. POOLE (Trans. Faraday Soc., Feb., 1926, advance proof).—The methods previously applied to gelatin jellies (A., 1925, ii, 519) have been used in the investigation of cellulose acetate jellies in benzyl alcohol as solvent. The load–strain curve is found to bend towards the load axis, and a two-phase fibrillar structure is therefore assumed. The elasticity of cellulose acetate jellies in benzyl alcohol containing a small, constant amount of water is found to be approximately proportional to the square of the concentration of solid component, which is interpreted on the basis of a reversible solvation equilibrium between solvent and solute. Unlike the case of gelatin, permanent deformation is found to occur to a very small extent when the compressed jellies are heated and cooled, from which it is concluded that the structure produced in gel formation is mainly a permanent one, and that the elasticity of the gel varies with degree of solvation, but in an opposite direction. Hysteresis in the recovery of elastic equilibrium after heating is noticeable, especially at higher temperatures. The forces between the cellulose acetate molecules are considered to have a strictly local character, the sphere of effective attraction being smaller than the molecule itself, so that the smaller molecules of solvent in their kinetic movements may enter this sphere and diminish the attraction.

The "creep" under stress is found to consist of a slow reversible part and an irreversible deformation of solid. The reversible creep follows the equations previously developed by the author for gelatin, and a "coefficient of inner resistance," measuring the force normal to a face required to produce unit velocity of creep in a unit cube of jelly in the hypothetical absence of all elastic controlling forces, is proposed for use in this connexion. When water or xylene progressively displaces benzyl alcohol as solvent, the above coefficient plotted against content of water or xylene gives curves of the same type as the corresponding viscosity curves of the parent sols plotted in the same way. Water produces a decrease of elasticity and therefore favours solvation; xylene increases elasticity and diminishes solvation.

C. H. D. CLARK.

Structure of gels. P. THOMAS and M. SIBI (Compt. rend., 1926, **182**, 314—316).—The dibenzoic acetal of sorbitol is known to yield a jelly when an aqueous solution, obtained by long boiling, is cooled. Gelation does not occur unless the water is nearly neutral, preferably with p_H 8·0—8·5. Solutions in various organic solvents gelatinise on cooling or evaporation. On prolonged agitation, the aqueous gel breaks up into flocculent fragments, leaving nothing in solution. When it is covered with acetone or other organic solvent and kept, incipient crystallisation is observed at the boundary. The view is favoured that the gel consists of a network of fine crystals holding a large volume of solvent in its meshes.

W. A. CASPARI.

Coagulation of clay. R. GALLAY (Koll. Chem. Beihefte, 1926, **21**, 431—489).—The effect of electrolytes on the coagulation of soil and clay has been investigated by means of mechanical analysis, and by reference to ultramicroscopical observations and viscosity measurements. In a suspension of clay, the coarse particles promote the coagulation of finer particles, so that the minimum electrolyte concentration required to produce coagulation increases with increasing dispersity of the suspension. During coagulation, the viscosity changes in a discontinuous manner, probably because the coarser particles have separated out before the fine particles commence to separate. If the clay holds the maximum amount of salts of univalent metals, then owing to base exchange the salts of bivalent metals lose some of their normal coagulative activity. Salts of univalent metals are unusually effective in coagulating clay containing considerable quantities of salts of bivalent metals for the same reason. The coagulative power of the univalent cations increases in the order Li, Na, NH_4, K, Rb, Cs, and of the bivalent cations in the order Mg, Ca, Ba. The effect of certain salt solutions on the physical structure of soil is considered from the point of view of the hydration theory.

R. CUTHILL.

Protein coagulation. E. FREUND and B. LUSTIG (Biochem. Z., 1926, **167**, 355—373).—Heat coagulation is a chemical process involving the absorption of water, increased alkalinity, increased free amino-groups, and increased amount of ether-soluble substances readily obtained by hydrolysis. The denaturation point coincides with the coagulation point after the addition of salt. P. W. CLUTTERBUCK.

Influence of p_H on the diffusion of dyes into gelatin gels. H. MOMMSEN (Biochem. Z., 1926, **168**, 77—87).—Acid dyes diffuse more slowly through acid than through alkaline gels, but accumulate to a larger extent in the former. With basic dyes, the reverse is the case. When the dye is caused to diffuse out of a gel into the acid or alkaline gel the anomaly disappears, and it would seem that the larger amount of acid dye which accumulates in the acid gel is due to adsorption. The differentiation between velocity of diffusion and adsorption effects is considered in relation to cell permeability.

R. K. CANNAN.

General colloid chemistry. XVIII. Analysis and constitution of colloidal gold. IV. Rate of migration. L. FUCHS and W. PAULI (Koll. Chem. Beihefte, 1926, **21**, 412—430; cf. A., 1925, ii, 390).—The rate of migration at 25° under unit fall of potential is $25{\cdot}5$—35×10^{-5} cm./sec. for pure sols prepared with formaldehyde and $25{\cdot}2$—$27{\cdot}3\times10^{-5}$ cm./sec. for pure acid sols. Undialysed sols and dialysed sols containing potassium carbonate give higher values, which are reduced and ultimately changed in sign by addition of aluminium sulphate or chloride. These latter also reduce the rate of migration of pure dialysed sols, but do not change its sign; Burton's results (A., 1906, ii, 841) are probably due to the presence of alkali carbonate. To obtain accurate values, it is essential that the electrolyte solution surrounding the electrodes should have the same conductivity as the sol. R. CUTHILL.

Kinetic theory of a highly ionised gas. E. PERSICO (Month. Not. Roy. Astr. Soc., 1926, **86**, 93—98).—Theoretical. The kinetic theory of gases deduced by means of the assumptions that each molecule is acted on by only one other molecule at any given time and that the time of action is short compared with the whole life leads to anomalous results because these postulates are incorrect. In the case of an ionised gas, the possibility of a particle being simultaneously acted on by several others may be taken into account by using a method similar to that applied by Debye and Hückel to strong electrolytes (A., 1923, ii, 459). This leads to expressions which can be evaluated for particular numerical conditions so as to give the coefficient of diffusion of the electrons among the ions and the viscosity. R. CUTHILL.

Dissociation constants of racemic proline and certain related compounds. C. M. MCCAY and C. L. A. SCHMIDT (J. Gen. Physiol., 1926, **9**, 333—339).—The fission of the pyrrolidine ring of proline by nitrous acid is not a factor of sufficient magnitude to account for the amino-nitrogen usually found in proline preparations. Racemic proline, free from amino-nitrogen, is obtainable from crude proline by repeated recrystallisation of the copper salt, followed by precipitation with phosphotungstic acid. The values found for K_a and K_b were: racemic proline, $2{\cdot}5\times10^{-11}$ and 1×10^{-12}, respectively (isoelectric point p_H 6·3); pyrrole-2-carboxylic acid, $4{\cdot}2\times10^{-5}$ and 3×10^{-13} (isoelectric point p_H 2·9). K_a was found to be $5{\cdot}6\times10^{-4}$ for pyrrolidone-2-carboxylic acid, and $1{\cdot}4\times10^{-4}$ for tetrahydropyromucic acid.

C. P. STEWART.

Influence of the size of the ions on the equation of state for strong electrolytes. J. FRENKEL and B. FINKELSTEIN (Z. Physik, 1925, **35**, 239—242).—The authors derive the formula $(p_o+p_e)(v-b)=\frac{2}{3}L$, in which p_o is the osmotic pressure, p_e the internal pressure due to electrostatic attraction in which the ions are regarded as points, b is four times the volume of the ions and represents the forces of repulsion, and L is the mean kinetic energy of all the particles of the dissolved electrolyte. Some of the assumptions of Debye and Hückel are criticised. The radius of the ions is calculated for the chlorides of sodium, potassium, and lithium at widely different concentrations; in the case of lithium chloride a high value is obtained for dilute solutions which is ascribed to hydration.

E. B. LUDLAM.

Activity coefficient of hydrochloric acid in concentrated solutions of strong electrolytes. H. S. HARNED (J. Amer. Chem. Soc., 1926, **48**, 326—342).—Measurements of cells of the type $H_2|HCl(m_1),MCl(m_2)|HgCl|Hg$ at constant total molalities have been made. The logarithm of the activity coefficient of the acid varies linearly with the acid concentration at constant total molality up to $3M$ total concentration. Revised measurements of the above cells containing $0{\cdot}01M$- and $0{\cdot}1M$-hydrochloric acid and chlorides at various concentrations have been made. The results with uni-univalent

electrolytes are shown to be calculable to within narrow limits by means of Hückel's approximate equation. The constants for the individual electrolytes were computed on the basis of Debye and Hückel's theory (A., 1923, ii, 459), and the results from data for the mixtures agree very well with the constants derived from the data for the individual electrolytes. The activity coefficients of calcium, strontium, and barium chlorides are found to be calculable by Hückel's approximate equation, and from these data it is shown that the activity coefficient of hydrochloric acid in these three salt solutions can be calculated. Debye and Hückel's theory cannot be applied to solutions of the alkali hydroxides without the introduction of another factor. W. THOMAS.

The p_H value of water. A. KLING and A. LASSIEUR (Compt. rend., 1925, **181**, 1062—1064).—The divergent results obtained experimentally for the p_H value of water indicate that ionisation does not take place in accordance with the usual assumption. The p_H value of water distilled in a platinum apparatus and protected from air has been determined using the colorimetric and potentiometric methods, in the latter case by adding potassium chloride to increase the conductivity. Both methods gave a p_H of 5·8, which remained unaltered after further purification and whether the water was kept in open or closed glass or in platinum vessels. This corresponds with a carbon dioxide concentration of 0·00001N, although 5 to 6 times the calculated quantities of baryta were required for titration. It is inferred either that the true p_H of water is 5·8, or that the methods available give incorrect results. J. GRANT.

Reaction of neutral and distilled water. I. M. KOLTHOFF (Biochem. Z., 1926, **168**, 110—121).—The use of methyl-red for the determination of the p_H of distilled water leads to large errors. The indicators recommended are 2:4:6:2′:4′:2″:4″-heptamethoxytriphenylcarbinol, the sodium salt of methyl-red or of chlorophenol-red. The p_H of distilled water in equilibrium with air is 5·9 to 6·0. For the examination of carbon dioxide-free distilled water the sodium salt of bromophenol-blue is recommended. Sodium methyl-red is suggested for the determination of the carbon dioxide of the air. Errors are discussed which are involved in the application of indicator methods to very dilute solutions of weak acids. R. K. CANNAN.

Indicator for acidimetry and alkalimetry. Turbidity indicators. K. NAEGELI (Koll. Chem. Beihefte, 1926, **21**, 305—411).—Addition of acid to alkaline solutions of *iso*nitrosoacetyl-*p*-aminoazobenzene and *iso*nitrosoacetyl-*p*-toluenazo-*p*-toluidine causes the appearance of turbidity at p_H 10·80—11·01 and 11·30—11·74, respectively. The narrowness of these ranges makes it possible to use these substances as "turbidity indicators" for the titration of weak acids with sodium hydroxide. In this way, boric acid, arsenious acid, *p*-chlorophenol, and tyrosine can be titrated with an accuracy of about 1%. Other weak acids give much less satisfactory results, probably owing to unsuitability of the above ranges. Carbon dioxide and large quantities of neutral salts should be absent, and the indicator concentrations be kept within narrow limits. Protective colloids do not alter the ranges, but delay the appearance of turbidity. The above indicators appear to be of the half-colloid type. R. CUTHILL.

Extension of the new fundamental equation for the law of mass action to the case of an addition to the components of one phase. R. LORENZ and J. J. VAN LAAR (Z. anorg. Chem., 1926, **150**, 329—334).—The equations previously derived (A., 1925, ii, 866) for a multiple-phase equilibrium of the type $PbCl_2+Cd \rightleftarrows Pb+CdCl_2$ are extended to the case in which an indifferent substance is added to one phase, *e.g.*, potassium chloride to the salt phase. Equations are deduced for the internal energy, entropy, and thermodynamic potential. A. GEAKE.

New mass action law. II. Discussion of the equations. R. LORENZ and M. MANNHEIMER (Z. anorg. Chem., 1926, **150**, 343—349; cf. Lorenz, this vol., 126).—For a reaction of the type $Pb+SnCl_2=PbCl_2+Sn$, in which the atom or mol. fractions of the four reactants are x, $1-y$, y, and $1-x$, it is shown mathematically that the curve of the new mass action equation must pass through the points $x=0$, $y=0$, and $x=1$, $y=1$. The ideal mass-action equation $x/(1-x)=Cy/(1-y)$ gives on differentiation $(dy/dx)_{x=0}=1/C$ and $(dy/dx)_{x=1}=C$; the curve is thus symmetrical. At the middle point where $y=1-x$, $(dy/dx)=1$. The slopes at $x=0$ and $x=1$ for the curve of the new equation are not reciprocals, and this is therefore unsymmetrical; in general, the slope at $y=1-x$ is not unity. A. GEAKE.

Effect of the presence of an "indifferent" gas on the concentration and activity of a vapour in equilibrium with a condensed phase or system of condensed phases. I. R. MCHAFFIE (Phil. Mag., 1926, [vii], **1**, 561—583).—The effect of the presence of air on the concentration of water in the gas phase in equilibrium with Na_2SO_4,$10H_2O$–Na_2SO_4 at 25° has been studied with increasing pressure up to 100 atm. The air was circulated in contact with the salt mixture, at constant pressure and temperature, until equilibrium was established. A small amount of this air containing water vapour was released to atmospheric pressure, and the amount of water vapour in a known volume determined. The results are somewhat anomalous, the curve representing stable equilibrium conditions apparently passing through a maximum at 16 atm. (about 1·25 millimol./litre), a minimum between 30 and 50 atm. (0·99 millimol./litre), and exhibiting a sharp break at 77·6 atm., above which the curve is linear. The minimum value is below the equilibrium value in the absence of air, 1·035 millimol./litre. By varying the conditions slightly, a metastable branch of the curve is obtained between 40 and 77·6 atm. This is linear and forms a continuation of the branch above 77·6 atm. When glass wool was mixed with the salts a branch exhibiting a sharp maximum at 25 atm. appeared. The thermodynamic theory of systems of the type of that investigated is developed, and the relative

activity coefficient for water vapour in equilibrium with $Na_2SO_4,10H_2O$–Na_2SO_4 at 25° has been calculated, on the assumption that the effect observed is due entirely to the deviation of water vapour from ideal gas behaviour. A. B. MANNING.

Absorption of hydrogen by praseodymium and neodymium. A. SIEVERTS and E. ROELL (Z. anorg. Chem., 1926, **150**, 261—276).—Between 700° and 1200°, the volume of hydrogen absorbed at atmospheric pressure by praseodymium is nearly the same as by cerium and lanthanum (A., 1924, ii, 185; 1925, ii, 854). The isotherms at 600°, 800°, and 1100° are also similar in form to those of cerium and lanthanum, and it is concluded that praseodymium and hydrogen do not form a stoicheiometric compound. The absorption compound is grey or black, according to the hydrogen content, and is slowly attacked by air, yielding a mixture of oxide and nitride. Neodymium behaves similarly to praseodymium, but absorbs somewhat less hydrogen.
A. GEAKE.

Intermetallic compounds, with special reference to certain compounds of tin. I—V. [Calcium–tin and magnesium–tin alloys.] W. HUME-ROTHERY (Inst. Metals, 1926, advance copy).—I.—The application of the phase rule to condensed systems is discussed. In the proof of the phase rule, it is assumed that compound molecules are in reversible equilibrium with their components, but in solid crystalline compounds no such equilibrium exists and the phase rule requires modification. The argument of Clendinnen and Rivett (J.C.S., 1921, **119**, 1337) that all solid phases must form solid solutions is unjustified. In condensed systems, it is justifiable to omit the pressure variable and the vapour phase, but the remaining solid and liquid phases should still be measured in volume concentrations. If weight-composition equilibrium diagrams are used, the phase rule will not apply where volume changes are unaccompanied by weight-composition changes.

II.—Intermetallic compounds are regarded as compounds in which some only of the available valency electrons are bound into octets or other stable groups, others remaining more loosely held. This accounts for the conductivity and metallic properties, and also for the irregular valency relations. A true intermetallic compound will very rarely give rise to the substitutional type of solid solution, whilst the interstitial type, although possible, will be very limited in extent.

III.—The β-series of solid solutions in alloys of copper, silver, and gold with zinc, aluminium, or tin are grouped round the compositions CuZn, Cu_3Al, Cu_5Sn, and similarly for gold and silver. If copper is assumed to be univalent, these all correspond with a ratio of 3 valency electrons to 2 atoms, and the phases are not real molecular compounds, but are space lattices of atoms and electrons existing only in the solid state, with the fundamental ratio of 3 : 2. The exact ratio 3 : 2 has the most symmetrical arrangement and hence the highest conductivity. This conception is in agreement with Lindemann's theory (A., 1915, ii, 47).

IV.—The equilibrium diagram of the system calcium–tin is determined. Three compounds are formed: $CaSn_3$ (m. p. 627°, d^0 6·01), CaSn (m. p. 987°, d^0 4·17), and Ca_2Sn (m. p. 1124°, d^0 3·47). $CaSn_3$ and Ca_2Sn correspond with maxima, and CaSn with a break in the liquidus curve. The eutectic temperatures are Sn—Sn_3Ca, 231°; Sn_3Ca—SnCa, 609°; $SnCa_2$—Ca, 759°. The properties of the compounds are examined. The oxidation of a natural crystal face is slower than that of a ground or polished section.

V.—The equilibrium diagram of the system magnesium–tin is determined. A very slight range of liquid immiscibility probably exists at the tin end of the diagram. The single compound has a molecular formula Mg_4Sn_2, m. p. 778°. It is bluish-black with octahedral cleavage, and resembles the compound Na_2Sn, which has octahedral cleavage and is the only sodium–tin compound showing a blue colour. When dropped into water, the compound Na_2Sn is completely decomposed, but retains its original form, the solid being honeycombed with fine cracks parallel to the octahedral cleavages. This new type of reaction of a solid also takes place between the compound $CaSn_3$ and dilute hydrochloric acid.
W. HUME-ROTHERY.

Diagram of state of calcium and mercury. A. EILERT (Z. anorg. Chem., 1926, **151**, 96—104).—Amalgams containing up to 3% of calcium are prepared by heating the components at 340°, and richer amalgams by slowly heating the poorer amalgams to the b. p. The cooling curves of amalgams containing 2—6% of calcium show a well-defined halt at 265°, 3·8—0% amalgams a halt at −39°, and 3·8—0·9% amalgams a slight halt at 84°, which is a maximum at 1·9% ($CaHg_{10}$=1·95%). The halt at 265° is a maximum at 3·9%, corresponding with $CaHg_5$ (3·84%), and becomes zero at 2·15%, and at 6·5%, corresponding with $CaHg_3$ (6·3%). It is concluded that the solid phase separating from amalgams containing more than 2·15% of calcium is the *compound* $CaHg_3$. At 265°, this reacts completely with a 2·15% amalgam, forming the compound $CaHg_5$. At 84°, the latter reacts partly with a 0·8% amalgam, forming the compound $CaHg_{10}$. Microscopical observations were made on amalgams frozen on plane glass or porcelain surfaces with solid carbon dioxide and ether. The surfaces were etched with atmospheric moisture and, to avoid decomposition, were observed in the freezing mixture. 0·9—3·9% Amalgams contain crystals ($CaHg_5$) in increasing quantity, the amount again decreasing with richer amalgams. Above 3·9%, a second type of crystals ($CaHg_3$) is formed in increasing quantity, and below 3·8% a third type ($CaHg_{10}$), increasing with decreasing calcium content. By pouring amalgams into water large crystals of the solid phase may be separated, and analysis corresponds with the formula $CaHg_5$. A. GEAKE.

Fusion curves and physical properties of the system benzene–toluene. S. MITSUKURI and A. NAKATSUCHI (J. Soc. Chem. Ind. Japan, 1926, **29**, 25—29).—The following data are recorded: benzene, m. p. 5·56°; toluene, m. p. −95·7°; eutectic −103° and 85% of toluene. The calculated heats of fusion are: benzene, 2490 cal., toluene, 1100 cal., at their

respective m. p. The densities and refractive indices of the system have been determined at 20°. The f. p. diagram has been applied in the determination of the composition of various fractions obtained on distillation of benzene–toluene mixtures.

K. KASHIMA.

Equilibrium between ethyl alcohol and the alkali and alkaline-earth salts. I. D. G. R. BONNELL and W. J. JONES (J.C.S., 1926, 318—321).—The solubilities of the bromides of calcium, barium, sodium, and lithium and of barium iodide in ethyl alcohol were determined between 0° and 85°. The following *alcoholates* were isolated: $CaBr_2$,4EtOH (below 17°), $CaBr_2$,3EtOH (between 17° and 73·9°), $CaBr_2$,EtOH (above 73·9°), and LiBr,4EtOH. The last-named substance, which forms deliquescent plates, occurs in a retroflex region between 13·2°, the eutectic point for anhydrous salt and alcoholate, and 23·8°, the congruent m. p. of the alcoholate. A considerable amount of heat is evolved when lithium bromide and barium iodide are dissolved in alcohol. The orange tint of the iodide solutions is due to the liberation of small quantities of iodine.

S. K. TWEEDY.

Dissociation pressures of alcoholates. I. D. G. R. BONNELL and W. J. JONES (J.C.S., 1926, 321—328).—The dissociation pressures of methyl, ethyl, *n*-propyl, and *n*-butyl alcoholates of calcium chloride and bromide were determined by a dynamical method. Identical results are obtained by the use of air currents which contain respectively more or less than the equilibrium amount of alcohol.

S. K. TWEEDY.

Diagrams of state for binary systems of which arsenic tribromide is one component. N. A. PUSCHIN and S. LÖWY (Z. anorg. Chem., 1926, **150**, 167—174).—Six systems were studied by thermal analysis. Arsenic and antimony tribromides form a continuous series of solid solutions. With aniline hydrochloride, a compound, $AsBr_3$,NH_2Ph,HCl, is formed which is stable below 133°. Resorcinol, phenol, α-naphthol, and ethylurethane do not combine or form solid solutions with arsenic tribromide; the last three show eutectic points at 7·5°, 20·8°, and 4°, and the eutectic mixtures contain 44, 80, and 59 mol. % of arsenic tribromide, respectively. A. GEAKE.

System ethyl alcohol–benzene–water. I. Turbidity surface. J. BARBAUDY (Rec. trav. chim., 1926, **45**, 207—213).—The turbidity curves at 25°, 60°, and 65°, the b. p. at 760 mm. of the ternary constant-boiling mixture, have been determined, refractivity and density measurements being used to ascertain the exact composition of the ternary mixtures. The measurements at 25° are in good agreement with existing data (Taylor, A., 1897, i, 402; Lincoln, A., 1900, ii, 392; Sidgwick and Spurrel, J.C.S., 1920, **117**, 1397; Wehrmann, Z. Elektrochem., 1921, **27**, 379). Comparison of the curves in the usual triangular diagram shows that the three isothermals are very similar; with increase of temperature, however, the curves move slightly away from the point which corresponds with pure alcohol.

J. S. CARTER.

Equilibrium between two liquid phases. II. System aniline–lactic acid–water. III. System o-toluidine–acetic acid–water. E. ANGELESCU (Bul. Soc. chim. România, 1926, **7**, 72—78, 79—90; cf. A., 1925, ii, 854).—II. The composition of conjugate pairs in the system aniline–lactic acid–water has been determined at 0° and 20°. For lactic acid concentrations of 13·27, 13·50, and 13·80%, complete miscibility occurs at 43·4°, 23°, and 1°, the aniline concentrations being 33, 32·4, and 31·5%, respectively. Data representing the partition of lactic acid between the two liquid layers at 20° are also recorded. Unlike the corresponding acetic acid system (Angelescu, *loc. cit.*), no closed solubility curves are obtained, confirming the theory that such curves are due to hydrolysis of the salt, acetic acid being a weaker acid than lactic acid.

III.—In the binary system *o*-toluidine–water complete miscibility is reached at a temperature of 216° and about 50% *o*-toluidine. In the ternary system *o*-toluidine–acetic acid–water the isothermals at 0° and 20° have been determined, and data are recorded which show the value of the partition coefficient of acetic acid at 20°, and the dependence of the temperatures of complete miscibility on the composition for acetic acid concentrations of 19·94, 21·84, 23·33, and 23·60%. Only one liquid phase is formed if the concentration of acetic acid exceeds 24·52%. The region of partial miscibility is characterised by the existence of both upper and lower critical temperatures. The behaviour of this system is said to be influenced by the hydrolysis of the *o*-toluidine acetate which is formed.

W. HUME-ROTHERY.

Three-component system iron–chromium–carbon. T. MEIERLING and W. DENECKE (Z. anorg. Chem., 1926, **151**, 113—120).—The cooling curves of alloys containing 0—20% of chromium and constant amounts (0·7% and 2·5%) of carbon have been followed, and agree with the space diagram of Fischbeck (cf. B., 1924, 635). Alloys containing 0·7% of carbon show halts at about 1460°, corresponding with the first precipitation, and about 700°, corresponding with pearlite formation. Alloys containing 2·5% of carbon begin to crystallise at about 1320°, ternary γ-iron mixed crystals separating. A second halt at about 1200° corresponds with the separation of γ-iron mixed crystals and cementite for alloys containing up to 5% of chromium, and with the separation of γ-iron mixed crystals and a needle-shaped double carbide (a solid solution of cementite in chromium carbide, Cr_5C_2) for alloys richer in chromium. The two branches of the curve intersect at 1120° in the ternary eutectic plane. A further feeble thermal effect occurs at about 1030°, and pearlite formation at 700—740°. With both 0·7% and 2·5% of carbon the temperature of pearlite formation at first rises and then falls with increasing chromium content; this may be due to the low reaction velocity of chromium-rich alloys. Very slow cooling of the former alloys produces much softer material. The solubility of carbon, determined by heating at 1100°, falls from 1·7% for pure iron to 0·7% when the chromium content is 15%, and over the same range

the pearlite point changes from 0·9 to 0·5% of carbon. A. GEAKE.

Phase equilibria of sulphates. E. JÄNECKE (Z. anorg. Chem., 1926, **151**, 289—308).—Schenck's treatment (A., 1925, ii, 1160) of the system lead–sulphur–oxygen is criticised on the ground that the amount of free lead present in the vapour phase in equilibrium with solid lead sulphide and sulphate was unjustifiably neglected. The system metal–sulphur–oxygen is discussed on the assumption that the metal M forms only the compounds MO, MS, and MSO_4. The application to sulphide roasting is considered, and the lines of extension to more complicated systems are indicated. R. CUTHILL.

Equilibrium in the system arsenic pentoxide–barium oxide–water (acid section). S. B. HENDRICKS (J. Physical Chem., 1926, **30**, 248—253).—In the acid section of the above system, the stable compounds at 30° are $BaH(AsO_4),H_2O$, $BaH_4(AsO_4)_2,2H_2O$, and $3As_2O_5,5H_2O$.

Alkaline hydrolysis of the compound $BaHAsO_4,H_2O$ with ammonium hydroxide gave the compound $BaNH_4AsO_4$ in some cases, and rarely the compound $Ba_3(AsO_4)_2$ (cf. Lefèvre, A., 1892, ii, 273; Salkowski, J. pr. Chem., 1868, **104**, 143).

Preliminary results in control field tests show that commercial barium arsenate has as great a toxic effect on *Anthonomus grandis*, Boh., as the corresponding calcium salt at present used. L. S. THEOBALD.

System ferrous oxide–phosphoric acid–water and some of its oxidation products. S. R. CARTER and N. H. HARTSHORNE (J.C.S., 1926, 363—374).—The above system was investigated at 70°. With increasing acid concentrations, the *solid* phases are $2FeO,P_2O_5,5H_2O$ (not previously described), $2FeO,P_2O_5,3H_2O$, and $FeO,P_2O_5,4H_2O$. The second compound (Debray, Ann. Chim. Phys., 1861, **61**, 437) was obtained in two forms, quasi-amorphous and crystalline, the latter having a slightly lower solubility. Atmospheric oxidation of the phases of low acid content leads to the successive deposition of two forms of normal ferric phosphate, $Fe_2O_3,P_2O_5,4H_2O$. The reddish-brown β-form, stable in presence of high ferrous iron concentrations, is considered to be true ferric phosphate, $FePO_4,2H_2O$; the pink α-form, stable at lower ferrous iron concentrations, is probably $Fe[Fe(PO_4)_2],4H_2O$. Five mols. of water were previously attributed, incorrectly, to this compound (J.C.S., 1923, **123**, 2223). S. K. TWEEDY.

Reduction equilibria for the system: zinc oxide–carbon monoxide. C. G. MAIER and O. G. RALSTON (J. Amer. Chem. Soc., 1926, **48**, 364—374).—Equilibria data have been obtained for the reaction $ZnO(s)+CO=Zn(g)+CO_2$ over a temperature range 500—850°. Standard free energy equations are derived for the reduction of zinc oxide by carbon monoxide, and the entropy and free energy of zinc oxide at 25° have been calculated to be 10·20 entropy units and −75·785 cal., respectively. The heat of formation of zinc has been found to be −83·285 cal. W. THOMAS.

Equilibrium between methyl formate and methyl alcohol, and some related equilibria. J. A. CHRISTIANSEN (J.C.S., 1926, 413—421).—The equilibrium constants for the reactions $2MeOH=2H_2+H\cdot CO_2Me$ and $MeOH+CO=H\cdot CO_2Me$ have been obtained at 200° and 100°, respectively, the value for the latter reaction being only approximate. From the results, with the aid of existing data, the following expressions for the influence of temperature on various equilibria have been derived: $\log_{10}[CO][H_2]^2/[MeOH]=-4896/T+8·43$; $\log_{10}[CO_2][H_2]^3/[MeOH][H_2O]=-3042/T+6·77$; $\log_{10}[CH_4][CO_2]/[MeOH][CO]=9170/T+2\log_{10}T-8·88$. The significance of the results is discussed. S. K. TWEEDY.

Reciprocal salt pair (Na,Ba)–(Cl,NO_3) in aqueous solution at 20°. A. FINDLAY and J. CRUICKSHANK (J.C.S., 1926, 316—318).—Investigation of the reciprocal salt pair (Na,Ba)–(Cl,NO_3) in aqueous solution at 20° indicates that the preparation of barium nitrate from barium chloride and sodium nitrate is facilitated by the use of a relatively large proportion of the latter salt. The mother-liquor, containing sodium nitrate, may be used again after evaporation and separation of sodium chloride. S. K. TWEEDY.

Equilibria underlying soap-boiling processes. System potassium oleate–potassium chloride–water. J. W. MCBAIN and W. J. ELFORD (J.C.S., 1926, 421—438).—The relations between the various forms of potassium soaps resemble those for sodium soaps (McBain and Burnett, *ibid.*, 1922, **121**, 1320; McBain and Langdon, A., 1925, ii, 537). All the soap phases in the above ternary system occur also in the binary potassium oleate–water system, which was also investigated, showing that "salting out" takes place even in the absence of salt. The limits of the field of existence of isotropic liquid solutions of potassium oleate both with and without potassium chloride were accurately determined for temperatures up to 210°. Crystalloidal solutions are included in this single phase, which ranges from pure water up to pure anhydrous liquid potassium oleate, both being completely miscible above 300°. Both neat and middle soap are shown to be typical conic anisotropic liquids. S. K. TWEEDY.

Elimination of salt from sea-water ice. W. G. WHITMAN (Amer. J. Sci., 1926, **11**, [v], 126—132).—Experiments show that in cakes of ice having a uniform content of 3·31% of sodium chloride a movement of salt towards the warmer end takes place when the cake is subjected to a temperature gradient of 18—21° between top and bottom. The cold end loses about 12% of salt, and the warm end gains about 17% in 5—6 hrs., whilst the total salt content drops to 2·35%. An explanation on the basis of the phase-rule equilibria near the f. p. is given. The phenomenon is well known in the Polar seas, where sea-ice that has been floating for two or three seasons yields potable water. W. A. CASPARI.

Plane representation of multicomponent systems. W. N. LODOČNIKOV (Z. anorg. Chem., 1926, **151**, 185—213).—The representation is by means

of an isosceles right-angled triangle with one of the equal sides horizontal and equal in length to the sum of the relative concentrations of the components. In such a figure, a three-component system is represented by a point, the concentrations being given by its vertical distance from the base and its horizontal distances from the other two sides. A four-component system is represented by a straight line parallel to the base, the concentrations being equal to its length, its vertical distance from the base, and the distance of its ends from the nearer of the other two sides. The application of the method to isothermal equilibrium in quaternary systems is discussed. R. CUTHILL.

Equilibria in systems in which phases [are] separated by semipermeable membranes. XI. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 812—820; cf. A., 1925, ii, 869, 975, 1062).—It is shown that previous considerations of systems in which water diffuses through a semipermeable membrane are equally valid for systems in which the water is replaced by other diffusible substances. F. G. TRYHORN.

Reaction regions. W. P. JORISSEN (Chem. News, 1926, **132**, 149—152).—See this vol., 246.

Thermal dissociation of metallic sulphates. (MLLE.) G. MARCHAL (J. Chim. phys., 1926, **23**, 38—60; cf. A., 1925, ii, 870, 1162).—Anhydrous calcium sulphate affords evidence of dissociation at 960° and the dissociation pressure reaches 9·7 cm. at 1230°. For a mixture of equal mols. of anhydrous calcium sulphate and amorphous silica the dissociation becomes evident at 870° and the dissociation pressure reaches 81·7 cm. at 1280°. The partial pressure of sulphuric anhydride at equilibrium is given by the equation $\log p_{SO_3} = -17818/T - 11{\cdot}87 \log T + 49{\cdot}27$, whence the heat of the reaction $CaSO_4 + SiO_2 \rightleftharpoons CaSiO_3 + SO_2 + 0{\cdot}5O_2$ is calculated to be 74·6 cal. at 15°, whilst that determined from thermochemical values is 76·6 cal. The dissociation pressure curves when quartz or amorphous silica is used are not sufficiently different to determine the heat of crystallisation of silica. When gas is removed, the system becomes polyvariant, due probably to dissolution of one of the solid phases in the other. Corresponding mixtures of alumina with calcium sulphate afford evidence of dissociation at 950°. The dissociation pressure reaches 16·7 cm. at 1270° and the total pressure at equilibrium is given by the expression $\log P = 76814/T + 136{\cdot}7 \log T - 484{\cdot}4$. By analogy with the results from silica mixtures, the reaction may be represented by the equation $Al_2O_3 + CaSO_4 = CaO,Al_2O_3 + SO_2 + 0{\cdot}5O_2 - 85{\cdot}6$ cal. The reaction between anhydrous calcium sulphate and anhydrous kaolin is assumed to take place according to the equation $2SiO_2,Al_2O_3 + 3CaSO_4 = CaO,Al_2O_3 + 2(CaO,SiO_2) + 3SO_2 + 1{\cdot}5O_2$. The reaction is univariant so long as no gas is removed. Different kaolins give different results. Generally the reaction becomes evident at 780° and the dissociation pressure attains 100 cm. at about 1160°. The reaction of the calcium sulphate with ferric oxide is complicated by the inner equilibria of the ferric oxide. It is assumed to follow the course $CaSO_4 + Fe_2O_3 = CaO,Fe_2O_3 + SO_2 + 0{\cdot}5O_2$, and is practically univariant so long as no gas is removed. The reaction is evident at about 1000° and the dissociation pressure attains 27·3 cm. at 1280°. Chromic oxide does not react with calcium sulphate. The bearing of the results on the recovery of sulphuric acid, in the Carmichael–Bradford process of lead smelting, and from gypsum, is discussed. A. E. MITCHELL.

Explosion regions. VIII. Explosion range of hydrogen–ammonia–air and hydrogen–ammonia–oxygen mixtures. W. P. JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1926, **45**, 225—231; cf. *ibid.*, 162).—An increase in the explosion range is also observed when oxygen replaces air in the gaseous system, hydrogen–ammonia–air. The following numbers represent the lower and upper limiting percentages, respectively, of hydrogen in explosive hydrogen–ammonia–air mixtures: 0% NH_3 (6·1, 66·9); 3% NH_3 (5·2, 53·7); 6% NH_3 (4·2, 40·9); 14% NH_3 (3·7, 6·9). The peak of the explosion region is at 3·5% H_2 and 14·9% NH_3. With air replaced by oxygen, the corresponding figures are: 0% NH_3 (6·1, 92·3); 3% NH_3 (5·1, 88·3); 8% NH_3 (4·5, 80·5); 12% NH_3 (3·1, 76·3); 48% NH_3 (upper limit 28·1); 60% NH_3 (upper limit 13·1). In the absence of hydrogen, the lower and upper limiting concentrations of ammonia in explosive mixtures are 18·9 and 69·5%, respectively. The explosion range for ammonia–oxygen–nitrogen mixtures has also been investigated. The ratio outside the parentheses represents the ratio $[O_2]/[N_2]$, whilst the numbers inside represent the lower and upper limiting percentages of ammonia, respectively: 95/5 (18·9, 69·5); 80/20 (18·9, 61·1); 60/40 (upper limit 51·5); 40/60 (22·9, 36·3); 35/65 (24·9, 30·3). The peak of the curve corresponds with a value of 32/68 for the ratio $[O_2]/[N_2]$. J. S. CARTER.

Conductivity of toluene. W. KUSNETZOV (Mitt. wiss.-tech. Arb. Republ. [Russ.], 1924, **13**, 5—6; from Chem. Zentr., 1925, II, 386).—The intensity of current i in toluene, using platinised or nickelled electrodes, is connected with the potential difference (V) by the relationship $i = f(V) + cV$, c being a constant and $f(V)$ being a function which increases with V and reaches its limiting value at 400 volts/cm.
G. W. ROBINSON.

Electrical conductivity of dielectrically individual compounds and metalloidal elements. I. M. RABINOVITSCH (Z. physikal. Chem., 1926, **119**, 59—69).—The electrical conductivities of acetic acid, of the three chloroacetic acids and their ethyl esters, and of methylene chloride were determined at various temperatures. The acids were investigated in both the liquid and solid states and the other substances in the liquid state. The differences in conductivity of the acids and esters are correlated with differences in the polarisation of the compounds, *i.e.*, the conductivities run parallel to those of the chloro- and nitro-derivatives of methane, which, in turn, increase as the dielectric constant increases.
L. F. GILBERT.

Electrical conductivity of dielectrically individual compounds and metalloidal elements. II. M. RABINOVITSCH (Z. physikal. Chem., 1926, **119**, 70—78; cf. preceding abstract).—Measurements have been made of the conductivities of ethyl ether, benzene, nitrobenzene, bromobenzene, naphthalene, α-bromonaphthalene, anthracene, *iso*valeric, *n*-octoic, palmitic, stearic, and benzoic acids, and of solutions of palmitic acid, stearic acid, naphthalene, and iodine in ether and in benzene; the conductivity of iodine in carbon disulphide was also measured. The conductivity of naphthalene is greater than that of benzene and is about the same as that of anthracene. Introduction of the polar groups NO_2, CO_2H, and Br into the benzene nucleus increases the conductivity. The conductivity of α-bromonaphthalene is greater than that of bromobenzene at the same temperature (25°); the conductivities of the fatty acids are less than those of aromatic acids. These experimental observations are connected with the constitution of the compounds concerned. The conductivities of solutions of palmitic and stearic acids in ether increases with time to a limiting value; this phenomenon is ascribed to slow solvolysis with the possible intermediate formation of etherates. It is considered that the conductivity of solutions of naphthalene and iodine is due to a slight ionisation of these substances. L. F. GILBERT.

Electrical conductivity of dielectrically individual compounds and metalloidal elements. III. M. RABINOVITSCH (Z. physikal. Chem., 1926, **119**, 79—86; cf. preceding abstracts).—The conductivities of liquid and solid bromine and iodine have been measured. It is pointed out that the conductivities of chlorine, bromine, and iodine near the m. p. run parallel with their dielectric constants. The mechanism of the electrolytic conductivity here obtaining is discussed. L. F. GILBERT.

Conductance of solutions of alkali metals in liquid ammonia and in methylamine. G. E. GIBSON and T. E. PHIPPS (J. Amer. Chem. Soc., 1926, **48**, 312—326).—The conductance of sodium and potassium in ammonia, and of cæsium, cæsium iodide, and potassium in methylamine, has been determined at various temperatures. The results in ammonia are in agreement with the measurements of Kraus (A., 1921, ii, 370). The temperature coefficient of conductance is an exponential function of the temperature at all dilutions. The metals are more highly ionised in ammonia than in methylamine, hence solutions in ammonia show a minimum at lower concentrations than those in methylamine, but the curves are of the same general type. The results are in accord with the hypothesis that the negative carriers are electrons largely combined with the solvent molecules, the degree of solvation diminishing as the temperature is increased. W. THOMAS.

Theory of electrolytic ions. XXXI. Transference numbers and ionic conductivities in lithium and potassium chlorides. R. LORENZ and J. WESTENBERGER (Z. anorg. Chem., 1926, **150**, 304—310).—Assuming complete dissociation of strong electrolytes, the ionic mobility (conductivity) of chlorine ion is calculated from the transference numbers of Bein and Goldhaber (A., 1898, ii, 553) for lithium chloride and of Bogdan and Jahn (A., 1901, ii, 540) for potassium chloride and the conductivity data of Kohlrausch. The mean for the two chlorides agrees well with Kohlrausch's ionic mobilities. Thus at a dilution of 0·0001*M* the values are 64·18 and 64·9 and at 0·01*M* 61·38 and 61·5. At higher concentrations, the difference again increases and is in the opposite direction. A. GEAKE.

Effect of pressure on the potential of the hydrogen electrode. G. TAMMANN and H. DIEKMANN (Z. anorg. Chem., 1926, **150**, 129—146).—The change with pressure of the potential of a hydrogen electrode has been calculated from the volume measurements of Amagat up to 3000 atm. The influence of pressure is somewhat greater than for an ideal gas. Eighteen concordant series of measurements were made of the *E.M.F.* of the cell $Pt|H_2|0{\cdot}1N\text{-}HCl|HgCl|Hg$ at both rising and falling pressures up to 3000 kg./cm.^{2} Similar measurements were made in which the platinum electrode was saturated with hydrogen, but no free hydrogen was present in the cell. In this case, the compressibility of platinum being low, the concentration of hydrogen is practically independent of the pressure; the fall of *E.M.F.* is represented by the equation $\Delta E=(p-400)^2/128{,}000-4$, in which p is the pressure in kg./cm.^{2} The differences between the two series of measurements agreed with the calculated potentials. It is noted that reproducible results were obtained in a particular case which agreed with the values calculated for the reaction $H_2 \longrightarrow H_2^+$; other abnormal results were obtained in some cases. The influence of neutral salts on the potential of the above cell is due partly to the effect of the change of internal pressure on the hydrogen and calomel electrodes and partly to a specific effect of the salt on the potential of the hydrogen ion. If internal pressure is assumed to have the same effect as external pressure, its influence on the hydrogen electrode is given by the equation above, and on the calomel electrode by the equation $\Delta E=-0{\cdot}7455\times10^{-6}p$ (cf. Hainsworth and MacInnes, A., 1922, ii, 467; Cohen, A., 1909, ii, 641). The specific salt action is proportional to its concentration, c, and thus the total effect of the addition of salt is $\Delta E=(p-400)^2/128{,}000-4+0{\cdot}75\times10^{-6}p+\sigma c$, where σ is a constant. Results thus calculated are in agreement with the measurements of Poma (A., 1915, ii, 210) and Michaelis (A., 1925, ii, 130) for potassium, sodium, calcium, magnesium, and lithium chlorides. The effect of neutral salts on the viscosity of water is similarly due partly to the change of internal pressure, and partly to specific salt action. Water has a minimum viscosity at a pressure of 1200 kg./cm.^{2}, and the effect of the addition of salts is given by the equation $\Delta\eta=(p-1200)^2/45{,}000-30+\sigma_\eta c$, which agrees with the measurements of Sprung (Pogg. Ann., 1876, **9**, 1). Addition of salts raises, in general, both the viscosity and the hydrogen-ion activity, and the latter effect is, therefore, not due to an increased migration velocity. A. GEAKE.

Potential of alloys of cadmium and magnesium. G. WINOGOROV and G. PETRENKO (Z. anorg. Chem., 1926, **150**, 254—257).—The potential

differences between magnesium and alloys of cadmium and magnesium in *N*-magnesium sulphate solution were measured in the expectation that the existence of the known compound MgCd would be revealed by a break in the composition–potential curve. The compound exists in two forms, stable above and below 245·5°, respectively. Alloys prepared by cooling the fused mixture, which therefore contained the β-form of the compound, show the expected break, and the slopes of the curve indicate the existence of solid solutions between 0 and 28·7 and 66·45 and 100 at.-% of cadmium. Alloys containing the α-form show a similar break and solid solutions are indicated between 0 and 12·6 and 80 and 100 at.-% of cadmium. These limits do not agree with those found by the fusion method or by the electrical conductivity. The difference of potential between the α- and β-forms is only about 70 millivolts. A. GEAKE.

Potential of alloys of thallium and antimony. G. WINOGOROV and G. PETRENKO (Z. anorg. Chem., 1926, **150**, 258—260).—The potential difference between thallium and alloys of antimony and thallium in contact with *N*-thallium chloride solution remains at the value for pure antimony until the thallium content reaches 75 atoms %; it then falls sharply and continuously to zero for pure thallium. The existence of a compound $SbTl_3$ (cf. Williams, A., 1906, ii, 673) is thus confirmed. This forms a continuous series of solid solutions with thallium, but no such solutions are formed with antimony. A. GEAKE.

Elimination of liquid potentials. A. H. W. ATEN and J. VAN DALFSEN (Rec. trav. chim., 1926, **45**, 177—190).—The extent to which liquid potentials are eliminated by intercalation of concentrated solutions containing cations and anions of approximately the same mobilities has been investigated by determining the *E.M.F.* at 18° of the cells:

$Hg|Hg_2Cl_2,0{\cdot}1M\text{-KCl}|KCl\ (or\ KI)|HCl\,n,H_2|Pt$ (*a*)
$Hg|Hg_2Cl_2,0{\cdot}1M\text{-KCl}|KCl\ (or\ KI)|KOH\,n,H_2|Pt$ (*b*)

n having the values 0·01, 0·10, and 1·0*M*. The concentrations of potassium chloride and iodide were varied over the ranges 0·01—3·70 and 0·01—6·0*M*, respectively. Measurements were made with the following cells in which a flowing junction was used:

$Hg|Hg_2Cl_2,0{\cdot}1M\text{-KCl}|KCl(KI)|HCl\,n,Hg_2Cl_2|Hg$ (*c*)
$Hg|Hg_2Cl_2,HCl\,n|HCl\,n,H_2|Pt$ (*d*)
$Hg|Hg_2Cl_2,0{\cdot}1M\text{-KCl}|KCl(KI)|KOH\,n,HgO|Hg$ (*e*)
$Hg|HgO,KOH\,n|KOH\,n,H_2|Pt$ (*f*)

The *E.M.F.* of cells of type (*a*) is the sum of those of types (*c*) and (*d*). Similarly, that of cells of type (*b*) is the sum of the *E.M.F.* of types (*e*) and (*f*). The discrepancies, usually of the order 0·5 millivolt, which exist between the present values and those of other investigators, are discussed in some detail. In those cells where a liquid potential comes into play the *E.M.F.* differ more markedly (about 3 millivolts) from those obtained by other observers using a stationary junction. Using dilute potassium chloride solutions as salt-bridge the difference between a flowing and a stationary boundary becomes less apparent. With cells of type (*a*), the *E.M.F.* decreases, and with cells of type (*b*) increases, with increasing concentration of potassium halide in the salt-bridge. Thus for a cell of type (*a*), $n=0{\cdot}01M$, the *E.M.F.* with 0·01*M*-potassium chloride or iodide as the intercalated solution is 0·4804 volt, whilst with 3·70*M*-potassium chloride and iodide the values are 0·4554 and 0·4545 volt, respectively.

Applying the method used by Fales and Vosburgh (A., 1918, ii, 424), and in agreement with their results, the authors find that a 4·15*M*-potassium chloride solution will eliminate the boundary potentials between 1·0 and 0·1, and between 0·1 and 0·01*M*-hydrochloric acid solutions. The corresponding concentrations of potassium iodide are 3·2 and 2·8*M*, respectively. The liquid potential between 1·0 and 0·1*M*-potassium hydroxide will be eliminated by 6·0*M*-potassium chloride or 6·4*M*-potassium iodide. If the method of Fales and Vosburgh is correct, it would appear that each pair of solutions requires a definite concentration of potassium chloride and iodide for the elimination of the liquid potential. The mobility difference of the constituent ions of the electrolyte in the liquid junction plays a part in the elimination process.

Application of the Bjerrum extrapolation to cells (*a*) and (*b*) containing potassium chloride in the salt-bridge leads in general to values which are 1—4 millivolts higher than the corresponding values for the cells containing potassium iodide. For the cells (*b*), $n=0{\cdot}01$ and $0{\cdot}10M$, the extrapolated *E.M.F.* are practically identical, and it is inferred that the extrapolated values, 1·0389 and 1·0934 volts, respectively, are correct. Modifying the method of Fales and Vosburgh by the replacement of concentrations by activities and using the activity coefficients given by Scatchard (A., 1923, ii, 606; 1925, ii, 398), the values 0·0658, 0·0554, 0·0615, and 0·0541 volt are found for the cells: $Pt|H_2,1{\cdot}0M\text{-HCl}||0{\cdot}1M\text{-HCl},H_2|Pt$, $Pt|H_2,0{\cdot}1M\text{-HCl}||0{\cdot}01M\text{-HCl},H_2|Pt$, and the two corresponding cells containing potassium hydroxide. The following numbers represent the values for the same cells obtained from the extrapolated values for cells (*a*) and (*b*) containing potassium chloride; the numbers in parentheses are those from the cells containing potassium iodide: 0·0659 (0·0703); 0·0580 (0·0591); 0·0587 (0·0571); 0·0547 (0·0544). The value of the liquid potential hence remains uncertain. Only for 0·01 and 0·10*M*-potassium hydroxide solutions will these values be exact to 0·5 millivolt. Elsewhere the uncertainty may amount to several millivolts. The Bjerrum process of extrapolation is held to be the best existing method, since the magnitude of the extrapolation gives some idea as to the extent of the possible error. J. S. CARTER.

Variation of the *E.M.F.* of a photo-active cell, containing a fluorescent electrolyte, when the amount of fluorescent material in solution is varied. W. RULE (Phil. Mag., 1926, [vii], **1**, 532—541).—The photo-*E.M.F.* of a cell with an electrolyte comprising 0·5 g. of sodium hydroxide per 100 g. of water and concentrations of fluorescein varying from 0·5 to 0·00016 g. per 100 c.c. of sodium hydroxide solution, has been measured. The *E.M.F.*

rises quickly to a maximum as the fluorescein concentration increases from zero, and then falls less rapidly as this concentration is increased still further. Similar results have been obtained with eosin in glycerol–water solution. Sodium hydroxide solution alone gives no photo-*E.M.F.* It is suggested that the active factor in building up such an *E.M.F.* is the activation of the fluorescent material in solution, and not, as suggested by Grumbach (A., 1923, ii, 108; Compt. rend., 1923, **177**, 395), that part of the *E.M.F.* is caused by the action of the fluorescent radiation emitted by the illuminated liquid. The results are discussed in connexion with several analogous phenomena. The theory of the variation of *E.M.F.* with the concentration of the fluorescent material is discussed and the results are explained on the basis of Perrin's assumptions (A., 1924, ii, 713).

A. E. Mitchell.

Electrochemical behaviour of chromium. G. Grube, R. Heidinger, and L. Schlecht (Z. Elektrochem., 1926, **32**, 70—79).—The behaviour of an anode covered with pure chromium in different solutions with varying current densities has been studied by potential measurements. Using an active chromium electrode (prepared by cathodic polarisation) with 0·02—0·2*N*-sulphuric and hydrochloric acid solutions, the anode potential is found to increase suddenly when the anode current density reaches a certain value. This critical value increases with the concentration of the acid and with increasing temperature. During the first stage, the chromium ions pass into solution entirely in the bivalent condition, and, during the second stage, entirely in the sexavalent condition. At the ordinary temperature, *N*-sodium chloride behaves similarly, but at higher temperatures the current density–potential curves are of somewhat different form, and their meaning is discussed in relation to the suggestion of Kuessner (A., 1910, ii, 927) that it is possible for chromium ions of varying valency to be formed simultaneously in solution. A different view is upheld, viz., that chromium goes primarily into solution as bivalent ions at lower current densities, and that these are immediately oxidised to the tervalent condition, whilst at higher current densities sexavalent ions are formed. The anode potential in *N*-, 4*N*-, 8*N*-, and 16*N*-potassium hydroxide solutions has also been studied at different temperatures; for low current densities, the curve is discontinuous as in acid solutions, and a similar explanation is adopted. In the alkaline solutions, the anode becomes coated with a fine grey powder, which apparently consists of a lower oxide of chromium. The results are discussed in relation to previous observations with iron and to suggested theories of passivity (layers of colloidal metal or of metallic salt). The oxide layer theory is upheld.

C. H. D. Clark.

Factors determining chemical stability. J. H. Hildebrand (Chem. Reviews, 1926, **2**, 395—417).

Reaction velocity and thermodynamics. M. E. Jouguet (Ann. Physique, 1926, [x], **5**, 5—72).—Theoretical. Using Duhem's concept of chemical viscosity, it is possible, with the aid of certain assumptions, to deduce thermodynamically the reaction rate expression of Marcelin (A., 1911, ii, 27; 1915, ii, 328). This latter leads to formulæ for the temperature coefficient similar to those of Trautz (A., 1909, ii, 557). It is applied to reactions in a homogeneous system, vaporisation, fusion, and allotropic transformation, but is not applicable to photo-chemical reactions. The van 't Hoff isochore is shown to be contained in it. R. Cuthill.

Reaction constant equation and a simple method of determining the end-point. R. C. Smith (Phil. Mag., 1926, [vii], **1**, 496—499).—The end-point of a unimolecular reaction is calculated from two values obtained at times such that one time is half the other. The effect of errors is discussed. The method may be applied to the results of multimolecular reactions, but the expressions for T_∞ become more complicated. A. E. Mitchell.

Explosive mixtures. VII. Influence of ethylene on the explosion limits of detonating gas [oxygen and hydrogen]. W. P. Jorissen and B. L. Ongkiehong.—See B., 1926, 179.

Kinetics of chemical reactions. I. Velocity of thermal decomposition of chlorous oxide. J. Zawidzki (Rocz. Chem., 1925, **5**, 504—508).—Certain results obtained by Hinshelwood and Prichard (J.C.S., 1923, **123**, 2730) for the thermal decomposition of chlorous oxide are said to point to this reaction being of an autocatalytic type, the autocatalyst being nascent oxygen.

R. Truszkowski.

Oxidation of ammonia to nitrite in aqueous solution by means of oxygen in presence of metallic and dissolved copper. E. Müller (Z. Elektrochem., 1926, **32**, 109—120).—When small concentrations of dissolved copper are used in the catalytic conversion of ammonia into nitrite by means of oxygen in presence of sodium hydroxide, the reaction velocity is approximately proportional to the concentration of copper, the pressure of oxygen, and the concentration of hydroxyl ions. The speed of nitrite formation increases with increasing ammonia concentration and also with rise in temperature. Addition of ammonium salts retards the change by removal of hydroxyl ions. When copper is present in the solid state, the activity appears to be due to the presence of copper in the liquid phase formed by solution in ammonia, an equilibrium $Cu + Cu^{\cdot\cdot} \rightleftharpoons 2Cu^{\cdot}$ being set up, forming the cuprous ion, which is particularly active. High reaction velocities are observed in presence of cuprous oxide as catalyst. The changes of potential of a copper anode in 2*N*-sodium hydroxide in presence and in absence of ammonia are consistent with the suggestion that the intermediate formation of tervalent copper ions plays a part in the catalytic mechanism. Thus bivalent copper ions may form tervalent ions by means of the charges of hydrogen ions which are oxidised to water; the tervalent ions then react with hydroxyl ions in presence of ammonia to give nitrite ions and re-form bivalent copper ions. Similarly, cuprous ions can form tervalent copper ions, which then behave in the same way. The general explanation of the catalytic phenomena is to be found

in the capacity of copper to build up higher oxidation products in solution. C. H. D. CLARK.

Velocity of hydrolysis of aqueous solutions of alkali metal cyanides. J. ZAWIDSKI and T. WITKOWSKI (Rocz. Chem., 1925, **5**, 515—528).—The velocities of hydrolysis of the alkali cyanides have been determined at 100°, 110°, and 120°, also the temperature coefficients. The value of k decreases with increasing at. wt. of the cation, falling from 169×10^{-5} for lithium at 100° to 121×10^{-5} for cæsium. The temperature coefficients vary only very slightly, from 1·80 to 2·07 between lithium and cæsium from 100° to 110°, and from 2·12 to 2·25 between 110° and 120°. A relation, $\alpha\sqrt[3]{k}=$const., is shown to exist between the degree of dissociation of the hydroxides and the velocity of hydrolysis of the alkali cyanides. The above data point to the reaction taking place in three stages: $R\cdot CN+H_2O\longrightarrow R\cdot OH+HCN$; $HCN+2H_2O\longrightarrow H\cdot CO_2NH_4$; $H\cdot CO_2NH_4+R\cdot OH\longrightarrow H\cdot CO_2R+NH_4OH$. For a reaction of this type, however, the velocity should increase with dilution of substrate, whilst in practice, for solutions below M, it is independent of the concentration. The kinetics of the hydrolysis of the alkali cyanides cannot therefore be considered as entirely elucidated. R. TRUSZKOWSKI.

Sulphite addition to unsaturated compounds. E. HÄGGLUND and A. RINGBOM (Z. anorg. Chem., 1926, **150**, 231—253).—As a measure of the degree of unsaturation of substances containing ethylene linkings, the determination of the velocity of sulphite addition has the advantages over that of bromine addition that the reaction is slower and that isomeric changes do not occur. The reaction proceeds according to the equation $:C:C:+NaHSO_3=:C(SO_3Na)\cdot CH:$, and bimolecular constants are given by crotonic acid (0·18), cinnamic acid (0·025), sorbic acid (0·025), fumaric acid (0·086), maleic acid (0·16), citraconic acid (0·042), and mesaconic acid (0·0015) at 80°. The velocity depends on the concentration of sodium hydrogen sulphite (or the ion HSO_3'); normal sulphite does not react. The strength of the unsaturated acid affects the velocity in so far as it controls the amounts of sulphurous acid, hydrogen sulphite, and normal sulphite. Generally, the reaction is most rapid when an excess of sodium hydrogen sulphite is added to the neutralised acid. The temperature coefficients between 80° and 90° for cinnamic and sorbic acids are 1·7 and 1·92, respectively. Of geometrical isomerides, the *cis*-form reacts more rapidly than the *trans*-form. Sodium hydrogen fumarate reacts more rapidly than the normal salt, but the reverse is the case for maleic acid. In general, the higher the mol. wt. of the compound the lower is the reaction velocity; triphenylacrylic acid does not react. Acrylic acid combines very rapidly, but does not give a bimolecular constant. Sorbic acid, which contains a pair of conjugated double linkings, combines with only 1 mol. of sodium hydrogen sulphite. A. GEAKE.

Reaction between sodium sulphite and sulphur. H. E. WATSON and M. RAJAGOPALAN (J. Indian Inst. Sci., 1925, **8**, A, 275—286; cf. Hargreaves and Dunningham, J.S.C.I., 1923, **42**, 147T).—The velocity of formation of sodium thiosulphate in aqueous solution at 60—80° from sodium sulphite and sulphur is increased by more efficient stirring, also by the addition of an excess of solid sulphur, the reaction being complete in 1 hr., when 4 g.-mol. of sulphur are present. The velocity of the reaction appears to depend almost entirely on the rate of dissolution of the sulphur, and not to be governed by the concentration of the sulphite. Dilution of the solution causes a slight increase in the percentage conversion. The catalytic effect of sodium sulphide on the reaction is confirmed. Fresh sulphur has a greater rate of dissolution at first than subsequently. The initial rate of dissolution is smaller for sulphur which has been used in a previous experiment. G. M. BENNETT.

Action of certain sugars and alcohols on the hydrolysis of methyl acetate. J. L. DONNELLY (Kolloid-Z., 1926, **38**, 165—168).—Conductivity measurements at 30° of 10% solutions of methyl acetate in water, to which 0·1, 0·2, and 0·3 g.-mol. of dextrose, sucrose, glycerol, or ethyl alcohol have been added, show that in each case the velocity of hydrolysis of the ester is reduced by the added sugar or alcohol. The decrease of hydrolysis is proportional to the quantity of sugar or alcohol added, the greatest effect being shown by glycerol, the least by ethyl alcohol. It is presumed that the added substance combines with a part of the water, the water so fixed being incapable of reacting hydrolytically with the ester. L. L. BIRCUMSHAW.

Kinetics of chemical reactions. III. Velocity of hydrolysis of acetylcitric acid. J. ZAWIDSKI (Rocz. Chem., 1925, **5**, 511—514).—The hydrolysis of acetylcitric acid according to the values obtained by Rath (A., 1908, ii, 94) is shown to be a semi-molecular reaction, in which only the anions undergo hydrolysis. Rath's numbers, when applied to the equation $dx/dt=k\sqrt{(1-x)}/\sqrt{a}$, where $(1-x)$ is the relative concentration of the substrate at time t, and a the original concentration, give fairly constant values for k. R. TRUSZKOWSKI.

Application of dilatometric and stalagmometric methods to kinetic investigations. A. BENRATH, DIDERICHS, J. GEUER, SASS, SCHLEICHER, VIEDEBANTT, and (FRL.) KRAHECK (Z. anorg. Chem., 1926, **151**, 53—67; cf. A., 1909, ii, 795).—Various reactions were followed dilatometrically in a 50-c.c. flask with a scale on the neck which enabled the volume to be read to 0·001 c.c. Ester formation involves expansion, and the esterification of acetic, propionic, and butyric acids with amyl alcohol could be followed. Contraction takes place during hydrolysis of acetamide with acid, and unimolecular constants were obtained with hydrochloric, hydrobromic, and nitric acids when the acid was in excess; the total contraction was independent of the concentration, but not of the nature, of the acid. The method is not applicable to sulphuric and phosphoric acids, with which the contraction varies with the acid concentration. The hydrolysis of bromoacetic, bromopropionic, and bromosuccinic acids with sodium hydroxide is accompanied by volume dilatation, the amount of which is constant when the alkali is in

excess. Bimolecular constants were obtained; bromosuccinic acid gave a unimolecular constant when an equivalent amount of sodium hydroxide was added, and bimolecular constants were obtained only over a small range of alkali concentration. The addition of sodium bromide or acetate to any of the acids, or of alcohol to bromoacetic acid, increased the reaction velocity, but diminished the change in volume.

The acid hydrolysis of acetamide may also be followed stalagmometrically, the surface tension being measured from time to time by the drop method. The surface tension of water is increased by the addition of ammonium chloride, but diminished by hydrochloric and acetic acids and by acetamide; the net effect of the hydrolysis is a decrease. Except in the case of acetic acid, the change is proportional to the concentration of solute. Hydrolysis by hydrochloric, nitric, and sulphuric acids gives bimolecular velocity constants when an equivalent amount of acid is taken, but unimolecular constants when the acid is in excess. The addition of an alkali chloride to an equivalent amount of hydrochloric acid also renders the constant unimolecular, and this is explained on the basis of Hantzsch's theory of hydroxonium salts. The results obtained with sulphuric acid are different from those obtained dilatometrically, because the surface tension is affected chiefly by the change in concentration of acetic acid and so measures this, whereas the dilatometric method measures the ammonium sulphate formed. When the concentration of sulphuric acid is increased, more hydrogen sulphate is obtained, and this influences the dilatometric results. The total surface tension change on hydrolysis is approximately proportional to the initial concentration of acetamide. A. GEAKE.

Kinetics of chemical reactions. II. Velocity of nitration of phenols. J. ZAWIDSKI (Rocz. Chem., 1925, **5**, 509—510).—Arnall (J.C.S., 1923, **123**, 3111) found that the nitration of phenols in alcoholic solution is a reaction autocatalysed by nitrous acid. This reaction is shown to have a velocity given approximately by $dx/dt=k(a-x)(b-x)(c-x)$, a, b, and c being the original concentrations of phenol, nitric, and nitrous acid, and x the decrement in time t. R. TRUSZKOWSKI.

Electrochemical precipitation of copper from solutions of its salts by zinc. I. A. GALECKI and T. ORLOWSKI (Rocz. Chem., 1925, **5**, 459—487).—The velocity of reaction in the heterogeneous system zinc–copper salt is measured with and without stirring. In the first case, k varies directly as the number of revolutions per minute of the stirrer, and, independently of the nature of the anion, increases with dilution, whilst the temperature coefficient is greater in more concentrated solutions. Little difference is observed whether cupric chloride or sulphate be used as the electrolyte, and the thickness of the copper deposit is shown to vary from 11μ to 108μ, this value varying inversely as the dilution and the rate of stirring. In the second case, k increases with concentration of electrolyte, is more than twice as great for cupric chloride as for sulphate, this difference being similar to that between the diffusion coefficients of the salts, and the temperature coefficient is practically independent of the concentration. The velocity of reaction under these conditions appears to be controlled by the diffusion coefficient, and thus affords a confirmation of Nernst's diffusion theory for heterogeneous systems. R. TRUSZKOWSKI.

Electrochemical precipitation of copper from solutions of its salts by zinc. II. A. GALECKI and W. KUCZYŃSKI (Rocz. Chem., 1925, **5**, 536—562; cf. preceding abstract).—The influence of hydrogen and of chlorate ions on the precipitation by zinc of copper from solutions of its salts is investigated. A study of the velocity of reaction in acid solutions of copper sulphate indicates an increase in k with increasing acidity, although the reaction is at first slow, pointing to the passivation of zinc under these conditions, since the induction period may be considerably shortened by the activation of the metal. The reaction proceeds periodically as a result of alternation in the passivity of the zinc during the course of the experiment. The temperature coefficient in acid solutions is low, its value being 1·2. The addition of potassium chlorate to neutral copper solutions produces a marked inactivation of the zinc, and in this case also the reaction shows a certain periodicity. The above observations are shown to be explicable on the basis of Ericson and Palmaer's theory of local currents. R. TRUSZKOWSKI.

Polymerisation and hydrogenation of ethylene by means of excited mercury atoms. A. R. OLSON and C. H. MEYERS (J. Amer. Chem. Soc., 1926, **48**, 389—396).—Ethylene decomposes and polymerises, and a mixture of ethylene and hydrogen reacts to form ethane under the action of resonated atoms. The rate of ethane formation is proportional to the square root of the hydrogen pressure. A mechanism for the reaction is proposed and the results of other investigations are correlated. W. THOMAS.

Theory of catalytic phenomena. B. K. MEREJKOVSKI (Bull. Soc. chim., 1926, [iv], **39**, 41—43).—The selective catalysis observed in homogeneous media in the action of bromine on hydrocarbons (A., 1923, i, 527) is inconsistent with Ostwald's theory of catalysis, and difficult to interpret on the theory of intermediate compounds. Chemical reaction is regarded as essentially modification of the valencies of the reacting atoms, and a catalyst is defined as a substance capable, for a given reaction, of modifying the valencies of the reacting substances, of reversible reactions with these substances, and of existing at the same temperature in at least two degrees of oxidation. Negative catalysis is attributed to formation of intermediate compounds with weaker valency forces. Variation in temperature may change negative into positive catalysis (cf. Zelinski, A., 1922, i, 1126). Selective catalysis is similarly attributed to the non-fulfilment of the condition of reversibility in certain cases. R. BRIGHTMAN.

Catalytic decomposition of hydrogen peroxide in an acid–chlorine–chloride solution. R. S. LIVINGSTON and W. C. BRAY (J. Amer. Chem. Soc., 1926, **48**, 405—406; cf. A., 1925, ii, 981).—An equation in the previous communication is corrected. W. THOMAS.

Catalytic effect of silver ammonia ion in the oxidation of ammonia by persulphates. D. M. Yost (J. Amer. Chem. Soc., 1926, **48**, 374—383).—The rate of oxidation of ammonia by the persulphate ion is found to be directly proportional to the concentration of the oxidising agent and to the concentration of the catalyst [the ion $Ag(NH_3)_2$]. The rate increases much less rapidly than the increase in concentration of the ammonia. Hydroxyl ion lowers the rate. A mechanism is suggested for the oxidation and the results are compared with those obtained in the oxidation of chromium (this vol., 261).

W. Thomas.

Inactivation of catalysts during the transformation of carbon compounds. N. D. Zelinski [with M. B. Turova-Pollak] (Ber., 1926, **59**, [*B*], 156—162).—The view has been recently emphasised (Zelinski, this vol., 277) that catalytic action may be ascribed to deformation of the activated molecules by the catalyst. A proportion of these molecules attains a temperature above the average and, in contact with the catalyst, undergoes a profound decomposition leading to the deposition of a thin film of carbon and consequent partial or complete paralysis of the catalyst under conditions in which specific contact poisons are not involved. The removal of the carbon layer must therefore lead to re-activation of the catalyst unless the surface layer has undergone a marked change owing to the deposition. This is found to be the case in an unexpected degree. Platinised asbestos, active birch charcoal, platinised and palladised charcoal are re-activated uniformly and almost completely when gently heated in oxygen; the very low temperature of the maximum rate of oxidation is remarkable. H. Wren.

Catalytic action of metals of the platinum group and their degree of subdivision. G. R. Levi and R. Haardt (Atti R. Accad. Lincei, 1926, [vi], **3**, 91—97).—Levi's method (Giorn. Chim. Ind. Appl., 1925, **7**, 410) of *X*-ray examination has been applied to determine the size of the particles of five specimens of finely-divided platinum. The preparations examined were a commercial platinum-black, two blacks prepared by the reduction of potassium chloroplatinate by aluminium, (*a*) in hot, acid solution, (*b*) in cold, neutral solution, and two specimens of platinum-sponge obtained by heating ammonium chloroplatinate at 320° and at 250°. Assuming the particles to be cubes, the values found for the edges of the particles of the preparations examined, in the above order, were: 6·93, 5·28, 4·8, 11·27, and 9·0 $\mu\mu$.

F. G. Tryhorn.

Fourth report of the committee on contact catalysis. H. S. Taylor (J. Physical Chem., 1926, **30**, 145—171).—Recent investigations on contact catalysis are shown to demand the assumption of a surface the catalytic activity of the component parts of which is not uniform (cf. A., 1925, ii, 562). For the varying atomic distances of Langmuir, there are substituted, in the new theory, varying degrees of saturation of the surface atoms, depending on position in the lattice, and these entail varying chemical reactivity and attractions for impinging molecules. Independent evidence for the theory is afforded by the work of Blench and Garner (J.C.S., 1924, **125**, 1288) on the heat of adsorption of oxygen on charcoal. Thermal data for materials having a high ratio surface mass should be greater than those obtained with coarsely crystalline material, and in this connexion unpublished work by Backström has shown that finely-ground Iceland spar has a higher heat of reaction with dilute acids than the coarser material (cf. also A., 1922, ii, 685).

A further consequence of the theory is that the initial rate of evaporation of catalytic metals should be greater than that of bulk material, which agrees with the sintering of metal catalysts at relatively low temperatures. In a composite metal catalyst surface with atoms ranging in saturation from those almost completely saturated to those held to the surface only by a single metal–metal linking, there will be a whole range of heats of evaporation of individual atoms from the surface. Using the Boltzmann equation, the rates of evaporation are shown to fall off exponentially as the number of atomic linkings increases, and this will explain the temperature sensitivity of active catalysts both to subsequent heat treatment and to the thermal effects accompanying preparation and reaction.

The high dissociation pressure of active manganese dioxide (Whitesell and Frazer, A., 1924, ii, 114) is in agreement with the present theory, as are the effects of interspersion of one oxide in altering the speed of reduction of another (cf. Armstrong and Hilditch, A., 1922, ii, 757). The extension of this theory, by Armstrong and Hilditch (A., 1925, ii, 562), that active atoms may be regarded as detached from the neighbouring metal atoms at the moment of catalytic interchange, is criticised. Recent experiments on promoter action are also discussed in relation to the theory.

With regard to specific activation, specificity of catalytic action may arise from an unsuitable ratio of the reacting gases on one hydrogenation catalyst as compared with a second (cf. Pease and Purdum, A., 1925, i, 798). The "spacing" theory of Adkins is criticised, his data being capable of an interpretation on the basis of contamination, in the main, by alkaline or salt poisons. Poisoning, and not "spacing," in fact, is the fundamental factor, as the latest work of Adkins and Bischoff shows (A., 1925, ii, 568).

The idea of a composite surface can be utilised to recast the concept of specific activity of catalysts. In certain decompositions, *e.g.*, acids to ketones, the bulk of the atoms in the catalytic surface are to be considered active, whereas in others, notably those of alcohols and esters, only a fraction of the surface composed of the less saturated atoms possesses catalytic activity sufficient to effect decomposition. The mode and nature of this will depend on the nature and arrangement of the extra lattice atoms, which factors are largely dependent on the preparation and subsequent treatment of the catalyst. L. S. Theobald.

Water and metals under the influence of electrolysis. R. Saxon (Chem. News, 1926, **132**, 170—171).—When a piece of copper, magnesium, zinc, mercury, bismuth, or tungsten is placed between,

but not touching, two electrodes immersed in water and a current is passed between the electrodes, the surface of the intermediate metal remains bright on the side nearest the cathode, but becomes oxidised on the side nearest the anode, whilst, in some cases, a mixture of oxygen and hydrogen in the ratio of $<1:2$ is evolved. A. R. POWELL.

Electrolysis of aqueous solutions of hydrogen chloride. A. HOLLARD (J. Phys. Radium, 1926, [vi], **7**, 25—32).—Contrary to the statements of Doumer (A., 1908, ii, 252, 349, 458), when the electrolysis is carried out between unattackable electrodes no gas whatever is evolved at applied voltages below 1·24. Between 1·24 and 3 volts, chlorine alone is produced, and above 3 volts a mixture of chlorine and oxygen. If the anode is of mercury or silver of sufficient area not to become immediately coated with oxide or chloride, no gas is evolved at any voltage. In no case has the formation of hypochlorous acid been detected. R. CUTHILL.

Direct oxidation of manganous ion to permanganate. A. N. CAMPBELL (Trans. Faraday Soc., Feb., 1926; advance proof).—The production of permanganate in the electrolysis of manganese sulphate (cf. A., 1924, ii, 555; 1925, ii, 305) has been studied with reference to the influence of conditions, measurements of anode potential being made against a normal calomel electrode. For a solution saturated with potassium sulphate and containing 198 g. of sulphuric acid and 0·7767 g. of manganese per litre, optimum conditions are obtained by electrolysing at 0° with a current density of 1·7 amp./dm.^{2}, in the absence of nitrates and chlorides. The statement of Sem (A., 1915, ii, 777) that manganic sulphate is produced at the same time is not confirmed by measurements of the absorption bands for the solution. It is suggested that the results may prove of use as a qualitative test for manganese. C. H. D. CLARK.

Photo-activation of chlorine. W. TAYLOR (Proc. Durham Phil. Soc., 1924—1925, **7**, 67—71).—See A., 1925, ii, 811.

After-effect in photo-chemical reactions. B. K. MUKERJI and N. R. DHAR (J. Indian Chem. Soc., 1925, **2**, 277—288).—Various reaction mixtures which are known to be photo-sensitive are exposed to a source of light for 5 min. and then removed to the dark. The velocity coefficients of these mixtures are compared with those of similar mixtures which have been kept entirely in the dark, the three coefficients being always calculated from the beginning of the reactions. It is claimed that after-effect is obtained in most of the examples taken. No comparison, however, appears to have been made of the velocity coefficients calculated from the time of removal of illumination with those obtained entirely in the dark. R. W. WEST.

Photo-chemical reactions in circularly polarised, plane polarised, and ordinary light. Velocity of reactions between bromine and (1) cinnamic acid, (2) stilbene. J. C. GHOSH and R. M. PURKAYESTHA (J. Indian Chem. Soc., 1925, **2**, 261—276).—The velocity coefficient in each case is independent of the concentration of the bromine, but increases as the initial concentration of cinnamic acid or stilbene increases. The life periods of the excited bromine molecules in the two series of experiments are calculated as being, respectively, $0·8\times10^{-9}$ sec. and $2·33\times10^{-9}$ sec. For the same intensity, ordinary light and plane polarised light are equally effective, whilst circularly polarised light appears to be less effective. The temperature coefficients are high for photochemical reactions, being 2·6 for stilbene and 2·8 for cinnamic acid. The reactions were all carried out in carbon tetrachloride solution. Application of Einstein's law of photochemical equivalence shows that one quantum of energy at 26° leads to the formation of 436 mols. of dibromophenylpropionic acid or 305 mols. of stilbene dibromide. R. W. WEST.

Photo-chemical disintegration of realgar. O. WEIGEL (Tsch. Min. Petr. Mitt., 1925, **38**, 288—308).—The well-known disintegration of realgar by the action of light to a reddish-yellow powder (consisting of a mixture of As_2S_3 and As_2O_3, with also As_4S_3) is connected with the photo-electrical conductivity of the substance. Detailed determinations were made of the refractive indices, absorption of light, and of the electrical conductivity when the crystal is exposed to light of different wave-lengths. The last shows maxima at 530 μμ and 550 μμ (green and greenish-yellow) for the α and γ vibrations, respectively. Fragments of realgar exposed to direct sunlight for 112 hrs. behind sheets of glass of various colours showed the greatest change with a green glass of maximum transparency near 520 μμ. It is concluded that the photo-chemical disintegration of realgar is due to the separation of electrons and the loosening of the atomic linkings, thus favouring oxidation of the arsenic. L. J. SPENCER.

Visible decomposition of silver halide grains by light. A. P. H. TRIVELLI and S. E. SHEPPARD.—See B., 1926, 173.

Action of dyes on the sensitivity of silver bromide-gelatin. L. GORINI and A. DANSI.—See B., 1926, 219.

Photo-chemical studies. VI. Mechanical actions on the photographic plate. A. REYCHLER.—See B., 1926, 219.

Sensitisation by nuclei of silver sulphide. S. E. SHEPPARD.—See B., 1926, 219.

Influence of sunlight on trinitrotoluene. D. LODATI.—See B., 1926, 220.

Zinc oxide as a photo-chemical sensitiser. A. PERRET (J. Chim. phys., 1926, **23**, 97—129).—Zinc oxide is a sensitiser for the photolysis of solutions of mercury and silver salts. The photolysis of silver salts proceeds according to the scheme $2AgNO_3+ZnO=2Ag+Zn(NO_3)_2+0·5O_2$ with silver peroxide as an intermediate product. The decomposition by chalk of silver salts in solution is not photo-sensitive as claimed by Schultze in 1727. The photolysis of mercuric chloride solutions proceeds according to the equation $2HgCl_2+ZnO=Hg_2Cl_2+ZnCl_2+0·5O_2$ and tends to establish an equilibrium. This reaction is greatly accelerated by dextrose and by sucrose, when

the reaction is of zero order. In the presence of air, the sensitising action of zinc oxide on the photolysis of mercurous chloride consists in the simultaneous oxidation and reduction of the salt. The photochemical decomposition of methylene-blue to the leuco-derivative and an oxidation product is sensitised by zinc oxide. The results are in accord with the views of Baur that methylene-blue is simultaneously an anodic and a cathodic depolariser according to the scheme

$$ZnO\begin{cases}\oplus + OH' + \text{methylene-blue} \longrightarrow \text{oxidation product} + 0{\cdot}5H_2O\\ \ominus + H^{\cdot} + \text{methylene-blue} \longrightarrow \text{leuco-derivative.}\end{cases}$$

During all these sensitising processes, the reduction potential of zinc oxide becomes the normal potential of hydrogen, whilst the oxidation potential approaches that of oxygen and even that of ozone.

A. E. MITCHELL.

Action of radium rays on rock-salt, fluorspar, and quartz. H. LEITMEIER (Tsch. Min. Petr. Mitt., 1925, **38**, 591—598).—Rock-salt when exposed to radium rays acquires a yellowish-brown colour, but this soon fades even in the dark. With the object of testing whether this colour may be due to the presence of impurities, pure sodium chloride was prepared by several recrystallisations from clear rock-salt and from metallic sodium. This purified material still showed the same colour change. The coloration is therefore no doubt due to a change in the material itself, and perhaps, as suggested by Przibram and Bělař (Sitzungsber. Akad. Wiss. Wien, Math.-naturw. Kl., 1924, IIa, **132**, 262), to a separation of electrons from the chlorine ions. All colourless fluorspars become cobalt-blue on exposure to radium, but material from different localities varies widely in the rate of the change and in the intensity of the colour produced. A fluorite from Cumberland exposed to a strong radium preparation until it became bluish-black was then exposed to sunlight, when it acquired a violet colour, which after five years is still stable. Colourless quartz becomes grey or smoky under the influence of radium, and this colour is permanent to light. To test the suggestion that this colour is due to the presence of sodium silicate (which also is browned by radium), colourless quartz from several localities was heated at 900° and 1100° (below and above the b. p. 1050° of sodium silicate) and afterwards exposed to radium, together with a piece of the unheated material; the colour change was the same for each of the three fragments, and cannot therefore be due to sodium silicate. It is concluded that in this case also the coloration is due to some change in the material itself and not to the presence of impurities.

L. J. SPENCER.

Coloration of minerals by radiation. C. DOELTER (Tsch. Min. Petr. Mitt., 1925, **38**, 456—463).—Minerals that have been coloured by radium frequently show subsequent changes in colour after having been stored in the dark for several years; those that have been afterwards decolorised by heat, sometimes show a slow return of the colour. Rock-salt, fluorite, and quartz buried for several months in powdered pitchblende showed in some cases very slight changes in colour. The author believes that the colours are due to pigments, and that his colloidal theory is still feasible (A., 1920, ii, 184).

L. J. SPENCER.

Effect of irradiation with radium on serum- and egg-albumin. A. FERNAU (Biochem. Z., 1926, **167**, 380—383).—Whereas salt inhibits the coagulation of serum-albumin by irradiation, no such protective action can be detected with egg-albumin.

P. W. CLUTTERBUCK.

Complex copper salts. A. BENRATH, H. NIEHAUS, H. MECKENSTOCK, and H. ESSERS (Z. anorg. Chem., 1926, **151**, 31—40).—The solubility of the double salt $5Cu_2S_2O_3,4Na_2S_2O_3,9H_2O$ in sodium thiosulphate solutions has been determined; the greater the concentration of sodium thiosulphate the smaller is the copper content of the residue. Of the three known cuprous potassium thiosulphates, $Cu_2S_2O_3,K_2S_2O_3,2H_2O$ (green), $Cu_2S_2O_3,2K_2S_2O_3,2H_2O$ (yellow), and $Cu_2S_2O_3,2K_2S_2O_3$ (white), the compositions of the first and third are confirmed, but the second is found to contain $3H_2O$. The green double salt decomposes very rapidly in air or water, and in dilute potassium thiosulphate solution it changes into the yellow salt. This also is metastable and changes into the white salt in water or aqueous potassium thiosulphate. At 15° and 35°, the solubility of the green double salt in potassium thiosulphate solutions increases with increasing concentration of the latter to a maximum, the sharp fall corresponding with the formation of the white salt. With gaseous ammonia, the *compounds* $Cu_2S_2O_3,2K_2S_2O_3,NH_3$, and $Cu_2S_2O_3,Na_2S_2O_3,2NH_3$ are formed. A co-ordination formula is proposed for the complex

$$2Na_2S_2O_3,Cu_2S_2O_3,CuS_2O_3,5NH_3.$$

The compositions of the three ammines of cupric cyanurate containing 2, 3, and 4 mols. of ammonia per mol. of cyanurate are confirmed. Higher or lower ammines could not be obtained. The solubility of the diammine at 20° in aqueous ammonia of increasing concentration shows breaks corresponding with the formation of the triammine and tetrammine, and the density–ammonia content curve also shows a break corresponding with the formation of the tetrammine. When basic cupric carbonate is treated with a solution containing 115 g. of potassium carbonate and 30 g. of potassium hydrogen carbonate to 50 c.c. of water, a dark blue complex *salt*, $K_6[Cu(CO_3)_4]$, is formed. This readily dissolves in water with decomposition, and the light blue salt, $K_2[Cu(CO_3)_2]$, is precipitated. This in turn is decomposed when stirred with water at 25°, forming the light green basic carbonate, $CuCO_3,Cu(OH)_2$. This also takes place in solutions containing 20 g. of potassium hydrogen carbonate and 0—80 g. of potassium carbonate in 100 c.c. of water, but if the neutral carbonate content is raised to 85—95 g., the grass-green normal carbonate, $CuCO_3$, is obtained. This is very sensitive to water, forming the basic carbonate.

A. GEAKE.

Formation of gold from mercury in an interrupted arc. A. MIETHE and H. STAMMREICH (Z. anorg. Chem., 1926, **150**, 350—354).—The formation

of gold from mercury in an arc occurs when the current changes, and experiments have been carried out in an apparatus rotating at 2000 revolutions per min. in which the circuit is broken at each revolution. Under these conditions, the weight of gold produced is approximately proportionate to the quantity of electricity, being always within 40% of 0·0004 mg. per amp.-hr. No gold was found when the apparatus was run with the current switched off. The *E.M.F.* was 110 volts, the current varied from 1 to 12 amp., and the time from 0·5 to 8 hrs.

A. GEAKE.

Constitution of bleaching powder. B. NEUMANN and F. HAUCK.—See B., 1926, 190.

Silicides of calcium and magnesium. L. WÖHLER and O. SCHLIEPHAKE (Z. anorg. Chem., 1926, **151**, 1—20).—Crucibles made from a mixture of bole and alumina (5 : 2) are not attacked by calcium silicides containing less than 85% of calcium, and soften at 1560°. Calcium silicides were studied by thermal analysis in such crucibles, the thermometer sheath and stirrer being made of the same material. Two silicides, CaSi and $CaSi_2$, of m. p. 1220° and 1020°, respectively, are definitely indicated, and a silicide, Ca_2Si, of m. p. 920°, is probable. Calcium monosilicide and dicalcium monosilicide are unstable and are decomposed by water, yielding silicon hydrides, which ignite spontaneously. They are, therefore, difficult to characterise. Potential measurements in an alcoholic solution of calcium chloride give definite potentials corresponding with calcium and the disilicide (−0·34 volt), but less definite indications of the two intermediate silicides.

As shown by Vogel (A., 1909, ii, 143), thermal analysis reveals the existence of only one magnesium silicide, Mg_2Si. The m. p. (1070°) and the eutectic points, 920° for 43% magnesium and 625°, are lower than found by Vogel. If a small quantity of magnesium and silicon is rapidly cooled from above 1050°, a second *silicide*, MgSi, is obtained; during slow cooling, decomposition to dimagnesium silicide and silicon takes place, the monosilicide being stable only above 1050°. When heated above 600°, dimagnesium silicide loses magnesium from its surface and the monosilicide is formed as an unstable intermediate product; decomposition does not, however, occur if volatilisation of magnesium cannot take place. Above 1100°, both silicides decompose into the elements. Photomicrographs of the alloys and potential measurements in a solution of magnesium chloride in alcohol revealed only dimagnesium silicide.

A. GEAKE.

Instantaneous decompositions on heating sulphides, carbides, silicides, phosphides, silicates, and spinels with alkaline-earth oxides. I. A. HEDVALL (Svensk Kem. Tidskr., 1925, **37**, 166—173; from Chem. Zentr., 1925, II, 1946; cf. A., 1925, ii, 125).—The author has studied the reactions which occur on heating the oxides of barium, strontium, calcium, and magnesium with zinc sulphide, silver sulphide, and cuprous sulphide in a stream of oxygen. The following reaction is typical: $CaO+ZnS+2O_2=CaSO_4+ZnO$. With zinc sulphide, the temperature of reaction increases in the order barium, strontium, calcium, magnesium. There is little or no formation of sulphur dioxide. The behaviour of silver sulphide is similar. From the reactions of cuprous sulphide, it is concluded that it has a transformation point slightly below 377°. In this case, also, no sulphur dioxide is formed. Chromium carbide, iron carbide, and calcium phosphide, respectively, heated with alkaline-earth oxides yield the corresponding carbonates, silicates, and phosphates, respectively, *e.g.*, $2CaO+FeSi_2+5{\cdot}5O=2CaSiO_3+0{\cdot}5Fe_2O_3$. Wollastonite, enstatite, sillimanite, and rhodanite, when heated with alkaline-earth oxides in a stream of nitrogen, undergo decomposition according to the equation $M'O+MSiO_3=MO+M'SiO_3$. A similar but less intense decomposition takes place with the spinels, *e.g.*, $CaO+CoO,Al_2O_3=CaO,Al_2O_3+CoO$.

G. W. ROBINSON.

Decomposition of alkaline-earth sulphates. I. J. ZAWIDSKI, J. KONARZEWSKI, W. J. LICHTENSTEIN, S. SZYMANKIEWICZ, and J. WACHSZTEJŃSKI (Rocz. Chem., 1925, **5**, 488—503).—The thermal decomposition of calcium sulphate has been studied, with the object of finding conditions under which this could be used for the technical production of sulphur dioxide. The two reactions $4CaSO_3 \longrightarrow CaS+3CaSO_4 \longrightarrow 4CaO+4SO_2$ take place at 600°, and lead to a condition of equilibrium in which the pressure of the sulphur dioxide depends on the temperature. At higher temperatures, there is a further reaction between sulphur dioxide and calcium oxide or sulphide, which leads to the separation of sulphur. Above 1150°, the only products of the interaction between sulphur dioxide and calcium oxide are calcium sulphate and sulphur. The decomposition of a mixture of 1 part of calcium sulphide to 3 parts of sulphate takes place at temperatures which are much lower than those required for the decomposition of pure calcium sulphate.

R. TRUSZKOWSKI.

Volatility of the compound of barium sulphate with sulphuric acid. F. KRAUSS (Chem.-Ztg., 1926, **50**, 33).—The compound formed when barium sulphate is dissolved in concentrated sulphuric acid is shown to be volatile by the green coloration of a Bunsen flame when (i) a platinum wire dipped in the solution is heated therein, (ii) a stream of air blown through the solution is directed towards the flame, (iii) the flame is brought near a mixture of barium sulphate, concentrated sulphuric acid, and methyl alcohol.

L. M. CLARK.

Two varieties of mercuric oxide, and direct formation of oxychlorides and oxybromides. H. PÉLABON (Bull. Soc. chim., 1926, [iv], **39**, 201—202).—See A., 1925, ii, 222, 697.

Behaviour of beryllium in the formation of complexes. R. FRICKE (Z. angew. Chem., 1926, **39**, 317—321).—From the position of beryllium in the periodic table, its small atomic volume, low atomic heat, and atomic configuration, beryllium compounds having a heteropolar structure should readily form stable co-ordinated additive compounds. Such compounds have been prepared by the direct

combination at the ordinary temperature of anhydrous beryllium chloride with various organic liquids. In compounds of the type $BeCl_2,2X$, where X is Me·CN, Me·CO·Me, C_5H_5N, Ph·NO_2, Ph·CHO, Ph·NH_2 or similar compounds, beryllium has the co-ordination number 4 and the chlorine ion is in the inner ring, whilst in the compounds $BeCl_2,4NH_3$, $BeCl_2,4Me·NH_2$, and $BeCl_2,4Ph·NH·NH_2$ the chlorine is in the outer ring. Compounds in which beryllium appears to have a co-ordination valency of 6 are formed by the addition of hydrazine to anhydrous beryllium chloride dissolved in ether, whereby white, powdery precipitates having the composition $BeCl_2,3N_2H_4$, $2BeCl_2,3N_2H_4,4H_2O$, and $2BeCl_2,5N_2H_4,2H_2O$ are formed. Under the same conditions, phenylhydrazine gives a stable precipitate, $BeCl_2,3Ph·NH·NH_2$, and evidence is given in support of a co-ordination valency of 6 for beryllium in this compound, although it is possible that the co-ordination valencies of the metal may not be fully saturated. Beryllium may be considered to have a co-ordination valency of 8 in the compounds $BeCl_2,2Me·CO·Me,4C_6H_6$ and $BeCl_2,2NH_3,4Me·CO·Me$; as neither acetone nor benzene is capable of displacing chlorine into the outer ring, the acetone molecules in the first compound and the ammonia molecules in the second must be, together with chlorine, in the inner ring, and the benzene in the first and the acetone in the second compound in the outer ring.

A. R. Powell.

Constitutional changes occurring in clays on heating. Research Staff of Gen. Electric Co. (J. F. Hyslop).—See B., 1926, 157.

Complex thallium compounds. A. Benrath [with H. Weiland, H. Hamacher, and E. Kircheisen] (Z. anorg. Chem., 1926, **151**, 21—30).—Thallium schönite, $CuSO_4,Tl_2SO_4,6H_2O$, crystallises from aqueous solution only in the presence of excess of copper sulphate. Similar double sulphates are formed with nickel (grass-green), zinc (colourless), cobalt (deep red), iron (light green), manganese (pale rose), and magnesium (white); excess of the sulphate of the bivalent metal is always requisite. Solutions of cadmium and thallous chlorides containing more than 6% of the former precipitate a double *salt*, $CdCl_2,2TlCl$, but the salt, $CdCl_2,TlCl$, which is formed in fused mixtures, could not be obtained from solutions.

Thallous thallic double sulphates have been studied in 14% sulphuric acid. Thallous sulphate is hydrolysed by water, and is much more soluble in 14% sulphuric acid, hence it is probable that an acid salt is formed. A double salt, $3Tl_2SO_4,Tl_2(SO_4)_3$, does not exist in the presence of this acid. The solubilities of mixtures, thallous sulphate, and the double salts $5Tl_2SO_4,Tl_2(SO_4)_3$ and $Tl_2SO_4,Tl_2(SO_4)_3$, have been determined at 18°, 45°, and 60°.

A. Geake.

Compounds of silicon and nitrogen containing a silicon bridge. R. Schwarz and W. Sexauer (Ber., 1926, **59**, [*B*], 333—337).—A solution of silicon hexachloride in anhydrous ether is gradually added to liquid ammonia, whereby ammonium chloride and polymeric *diamidodi-iminodisilane*,

$NH_2·Si(:NH)·Si(:NH)·NH_2$,

are formed; the ammonium chloride is removed by solution in liquid ammonia and the product subsequently exposed to a current of nitrogen at −20° to remove adsorbed ammonia. At about −10°, the compound loses ammonia and forms polymeric *tri-iminodisilane*, $\begin{matrix}Si(:NH)\\Si(:NH)\end{matrix}>NH$. The latter substance is stable at the atmospheric temperature; it decomposes above 400°, chiefly with rupture of the silicon bridge, but to some extent with formation of "silicocyanogen," Si_2N_2. The compounds are characterised by unusual sensitiveness to oxygen and particularly to moisture.

The action of magnesium phenyl bromide on silicon hexachloride leads to rupture of the silicon bridge and formation of a mixture of derivatives of monosilane from which *dichlorodiphenylmonosilane*, $SiPh_2Cl_2$, b. p. 166°/17 mm., has been isolated.

H. Wren.

Some double fluorides of zirconium. M. M. Windsor (J. Amer. Chem. Soc., 1926, **48**, 310—312).—Double *fluorides* of zirconium with aniline, brucine, cinchonine, quinine, quinidine, and strychnine were prepared by dissolving the dioxide in hydrofluoric acid and adding an alcoholic solution of the base, followed by crystallisation or by precipitation with acetone.

W. Thomas.

Tin dihydride and tin tetrahydride. E. J. Weeks (Rec. trav. chim., 1926, **45**, 201—202).—Addition of pure aluminium foil to an alkaline solution of potassium stannite yields a light grey deposit of *tin dihydride*, $2KHSnO_2+2Al=2KAlO_2+Sn_2H_2$. The substance quickly oxidises in air and when heated gives tin and water. In the absence of air, tin and hydrogen are formed. With fused potassium nitrate, nitrogen peroxide is formed, $Sn_2H_2+5KNO_3=KNO_2+H_2O+2K_2SnO_2+4NO_2$. Heating in an atmosphere of pure hydrogen yields gaseous *tin tetrahydride*, which reacts with aqueous silver nitrate to give a dark brown precipitate, $SnH_4+4AgNO_3=SnAg_4+4HNO_3$.

J. S. Carter.

Pyrocatechol and pyrogallol compounds with stannic acid. R. Weinland and M. Maier.—See this vol., 398.

Quadrivalent lead salts of the pseudohalogens. H. P. Kaufmann and F. Kögler (Ber., 1926, **59**, [*B*], 178—186; cf. A., 1925, i, 1252).—Potassium selenocyanate dissolved in anhydrous acetone reacts with a solution of lead tetra-acetate in chloroform, yielding lead selenocyanate and selenocyanogen, which is identified by converting it into *diantipyryl selenide*, $C_{22}H_{22}O_2N_4Se$, m. p. 236° (decomp.) (prepared also from antipyrine and selenium bromide or selenocyanogen from iodine and silver selenocyanate). Selenocyanogen is hydrolysed by water according to the equation $2(SeCN)_2+3H_2O=H_2SeO_3+HCN+3HSeCN$; the selenocyanic acid is stable only in neutral or alkaline solution. Potassium selenocyanate may be determined by addition of an excess

of iodine to its solutions in the presence of much sodium hydrogen carbonate and titration of the unused iodine after 1 hr. by sodium thiosulphate in the presence of a little carbon disulphide; the reaction involved is expressed by the scheme $KSeCN+6I+3H_2O=H_2SeO_3+KI+4HI+ICN$. Selenocyanogen undergoes polymerisation when heated in carbon disulphide solution, yielding selenium diselenocyanide, $Se(SeCN)_2$, and selenium dicyanide.

Cyanic acid and lead tetra-acetate react in chloroform solution, yielding *lead tetracyanate* as a non-crystalline substance, which gradually decomposes even in a vacuum and is hydrolysed by water to lead dioxide and cyanic acid; evidence of the production of oxycyanogen was not obtained. H. WREN.

Ammonium carbonates. C. BONNIER (Ann. Chim., 1926, [x], **5**, 37—94; cf. A., 1923, ii, 858).—Ammonium hydrogen carbonate when heated in air loses weight without change of composition. In a closed vessel, the partial pressure of the water vapour reaches its maximum at 33°, condensation taking place at this temperature. This is followed by change of equilibrium due to increase in the pressure of carbon dioxide. In distilling ammonium carbonate, a similar phenomenon occurs on sudden cooling; condensation of water is accompanied by crystallisation of more basic carbonate. The action of water on ammonium hydrogen carbonate is not that of a solvent, but of a reagent which displays affinity for ammonia, as the acid carbonate is decomposed with liberation of carbon dioxide. In a closed vessel, this decomposition continues until the pressure of carbon dioxide reaches a value such that its concentration in the solution inhibits the reaction. This value, which is conditioned by the concentration of the solution, the relative volume of the gaseous phase, and the temperature, may become greater than 1 atm. In air, carbon dioxide is evolved and the solution may be evaporated to dryness without any definite compound crystallising out. Addition of ammonia to a solution of ammonium hydrogen carbonate lowers the vapour pressure considerably; the minimum value thus attained corresponds with a composition which is approximately that of the normal carbonate. The various equilibria studied are treated mathematically, coefficients based on experimental results being determined.

H. J. EVANS.

Oxidation of combined nitrogen to potassium nitrate at low temperatures and reduction of potassium nitrate to cyanide. K. A. HOFMANN, W. LINNMANN, H. GALOTTI, H. HAGENEST, and A. HOFMANN (Ber., 1926, **59**, [*B*], 204—212; cf. Hofmann and Linnmann, A., 1924, ii, 477).—Interaction of nitric oxide and potassium chlorate with production of potassium nitrate, chlorine, and oxygen commences at 210° and is accelerated by increasing the temperature to 300°; since the liberated oxygen oxidises the nitric oxide to some extent, potassium nitrite is also formed. Nitrous oxide, probably on account of its saturated nature, does not react with potassium chlorate, which also behaves very sluggishly towards hydrogen or carbon monoxide, in striking contrast to its behaviour towards ammonia (*loc. cit.*). The ready oxidisability of combined nitrogen is shown by the production of nitrate from potassium cyanate and potassium chlorate or from magnesium nitride, calcium cyanamide, or carbamide and sodium or barium peroxide at very moderate temperatures. Potassium cyanate is converted into potassium nitrate by air at 400°; the action is facilitated by the addition of copper or nickel powder, basic copper carbonate, nickel carbonate, or, preferably, gold or silver powder; the presence of a little water vapour in the air is advantageous. Conversely, potassium nitrate is reduced to cyanide by carbon, but the conditions under which the change occurs are so different from those under which nitrate is produced that the one process cannot be regarded as the reverse of the other. Oxidation of ammonia to nitrate by air proceeds readily at 380—400° in the presence of a basic contact agent such as soda-lime and can be accelerated in an unusual degree by increase of pressure. Copper carbonate, nickel powder, silver powder, and nickel carbonate accelerate the reaction in order of increasing efficiency. Soda-lime may be replaced by the oxides or carbonates of the alkaline earths, provided that the maximum temperature does not exceed the temperature of decomposition of the corresponding nitrate. Technical "nitrolim" is readily nitrified at temperatures below 200° if mixed with soda-lime and copper oxide and exposed in thin layers to the air during several days.

In all the cases of oxidation of nitrogen described above, the presence of nitrite can be readily detected at the commencement of the action, particularly when oxidation takes place rapidly. Towards the end of the change, when the nitrate formation has attained its maximum, the nitrite content diminishes. The tervalent nitrogen of ammonia or its derivatives passes therefore into the tervalent oxidised condition in the nitrite, which, under the conditions of the experiments, is invariably oxidised to nitrate with considerable rapidity. H. WREN.

Oxidation of hydrazine. I. Potassium azodisulphonate. E. KONRAD and L. PELLENS (Ber., 1926, **59**, [*B*], 135—138).—*Pyridine hydrazinedisulphonate* is prepared in 80—85% yield by the action of chlorosulphonic acid on a suspension of hydrazine sulphate in cold pyridine and subsequent precipitation of the salt by addition of ethyl alcohol; the corresponding *ammonium* ($+H_2O$), *sodium* ($+2H_2O$), and *barium* ($+2H_2O$) salts are described. The pyridine salt is oxidised by sodium hypochlorite in the presence of water at −20° to the azo-compound, isolated by addition of potassium chloride as *potassium azodisulphonate*, $SO_3K{\cdot}N{:}N{\cdot}SO_3K$.

H. WREN.

Heavy-metal vanadates and their ammoniacal compounds. F. EPHRAIM and G. BECK (Helv. Chim. Acta, 1926, **9**, 38—51).—Decomposition of alkali vanadates by solutions of heavy-metal salts gives, with few exceptions, complex salts containing both metals (A., 1887, 339; 1889, 351). Double decomposition of barium metavanadate and the heavy-metal sulphates gives products difficult to

separate from barium sulphate, but good results are obtained by use of an *acid barium vanadate*,

$$2BaO,3V_2O_5,12H_2O.$$

Precipitation with alcohol or alcohol–ether mixtures is usually necessary. The salts have the general formula $2MO,3V_2O_5,12$ or $15H_2O$. Less frequently they approximate to the composition $3MO,5V_2O_5,nH_2O$, although the analytical difference is small. They lose their water of crystallisation largely or completely at 220° with decomposition in the case of oxidisable heavy metals.

For the preparation of the acid barium vanadate, ammonium metavanadate (30 g.) is boiled with lime (15 g.) and water (200 c.c.) until the odour of ammonia disappears. Concentrated hydrochloric acid is added until the colour remains yellow, when 500 c.c. of 2*N*-acetic acid are added. The solution is precipitated with barium chloride (30 g. in 300 c.c. of water and 100 c.c. of 2*N*-acetic acid). The barium salt is filtered after 2—3 hrs. Salts of the following metals are then prepared: *nickel*, $3NiO,5V_2O_5,24H_2O$; *cobalt*, $2CoO,3V_2O_5,15H_2O$; *copper*, $3CuO,5V_2O_5,22H_2O$; *beryllium*, $2BeO,3V_2O_5,11H_2O$; *zinc*,

$$2ZnO,3V_2O_5,15H_2O;$$

cadmium, $2CdO,3V_2O_5,15H_2O$; *manganese*,

$$2MnO,3V_2O_5,11H_2O,$$

and thence *lead*, $3PbO,2V_2O_5,2H_2O$. Further salts of the following metals are described: *zinc*,

$$3ZnO,5V_2O_5,8H_2O$$

(from barium metavanadate); *calcium*,

$$2CaO,5V_2O_5,5H_2O;$$

strontium, $3SnO,2V_2O_5,2H_2O$ (anhydrous form known).

The heavy-metal vanadates take up ammonia very slowly with formation of ammoniacal compounds containing, as a rule, 6 mols. of ammonia for each heavy-metal atom. These are more readily obtained by digestion with liquid ammonia. They are regarded as hexammines, and appear, from examination of the ammonia-content with rising temperature, to break down into triammines and, frequently, monoammines. Ammoniacal *compounds* of this type are described for salts of nickel, copper, beryllium, zinc, calcium, and manganese. M. CLARK.

Bettendorf's reaction. K. ZWICKNAGL (Z. anorg. Chem., 1926, **151**, 41—52).—Favourable conditions for Bettendorf's reaction, in which elementary arsenic is precipitated from solutions of arsinic trichloride in hydrochloric acid by stannous chloride, are high concentration of hydrochloric acid, excess of stannous chloride, and warming. The reaction is exothermic, and the heat evolution is about 20,000 cal. per g.-atom of arsenic, depending on the conditions. When arsenic is precipitated from a solution of the trioxide in pure hydrochloric acid, the precipitate has the composition 98·18% As, 1·85% Sn. By exposure to the air, the greater part of the arsenic is re-oxidised. The precipitate from a crude acid contained 94·34% As, 2·35% Sn, 3·23% Se. After treatment with stannous chloride, the solution was freed from tin by distillation through a fractionating head, and from hydrochloric acid by evaporation with potassium chlorate. Four litres of acid were then concentrated to a few c.c., and by testing in Marsh's apparatus no arsenic was found. By Bettendorf's reaction, arsenic may be separated from antimony, but it is only available in concentrated hydrochloric acid; selenium, gold, and mercury are also precipitated. A. GEAKE.

Preparation and properties of antimonic acid solutions. S. GLIXELLI and (MLLE.) DENISZCZUKOWNA (Compt. rend., 1926, **182**, 521—523).—By the hydrolysis of a concentrated aqueous solution of antimonic chloride at 0° for 12—24 hrs., with subsequent removal of hydrochloric acid with ice-water, a precipitate of antimonic oxide has been prepared. Solutions containing 150 g. per litre were slightly opalescent, and very stable at 0° if the preparation was carried out as described. The f. p. was below 0°, but mol. wt. determinations made by this method were influenced by the concentration. For a solution containing 1 g.-mol. of Sb_2O_5 per litre, $\mu=45{\cdot}4$; μ falls to a minimum with dilution, and then increases to 207·9 at 0·00048 g.-mol. per litre. This is analogous to the behaviour of soap solutions. Measurements of p_π have enabled the number of ions associated with the colloidal anion in each micelle to be found at various dilutions, and the f. p. and conductivity phenomena are attributed to the decomposition of these micelles and subsequent ionisation on dilution. For concentrated solutions, the conductivity decreases with time, but for dilute solutions it rises through a maximum and then falls. These solutions are not ultra-filterable, but they can be made so by prolonged heating. Stable colloidal solutions then result which yield a mol. wt. of the order of 10,000. The molecular conductivities are small, and increase with time, especially in dilute solutions, where the micelles split up into molecules. They are coagulated by cations according to the Hardy–Schultze rule. J. GRANT.

Bismuth ammines and complexes. A. C. VOURNAZOS (Z. anorg. Chem., 1926, **150**, 147—156).—Bismuth halides form complex compounds with a great variety of amines and ammonium salts. These may be divided into three classes: (1) compounds with inorganic or organic ammonium salts, *e.g.*, $NH_4[BiBr_4]$ and $NH_4[BiBr_3OAc]$, (2) compounds with salts of aliphatic or aromatic primary, secondary or tertiary amines, *e.g.*, $[BiBr_3,NH_3MeBr]$, (3) compounds with salts of primary or secondary hydrazines, or with azo- or diazo-compounds, *e.g.*,

$$[BiCl_3,NH_2{\cdot}NH_2,(AcOH)_2],\ [BiI_3,C_6H_5N_2{\cdot}C_6H_4Cl],$$
$$[BiBr_3,C_6H_5N_2Cl].$$

These bismuth ammines are mostly readily hydrolysed by water, and they are therefore prepared by mixing the reactants in a suitable non-aqueous solvent, generally acetic acid. The ammines are less soluble than the simple salts and are obtained as crystalline or amorphous precipitates. Bismuth iodide being only slightly soluble, the more soluble double salts, $K_3[BiI_6]$, $Na_3[BiI_6]$, and $K_3[BiBr_3I_3]$, were used. The following complex pyridine and quinoline *compounds* were obtained: $[BiCl_3,C_5H_5N,AcOH]$,

$$[BiCl_3,C_9H_7N,AcOH],$$
$$[BiBr_3,C_5H_5N,CHMe(OH){\cdot}CO_2H],$$
$$[BiBr_3,C_9H_7N,HBr],$$

$[BiF_3,C_5H_5N,H{\cdot}CO_2H]$, $[BiF_3,C_9H_7N,H_2SO_4]$. Some

amine salts are attacked by acetic and other volatile fatty acids, and in such cases the complex compounds are prepared from acetone solutions. The iodides of bismuth, antimony, tin, lead, copper, and silver are only slightly soluble in acetone. These and other halides form very stable complex compounds with alkali halides, the following being obtained: $K_3[BiI_6]$, $K_3[BiI_3Br_3]$, $K_3[BiI_3(CN)_3]$, $K_3[SbI_3Br_3]$, $Na_3[SbI_3(CN)_3]$, $K_2[SnI_2Br_2]$, $Na_2[SnCl_2Br_2]$, $K_2[PbI_2Br_2]$, $Na_2[Cu_2I_2(CN)_2]$, K[AgICN]. A. GEAKE.

Transformation and oxidation of chromium sesquioxide. L. BLANC and G. CHAUDRON (Compt. rend., 1926, **182**, 386—388).—The exothermic reaction αCr_2O_3 (blue precipitated form) $\longrightarrow$ βCr_2O_3 (olive-green) occurs at 500° in air and 750° in a vacuum. The blue oxide absorbs oxygen rapidly at 200°, forming the oxides CrO_2 (CrO_3,Cr_2O_3) and Cr_5O_9 ($CrO_3,2Cr_2O_3$). Both these oxides give rise to β-chromic oxide and a black oxide at 440°; if they are maintained for several hrs. at 350°, the black oxide is formed in larger amount. It is, however, decomposed endothermically at 450—500°, yielding β-chromic oxide. Guignet's green (finely-divided β-chromic oxide) yields the black oxide Cr_5O_9 on oxidation. The results prove the existence of two oxides having the formula Cr_5O_9, the transition temperature being 440°. R. A. MORTON.

Isomerism of Guignet's green. L. WÖHLER and J. DIERKSEN.—See B., 1926, 166.

Compounds of molybdic acid, tungstic acid, and quinquevalent molybdenum with polyhydric phenols and phenolic acids. R. WEINLAND, A. BABEL, K. GROSS, and H. MAI.—See this vol., 397.

Quadrivalent uranium compounds. M. LOBANOW (Rocz. Chem., 1925, **5**, 437—448).—The following compounds of quadrivalent uranium are prepared by the addition of the appropriate acid in the requisite proportions to acid solutions of uranic sulphate: the *basic iodate*, $UO(IO_3)_2$; *normal iodate*, $U(IO_3)_4$; *acid iodate*, $U(IO_3)_4,2HIO_3$; *basic selenite*, $UOSeO_3,U(SeO_3)_2$; *normal selenite*, $U(SeO_3)_2$; all unstable, green, amorphous powders; the *secondary phosphite*, $U(HPO_3)_2,4H_2O$; *acid phosphite*, $UHPO_3,2H_2PO_3,2{\cdot}5H_2O$; *hypophosphite*, $U(H_2PO_2)_4$; *acid hypophosphite*, $U(H_2PO_2)_4,H_3PO_2$; *basic cyanoplatinate*, $UOPt(CN)_6,4H_2O$, all stable crystalline substances; *basic chloroacetate*, $UO(CH_2Cl{\cdot}CO_2)_2,2{\cdot}5H_2O$, unstable [readily changing to *uranyl chloroacetate*, $UO_2(CH_2Cl{\cdot}CO_2)_2$]; *basic dichloroacetate*, $UO(CHCl_2{\cdot}CO_2)_2,2H_2O$ (readily oxidising to *uranyl dichloroacetate*); *tartrate*, $U(C_4H_4O_6)_2,2H_2O$; *citrate*, $U_3(C_6H_5O_7)_4$; *basic cinnamate*, $UO(C_6H_5{\cdot}CH{:}CH{\cdot}CO_2)_2,H_2O$, and *basic salicylate*, all green, amorphous powders. R. TRUSZKOWSKI.

Disulphito- and diselenito-complexes of bivalent central atoms with four co-ordination positions, and the preparation of sodium trisulphitocobaltiate. F. L. HAHN, H. A. MEIER, and H. SIEGERT (Z. anorg. Chem., 1926, **150**, 126—128).—The preparation of salts of the anions $[M^{II}(SO_3)_2]$ and $(M^{III}(SO_3)_3]$ is difficult, because the simple sulphites are sparingly soluble in water. They are, however, soluble in solutions of ammonia, alkali acetates and acetic acid, and sulphur dioxide. The double salts are obtained by adding excess of alkali sulphite to such solutions, and evaporating off the ammonia or sulphur dioxide when necessary. Ammonium salts of complexes having the central atoms magnesium, zinc, cadmium, iron, manganese, cobalt, nickel, copper, and uranyl, and sodium and potassium salts with cobalt, copper, and manganese, were obtained. The corresponding *selenito*-salts are obtained when the simple selenites are dissolved in a warm, concentrated solution of ammonium selenite, and the solution is cooled. Ammonium salts with central atoms cobalt, manganese, cadmium, zinc, nickel, copper, and thallium (NH_4TlSO_3) were prepared. Sodium trisulphitocobaltiate is prepared by adding a boiling solution of sodium sulphite to a solution of cobalt nitrate in dilute acetic acid. A. GEAKE.

Constitution of sulphitocobaltiates. R. KLEMENT (Z. anorg. Chem., 1926, **150**, 117—125).—By digesting carbonatotetramminecobaltic chloride, $[(NH_3)_4CoCO_3]Cl$, with ammonium sulphite, ammonium disulphitotetramminecobaltiate, $NH_4[(SO_3)_2Co(NH_3)_4],3H_2O$, is obtained. The two sulphito-groups probably occupy *cis*-positions, as the single carbonato-group must do so. Attempts to confirm this by replacing the ammonia by 2 mols. of ethylenediamine and separating the optical isomerides of the compound thus obtained were unsuccessful. Only one ethylenediamine molecule reacts, yielding *ammonium* cis-*disulphitoethylenediamine*-trans-*diamminecobaltiate*, $NH_4[(SO_3)_2Co\ en\ (NH_3)_2],3H_2O$. The sodium salt, *sodium* cis-*disulphitodiethylenediaminecobaltiate*, $Na[(SO_3)_2Co\ en_2],3H_2O$, is formed from carbonatodiethylenediaminecobaltic chloride and sodium hydrogen sulphite, but alkaloid salts could not be prepared from it. It differs markedly in solubility, however, from the ammonium *trans*-disulphitodiethylenediaminecobaltiate of Riesenfeld and Petrich (A., 1924, ii, 342), confirming its *cis*-configuration. By the action of concentrated hydrochloric acid on the sodium salt, *trans*-dichlorodiethylenediaminecobaltic chloride is obtained, but it is probable that by such vigorous treatment inversion occurs. Sodium disulphitodiamminecobaltiate, in which each sulphito-group occupies two co-ordination positions, is formed when sodium trisulphitocobaltiate is boiled with sodium hydrogen sulphite and ammonia. Alkaloid salts could not be obtained. By the action of concentrated hydrochloric acid dichloroaquotriamminecobaltic chloride is formed. A. GEAKE.

Hydrides of nickel, cobalt, iron, and chromium. T. WEICHSELFELDER and B. THIEDE (Annalen, 1926, **447**, 64—77; cf. A., 1924, ii, 189).—Whilst the production of nickel hydride by the

action of ethereal magnesium phenyl bromide on nickel chloride is probably preceded by the formation of nickel diphenyl, this compound could not be isolated in a pure condition, probably owing to its ready decomposition with formation of diphenyl, as the proportion of the latter normally found in a solution of the above Grignard reagent is appreciably increased when the latter is treated with nickel chloride in an atmosphere of nitrogen. The existence of the compound NiH_4, previously reported, is not confirmed. The reaction between cobalt chloride and hydrogen in presence of magnesium phenyl bromide proceeds similarly to that in the case of the nickel salt, the *compound* CoH_2 being produced. Ferrous chloride behaves similarly, with formation of *iron dihydride*, FeH_2, a black powder, whilst ferric chloride affords analogously *iron hexahydride*, FeH_6, a black, viscous oil. Treatment of ferric chloride with magnesium phenyl bromide in ether in an atmosphere of nitrogen affords a light brownish-red, flocculent precipitate which immediately turns black, together with colourless crystals. The mixture ignites spontaneously on access of air, an odour of diphenyl being apparent, but an iron phenyl could not be isolated. Hydrogen is absorbed slowly by an ethereal solution of magnesium phenyl bromide and chromium chloride, *chromium trihydride*, CrH_3, being formed as a black precipitate. Preliminary experiments indicate the analogous formation of a tungsten hydride. F. G. Willson.

Oxidation complexes of nickelocyanides in presence of hydroxylamine. A. Job and A. Samuel (Compt. rend., 1926, **182**, 579—581; cf. A., 1923, i, 904).—When the intense violet complex formed from potassium nickelocyanide by atmospheric oxidation in presence of hydroxylamine is treated in neutral solution with mercuric chloride the solution turns blue. Extraction with amyl alcohol affords a blue compound free from potassium and containing only two cyano-groups for each atom of nickel. If aqueous potassium cyanide is added to the solution in amyl alcohol, the violet colour reappears when 1 mol. of potassium cyanide is added for each atom of nickel. If a strongly alkaline solution of the violet compound is treated with sufficient mercuric chloride, the complex is destroyed, yielding nickel cyanide and nitrogen, nitrous and nitric oxides, in exactly the same proportions as when hydroxylamine alone is oxidised under the same conditions, showing that the complex anion contains hydroxylamine; the hydroxylamine molecule connects two nickel atoms. The interaction of the violet compound and red nickel tricyanide in the presence of potassium cyanide affords hydroxylamine and normal potassium nickelocyanide. The blue complex is formulated $(CN)_2(OH)Ni^{III}NH_2(OH)Ni^{III}(OH)(CN)_2$ and the violet complex anion

$$[(CN)_3(OH)Ni^{III}NH_2(OH)Ni^{III}(OH)(CN)_3]''.$$

R. A. Morton.

Oxidation of platinum complex compounds. I. Oxidation by hydrogen peroxide and ozone. L. Tschugaev and W. Chlopin [with E. Fritzmann] (Z. anorg. Chem., 1926, **151**, 253—268).—The general action of hydrogen peroxide on complex compounds of bivalent platinum is to render the platinum quadrivalent and thereby add two hydroxyl groups to it. Thus Peyronne's chloride gives the *dihydroxy*-compound, $[Pt,2NH_3,Cl_2(OH)_2]$, and, in presence of ammonium carbonate, ammonium chloroplatinite is acted on similarly. Ozone in hydrochloric acid solution increases the valency, but adds two chlorine atoms; in alkaline solution both addition and substitution may occur simultaneously. In this way, Peyronne's chloride in presence of ammonia and ammonium carbonate forms a new *hydroxypentammineplatinum carbonate*, $[Pt,5NH_3,OH]_2(CO_3)_3$, whereas the *trans*-isomeride (the chloride of Reiset's second base) forms the chloropentammine chloride, $[Pt,5NH_3,Cl]Cl_3$. If ozone be passed into a solution of platinum methylethylglyoxime in sodium hydroxide, a *sodium* salt is formed by replacement of a hydrogen atom by a chlorine atom. R. Cuthill.

Separation of hafnium and zirconium by fractional precipitation as phosphates from oxalic acid solution. J. H. de Boer (Z. anorg. Chem., 1926, **150**, 210—216).—Freshly-precipitated zirconium phosphate is soluble in oxalic, sulphuric, and phosphoric acids. From oxalic acid solution it is reprecipitated by boiling, or by adding alcohol or a mineral acid; and from sulphuric and phosphoric acids by dilution. If a solution containing zirconium and hafnium phosphates is fractionally precipitated, the hafnium accumulates in the precipitate. The precipitates obtained from sulphuric and phosphoric acids are difficult to filter, but that obtained by adding hydrochloric or sulphuric acid to an oxalic acid solution filters well and gives a comparatively rapid separation of the elements. One hundred kg. of a preparation containing 47·5% of zirconium and less than 0·5% of hafnium were treated, and after 26 fractionations hafnium containing not more than 1% of zirconium was obtained. The hafnium content of each fraction was determined with an *X*-ray spectrograph and confirmed chemically at intervals. This method of separation has the advantages over fractional crystallisation of the double fluorides that it is more rapid, and that the hafnium accumulates in the less, instead of in the more, soluble fraction. From the pure hafnium phosphate, the metal (d 12·1) was prepared by way of the hydroxide, oxide, chloride, metal, iodide, metal. A. Geake.

Preparation of lead arsenates. L. Cambi and G. Bozza.—See B., 1926, 191.

Preparation of pure nickel monoxide. M. Le Blanc and H. Sachse (Z. Elektrochem., 1926, **32**, 58—62).—A study of methods available for the preparation of pure nickel monoxide by heating normal or basic nickel carbonate under varying conditions. The different colours of samples of nickel monoxide may be explained by the presence of the darker-coloured oxide, Ni_2O_3. The quantity of higher oxide may be determined in terms of available oxygen equivalent to the iodine set free when the sample is treated with potassium iodide in presence of hydrochloric acid. By raising the decomposition temperature towards 1200°, the content of higher oxide in the product steadily diminishes.

The oxidation of reduced nickel at about 450° leads to a product containing 2—3% of higher oxide. The best method for preparing the pure monoxide consists in heating the carbonate in a high vacuum at 280°. A yellowish-brown oxide is obtained, containing 0·1% of higher oxide with about 0·5% of water, which darkens rapidly in presence of minute quantities of oxygen. When heated under reduced pressure in the presence of a stream of indifferent gas (carbon dioxide or nitrogen dry and free from oxygen), the carbonate yields the pure monoxide, with about 5% of water. C. H. D. CLARK.

Use of measurements of magnetic rotation for analysis of mixtures. M. JACOB (Compt. rend., 1926, **182**, 573—574).—Analytical applications of rotation and rotatory dispersion are confined to the relatively few substances which display optical activity, whereas the general property of magnetic rotation does not suffer this limitation. A null method, independent of variations in electrical supply, is described whereby a measured magnetic rotation of a standard liquid is balanced against an unknown rotation of opposite sign. The marked differences shown by saturated and benzenoid hydrocarbons enable the method to be of service in the rapid analysis of fuels for aviation. R. A. MORTON.

Sodium chloride solution as a confining liquid for gas analysis. F. G. HOFFMANN.—See B., 1926, 146.

Errors in electro-analysis. BOEHM (Chem.-Ztg., 1926, **50**, 109).—Where the source of current for electrolysis is an alternating supply, it is not satisfactory to employ a motor-generator directly, since the condensation of fumes etc. on the brushes may make the output current irregular, but the motor-generator should be used to charge accumulators, which constitute a satisfactory source of direct current. S. I. LEVY.

Filling of micro-burettes. F. v. KRÜGER (Biochem. Z., 1926, **167**, 66—67). E. C. SMITH.

Multimicroelectrode for simultaneous determinations of p_H. B. SOLOVIEV (Biochem. Z., 1925, **167**, 54—57).—A modification of Lehmann's electrode (A., 1923, ii, 608). E. C. SMITH.

Direct reading off of p_H by a compensatory potentiometric method. A. KANITZ (Biochem. Z., 1926, **167**, 474—478). P. W. CLUTTERBUCK.

Electrometric method of p_H determination. H. MENZEL and F. KRÜGER (Z. Elektrochem., 1926, **32**, 93—97).—A discussion of refinements and precautions which the authors have found to be desirable in the accurate determination of p_H by the electrometric method, using a capillary electrometer. C. H. D. CLARK.

Application of the quinhydrone electrode to the measurement of p_H values in solutions containing copper ions and other bivalent ions. J. B. O'SULLIVAN (Trans. Faraday Soc., 1925, **21**, 319—325).—See A., 1925, ii, 822.

Preparation of solutions of standard hydrogen-ion concentration and the measurement of indicator ranges in an acetone–water mixture containing 10% by volume of water. F. M. CRAY and G. M. WESTRIP (Trans. Faraday Soc., 1925, **21**, 326—337).—Solutions of standard p_H values covering the range from 12·5 to 2, and consisting of solutions of organic acids and their salts, of diethylaniline and its hydrochloride, and of potassium chloride and hydrochloric acid, have been prepared in a solvent consisting of acetone and water and containing 10 vol. % of water and calibrated by means of the quinhydrone electrode. Tables of large numbers of indicators, with the colour changes and p_H ranges in this mixture and in water, have been prepared. S. I. LEVY.

Buffer mixture for the alkaline range of hydrogen-ion concentration determinations. W. R. G. ATKINS and C. F. A. PANTIN (Biochem. J., 1926, **20**, 102—104).—The buffer mixture consists of (*a*) a solution containing 12·4048 g. of boric acid and 14·912 g. of potassium chloride per litre, and (*b*) a solution containing 21·2000 g. of sodium carbonate per litre. The range of this buffer mixture is p_H 7·8—10·8. Between p_H 7·8 and 9·6, the indicators thymol-blue and xylenol-blue are recommended. Phenolphthalein may be used up to p_H 10·5. Beyond this range (p_H 10·1—12·1) alizarin-yellow G (*p*-nitrobenzeneazosalicylic acid) was found suitable. S. S. ZILVA.

Determination of water in mineral oils. S. REINER.—See B., 1926, 146.

Accurate determinations based on measurement of gaseous volume. L. HACKSPILL and G. D'HUART (Ann. Chim., 1926, [x], **5**, 95—133).—The methods previously described (Hackspill and de Heeckeren, A., 1923, ii, 578; Hackspill and d'Huart, A., 1924, ii, 625) are treated in greater detail and applied to the measurement of moisture in gases as well as to the determination of carbon in steel as carbon dioxide. In the former, there is a small but constant error which necessitates a correction; in the latter, the method is claimed to be accurate for very small carbon content and is applicable directly to chromium steels. The apparatus used in this work may be readily applied to vapour-density determinations of many organic compounds, and for this purpose gives accurate results. H. J. EVANS.

Sensitivity of the *o*-tolidine and starch–iodide tests for free chlorine [in water]. A. M. BUSWELL and C. S. BORUFF.—See B., 1926, 174.

Determination of the chlorine ion in water. H. W. VAN URK.—See B., 1926, 174.

Analysis of iodides, and standardisation of permanganate and thiosulphate solutions. G. ALSTERBERG (Biochem. Z., 1925, **166**, 1—23).—McCulloch's method for the determination of iodides by titration with permanganate in the presence of potassium cyanide (A., 1888, 626), which is applicable only to relatively concentrated solutions of iodide (0·1—0·05*N*), has been modified to permit of the

determination of much lower concentrations. Permanganate is added in excess, and the cyanogen iodide formed is titrated with thiosulphate after removal of excess of permanganate with oxalic acid. Bromides are removed by the addition of salicylic acid. The method is also applied to the standardisation of permanganate and thiosulphate solutions. E. C. SMITH.

Test for iodate ion. J. BICSKEI (Z. anorg. Chem., 1926, **151**, 127—128).—When sulphuric acid, starch, and potassium thiocyanate are added to a solution of an iodate, a blue colour is obtained, in accordance with the equation

$5HCNS+6HIO_3+2H_2O=5H_2SO_4+5HCN+6I$.

The test is sensitive to 0·00005 g. of potassium iodate in 10 c.c., and is unaffected by bromates, chlorates, and nitrates; too great an excess of thiocyanate should not be used. A. GEAKE.

Determination of nitrogen by Kjeldahl's method. A. C. ANDERSEN and B. M. JENSEN (Z. anal. Chem., 1926, **67**, 427—448).—As a result of an investigation into the possible sources of error in the determination of nitrogen in organic compounds by Kjeldahl's method, the following procedure is recommended: The substance is decomposed by boiling gently but steadily with 20 c.c. of concentrated sulphuric acid, 10 g. of potassium sulphate, 1 g. of copper sulphate, and 0·75 g. of mercuric sulphate, together with about 0·01 g. of specially prepared graphite to prevent bumping, care being taken to avoid undue evaporation of the acid. Practically all organic substances are decomposed in 2—4 hrs. by this treatment. If the substance evolves hydrogen chloride on treatment with sulphuric acid, the mercuric sulphate is not added until this has been completely expelled. The mercury is precipitated by the addition of sodium sulphide to the alkaline solution immediately before distillation and copper sulphate is added to destroy the excess of alkaline sulphide. The graphite used is prepared as follows: 5 g. of commercial graphite are heated with 15 c.c. of 20% sulphuric acid, and 20 c.c. of a saturated solution of potassium permanganate are slowly added. The mixture is evaporated to dryness in a silica dish and the residue heated until a light, powdery mass remains; this is used in the analysis without further treatment. A. R. POWELL.

Sensitive and specific reactions for nitrate and hydroxylamine. J. BLOM (Ber., 1926, **59**, [*B*], 121—125; cf. Hahn and Jaeger, A., 1925, ii, 1199).—In the absence of nitrite, the solution under investigation (5 c.c.) is treated with sodium acetate if acid or acidified with acetic acid if neutral or alkaline; 1 c.c. of sulphanilic acid solution (10 g. in 1000 c.c. of 30% acetic acid) and 1 c.c. of α-naphthylamine solution (3 g. in 700 c.c. of water+300 c.c. of acetic acid) are added, followed by a small piece of zinc or a few cg. of zinc dust. The gradual development of a red colour or formation of a red precipitate shows the presence of nitrate. For the detection of hydroxylamine in the absence of nitrite, the acetic acid solution is treated with 1—2 c.c. of sulphanilic acid solution and 0·5 c.c. of a solution of iodine (1·3 g.) in glacial acetic acid (100 c.c.); after 2—3 min., the excess of iodine is removed by cautious addition of a slight excess of sodium thiosulphate (2·5 g. in 100 c.c. of water). Production of a red colour after addition of α-naphthylamine solution establishes the presence of hydroxylamine. The method permits the detection of 1 mg. of nitrate or 0·01—0·003 mg. of hydroxylamine per litre. Nitrite may be destroyed previous to testing for nitrate by means of carbamide or ammonium carbonate or by treatment with sulphanilic acid in acetic acid solution, followed by decomposition of the diazobenzenesulphonic acid by heating the solution for 3—4 min. on the water-bath; when the presence of hydroxylamine is being investigated, the latter procedure must be followed, since the other reactions occur sufficiently slowly to permit interaction of nitrous acid and hydroxylamine with formation of nitrous oxide. H. WREN.

Determination of nitrate. K. KÜRSCHNER and K. SCHARRER.—See B., 1926, 155.

Iodometric determination of arsenic acid. B. ORMONT (Z. anal. Chem., 1926, **67**, 417—426).—The arsenic acid solution is treated with sulphuric acid until it contains 15—20% by volume, and then with sufficient potassium iodide to reduce the arsenic acid to arsenious acid. The solution is heated at 80—90° and a current of carbon monoxide and dioxide generated by the action of sulphuric acid on oxalic acid is passed through until the iodine is almost completely expelled (20—30 min.). Sodium sulphite solution is then added drop by drop until the liquid is completely decolorised. After cooling, the acid is neutralised with sodium hydroxide, and the arsenious acid titrated with iodine in the usual way. If all the iodine liberated by the reduction of the arsenic acid is removed by addition of sodium sulphite, the results obtained are not so exact. The sulphuric acid used may be replaced by 10—12% of hydrochloric acid without danger of losing arsenic during the expulsion of the iodine in the gas stream. A. R. POWELL.

Absorption of carbon monoxide by solutions of cuprous chloride. L. MOSER and F. HANIKA (Z. anal. Chem., 1926, **67**, 448—456).—The maximum absorption of carbon monoxide by acid solutions of cuprous chloride is obtained when the composition of the solution is 16—18% of cuprous chloride, 24—27% of hydrochloric acid (*d* 1·19), and 60—55% of water. Addition of 0·2% of stannous chloride still further increases the absorptive power, but larger amounts decrease it. Maximum absorption in ammoniacal solution is obtained with a composition of 11—12% of cuprous chloride, 13—14% of ammonia, and 76—74% of water; 1 c.c. of this solution absorbs 31 c.c. of carbon monoxide at 20°, and this solution is therefore more efficient than the acid solution. A. R. POWELL.

Detection and determination of traces of carbon disulphide in small gas volumes. W. J. HUFF.—See B., 1926, 146.

Determination of sodium sulphide. P. BUDNIKOV.—See B., 1926, 154.

Separation of small quantities of calcium from large amounts of magnesium in water. H. NOLL.—See B., 1926, 221.

Determination of permanent hardness of water by Pfeifer and Wartha's method. A. LUMSDEN-BEDINGFELD.—See B., 1926, 222.

Precipitation of magnesium with aluminium hydroxide. A. LASSIEUR (Compt. rend., 1926, **182**, 384—386).—Pariselle and Laude (A., 1925, ii, 903) have shown that precipitation of aluminium in presence of magnesium by four equivalents of ammonium hydroxide causes co-precipitation of magnesium unless ammonium salts are present in great excess. It is possible to separate aluminium and magnesium accurately, even in the absence of added ammonium salts, by adding ammonium hydroxide until a p_H value of 7 is reached (blue tint with bromothymol-blue). Magnesium is carried down as soon as the p_H exceeds 7. When ammonium hydroxide is added in excess to solutions containing aluminium and calcium salts, the separation is straightforward. R. A. MORTON.

Direct titration of thallous salts by potassium iodate. A. J. BERRY (Analyst, 1926, **51**, 137—139).—Quantitative oxidation of thallous compounds (*e.g.*, hydroxide, iodide, thiocyanate, etc.) to the tervalent thallic condition may be effected by potassium iodate in the presence of a large excess of hydrochloric acid. It is necessary to free the hydrochloric acid from chlorine. Bromides do not interfere, as in the titration the violet colour in the chloroform disappears sharply before any visible yellow or brown colour due to bromine appears. D. G. HEWER.

Theory of the time factor in the de Haen–Low method of determining traces of copper. H. B. DUNNICLIFF and K. RAM (Kolloid-Z., 1926, **38**, 168—174).—The de Haen–Low (iodide) method is recommended for the determination of traces of copper, and may be used to detect 1 part of copper in 5,000,000 parts of solution. The reaction between free iodine and starch is instantaneous. (Limits, iodine$=1{\cdot}5\times10^{-5}$ g. per c.c., starch$=5\times10^{-5}$ g. per c.c.) The observation is confirmed that with given starch and iodine concentrations, and increasing potassium iodide concentration, the colour appears more quickly and is more intense. The possible causes of the time lag in the appearance of the colour are reviewed. It is not due to adsorption of iodine by starch, nor does it depend on the rate of reaction of potassium iodide and copper sulphate. On addition of colloidal cuprous iodide solution to the copper sulphate solution before addition of starch and potassium iodide, the time factor is higher. It is suggested that this can be traced to the adsorption of iodine by the cuprous iodide. Another possible cause is the adsorption of copper ions by starch. The time factor is not influenced by slight acidity, nor by the potassium sulphate formed. It decreases uniformly between 0° and 30°, above 30° it increases, until at 68° no colour appears in dilute solution. Directions are given for the determination of traces of copper by this method, which gives results in good agreement with those obtained by other colorimetric methods. L. L. BIRCUMSHAW.

Spectroscopic detection of minute quantities of mercury. J. J. MANLEY (Proc. Physical Soc., 1926, **38**, 127—128).—Details are given of a method whereby vertical spectrum tubes can be critically examined for vanishingly small quantities of mercury. The tubes have two U-limbs partly immersed in insulated water, which serve as external electrodes. An end-on view of the glow within the tube is obtained by a totally reflecting prism formed on the summit of one of the limbs, the light being reflected horizontally and received in a spectrometer. C. J. SMITHELLS.

Use of water–alcohol mixtures in the electrometric study of precipitation reactions. J. A. ATHANASIU (Compt. rend., 1926, **182**, 519—521).—Electrometric titrations of cerous and cupric ions using potassium ferrocyanide, and of lead, barium, and mercurous ions using potassium chromate solutions have been carried out in a 30% ethyl-alcoholic medium. The anomalous effects due to solution and adsorption in the case of water have not been noted, *i.e.*, there is no potential fall at the beginning of the reaction, the time-effect is absent, and the potential-curve is quite regular. The point of inflexion is not displaced, and is marked by a potential fall of three to ten times that produced using water. This point is unaffected by the presence of sodium and calcium ions. When, however, the strength of the alcohol exceeds 40%, the platinum electrode loses its sensitivity. J. GRANT.

Rapid detection of small amounts of aluminium in certain non-ferrous materials [alloys]. G. E. F. LUNDELL and H. B. KNOWLES.—See B., 1926, 195.

Potentiometric evaluation of titanous chloride solutions. I. M. KOLTHOFF, O. TOMIČEK, and C. ROBINSON (Z. anorg. Chem., 1926, **150**, 157—162; cf. Kolthoff and Tomiček, Rec. trav. chim., 1924, **43**, 775).—The use of potassium dichromate as a standard for evaluating titanous chloride solutions potentiometrically has the advantage that the iron content may also be determined. When titanous chloride is added to the dichromate, the first break in the curve corresponds with oxidation of both the titanium and the iron, and, on continuing the addition, a second break occurs when the iron has been reduced again to the ferrous state. If copper sulphate is used as a standard (cf. Zintl and Rauch, A., 1925, ii, 1003), somewhat too much titanous chloride is always required, and the change of potential at the end-point is small. These difficulties may be overcome by the addition of a little potassium thiocyanate, but the use of copper sulphate is, nevertheless, not recommended. The titration with potassium dichromate is slow, but is accelerated in the neighbourhood of the end-point by the addition of a little copper sulphate or ferric salt. A. GEAKE.

Detection of titanium and uranium by spot analysis. N. A. TANANAEV and G. A. PANTSCHENKO (Z. anorg. Chem., 1926, **150**, 163—166).—The most sensitive test for titanium is that with hydrogen peroxide, but this is not suitable for spot analysis on filter-paper. For this purpose, the best test is the red colour given by chromotropic acid (1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid), which is only slightly weakened by stannous chloride. Colorations given by other metals with this acid either are destroyed by stannous chloride or do not interfere with the test. If a mineral is to be tested, a pin-head of it is fused with potassium hydrogen sulphate, treated with water on a watch-glass, and spotted on filter-paper with chromotropic acid; alternatively, stannous chloride and chromotropic acid may be added to the mass on the watch-glass. The test is sensitive to 0·005 mg. of titanium dioxide in 1 drop of solution. The most sensitive reaction for uranium is the brown colour produced by potassium ferrocyanide. Colorations due to ferric and cupric ions are avoided by reducing with potassium iodide and decolorising the iodine with thiosulphate. Titanium gives a yellow colour, and, if present, must first be precipitated. The test is sensitive to 0·001*N*-solutions. A. GEAKE.

Separation of germanium. I. WADA and S. KATO (Sci. Papers Inst. Phys. Chem. Res., 1925, **3**, 243—262).—For the detection of germanium in an ore or alloy, the substance is digested with 6*N*-nitric acid and, after dilution, the residue is collected and dissolved in hydrofluoric acid. The solution so obtained is evaporated to dryness with nitric acid and the residue extracted with nitric acid, the solution being added to that first obtained and the residue again digested with hydrofluoric acid. The second fluoride solution is diluted, treated with 1 c.c. of sulphuric acid, and saturated with hydrogen sulphide; the filtrate is evaporated with sulphuric acid to expel hydrofluoric acid and heated in a pressure flask with ammonia and ammonium sulphide; the filtered solution is united with the two nitric acid solutions previously obtained. The mixture is evaporated to dryness on the water-bath, the residue dissolved in water with 10 c.c. of hydrobromic acid, and the solution distilled in a current of air saturated with bromine. The cold distillate is treated with a current of air to expel bromine, saturated with sulphur dioxide, and filtered, after addition of 1 c.c. of 10% potassium iodide solution. The filtrate is treated with 10 c.c. of fuming nitric acid, then with a current of air to expel bromine, and evaporated to dryness. The residue is dissolved in hydrochloric acid and the solution distilled in a current of chlorine. The distillate contains the whole of the germanium free from arsenic and selenium. A. R. POWELL.

Determination of iron by the dichromate method. A. BESOMBE (Bull. Soc. chim. Belg., 1925, **34**, 338—342).—The dichromate method for determination of iron is usually regarded as unsatisfactory for amounts of iron of the order 0·2% to a few %, the ferricyanide end-point being too indefinite. The reasons for this indefiniteness are discussed from the point of view of the law of mass action, and it appears that a higher concentration of ferrous iron is necessary to ensure a sharp end-point. Satisfactory results are obtained when 100 c.c. of the solution are evaporated to 5 c.c., a few drops of stannous chloride solution added until the mixture is colourless, 10 c.c. of a 5% mercuric chloride solution added, and the titration then carried out with 0·02*N*-dichromate solution. G. M. BENNETT.

Separation of tantalum and niobium and detection and determination of small quantities of tantalum in niobium compounds. A. R. POWELL and W. R. SCHOELLER (Z. anorg. Chem., 1926, **151**, 221—238).—See A., 1925, ii, 1096.

Determination of gold dissolved in mercury. G. TAMMANN and K. KOLLMANN (Z. anorg. Chem., 1926, **151**, 269—270).—If gradually increasing quantities of zinc are added electrolytically to the amalgam, its potential, measured by the cell $Hg|0{\cdot}5M\text{-}ZnSO_4,Hg_2SO_4|Hg$, is scarcely changed until the amount of zinc is sufficient to convert all the gold into the compound AuZn, after which it suddenly increases. R. CUTHILL.

Separation of the platinum metals. L. WÖHLER and L. METZ.—See B., 1926, 160.

Electric vacuum furnace. J. R. PARTINGTON and N. L. ANFILOGOFF (Trans. Faraday Soc., 1925, **21**, 360—373).—See this vol., 41.

All-metal mercury-vapour pump. G. W. C. KAYE (Phil. Mag., 1926, [vii], **1**, 349—353).—The pump described previously by Backhurst and Kaye (A., 1924, ii, 468) has been considerably improved. The pump is a single-stage type and requires a backing pressure of 4—5 mm. for most purposes, whilst the highest vacua may be obtained with a backing pressure of 1·5 mm. Special attention is directed to the shape and dimensions of the inverted annular jet and the boiler portion has been modified to give a higher boiler pressure and increased jet velocity. A useful form of micrometer valve "constant-leak" device is described. A. E. MITCHELL.

Continuous dialysis or extraction apparatus. M. T. HANKE and K. K. KOESSLER (J. Biol. Chem., 1925, **66**, 495—499).—An apparatus for continuous dialysis under reduced pressure is described, in which the dialysate is kept in constant circulation, its total volume being maintained constant (cf. Mann, A., 1921, ii, 23). C. R. HARINGTON.

Wiegner's elutriation apparatus and its practical application. H. GESSNER (Kolloid-Z., 1926, **38**, 115—123).—The apparatus can be used to determine the rate of settling of the particles in any polydisperse system, the diameter of the particles lying between 2 mm. and 2 μ. It consists of a wide tube, containing the suspension, connected by means of a tap to a narrow tube which contains water. The rate at which the water column sinks in the narrow tube is registered by a photographic method. A graphical method is deduced for determinirg the curve denoting the rate of settling. The possible sources of error in the method are discussed, the chief

difficulty being the preparation of a sample free from electrolytes. The best method of treating samples for analysis appears to be washing with distilled water followed by boiling for 1 hr. A number of examples are given of the use of the apparatus in the investigation of soils. L. L. BIRCUMSHAW.

Apparatus to determine different melting points at the same time. M. SPETER (Chem. Weekblad, 1926, **23**, 135).—The apparatus consists of a tube carrying a bulb at the lower end, the bulb being perforated to allow of the insertion of 5 or 6 capillary m. p. tubes. The thermometer is placed inside this tube, and the whole placed in a wider heating tube. S. I. LEVY.

Storage of small quantities of gas at low pressures. J. J. MANLEY (Proc. Physical. Soc., 1926, **38**, 129—131).—An apparatus for storing small quantities of gases in such a way that contaminating air is excluded, is described. It is designed for use with a Sprengel pump, which withdraws the gas from any experimental plant and delivers it into the storage apparatus. With the aid of barometric traps etc. the gas can be readmitted either partly or wholly into the experimental plant. C. J. SMITHELLS.

Warning against the customary method of preparing cooling mixtures with combustible compounds and liquid air. H. STAUDINGER (Z. angew. Chem., 1926, **39**, 98).—Mixtures of organic compounds with liquid air are very sensitive to impact and friction, and should never be used as cooling mixtures. For example, if 1 c.c. of ether is added to 2—2·5 c.c. of liquid oxygen (old liquid air) and, immediately after mixing, an electric spark is passed about 1 cm. above the mixture, an extremely violent detonation, equivalent to that of about 3 litres of a mixture of hydrogen and oxygen or of 4 g. of glyceryl nitrate, usually results. W. T. K. BRAUNHOLTZ.

New carbon electrode. C. BECKER.—See B., 1926, 198.

Single electrode arc. N. R. DAVIS and C. R. BURCH (Nature, 1926, **117**, 342).

Photo-electric polarimetry. J. KENYON (Nature, 1926, **117**, 304).—An application of a selenium or alkali-metal photometer to polarimetry is described whereby the half-shadow device is eliminated and an accuracy of 0·01° in the red end of the spectrum and 0·1° in the violet has been obtained with apparatus of a preliminary nature. A. A. ELDRIDGE.

Measurement of radiation intensities by photographic methods. I. O. GRIFFITH (Nature, 1926, **117**, 344; cf. Toy, this vol., 135; Houstoun, *ibid.*, 253).—The use of an optical wedge is more convenient and accurate than that involving application of the inverse square law. A. A. ELDRIDGE.

Device for working a thermostat at low temperatures. C. J. J. FOX and C. L. MANKODI (J. Indian Chem. Soc., 1925, **2**, 292—295).—The apparatus is similar to that described by Hickman (J.C.S., 1923, **123**, 3416). Certain modifications are introduced which render the apparatus more efficient, the consumption of ice being considerably reduced. R. W. WEST.

Simple and efficient hydrogen electrode. C. P. SIDERIS (Science, 1925, **62**, 331—332).—The 3-holed rubber stopper of a cylindrical cell carries the hydrogen inlet tube, terminating (upwards) 2 mm. below the conical spiral platinum-wire electrode, and a salt bridge. Equilibrium is reached in a relatively short time. A. A. ELDRIDGE.

Simple nephelometer and colorimeter. H. DOLD (Münch. med. Woch., 1925, **72**, 1325—1326; from Chem. Zentr., 1925, II, 1880).—The height of a liquid column through which a grating on a milk glass plate is visible may be measured by means of an apparatus which is readily sterilisable and requires only small quantities of liquid. The apparatus may be used both for relative and absolute determinations. It may also be used as a tintometer. G. W. ROBINSON.

Turbidimeter for accurate measurement of low turbidities. J. R. BAYLIS (Ind. Eng. Chem., 1926, **18**, 311—312).—The instrument consists of long glass tubes so arranged that a perfectly blue light is underneath. Any suspended matter will reflect white light and cut out some of the blue, and by this means a turbidity of 1 part per million parts may be detected. Standards are prepared by diluting a stock solution made from 2—3 g. of fuller's earth in 1 litre of water, and with a reading between 25 and 45 with the Jackson candle turbidimeter, and the sample under examination is matched with a suitable dilution. D. G. HEWER.

Discovery of aluminium. N. BJERRUM (Z. angew. Chem., 1926, **39**, 316—317).

Arabic text of Avicenna's "Mineralia." E. J. HOLMYARD (Nature, 1926, **117**, 305).—Avicenna's "Mineralia," of hitherto disputed authenticity, is a close Latin translation of the Arabic text of parts of "Al-Shifā'" which is undoubtedly authentic. A. A. ELDRIDGE.

Mineralogical Chemistry.

Cause of the blackening of the sand in parts of the Clyde estuary. D. ELLIS (J. Roy. Tech. Coll. Glasgow, 1925, [2], 144—156).—In various localities in the Clyde estuary the sand is deep black in colour and when freshly gathered has a strong odour of hydrogen sulphide. On exposure to the air it slowly loses its black colour and becomes brown. The fresh sand swarms with saprophytic bacteria and contains sufficient moisture and organic matter to provide for their development, during the course of which they

evolve hydrogen sulphide. This gas reacts with the ferruginous minerals in the sand and with the iron compounds brought down by the river, both in solution and in suspension, and the iron sulphide so formed is deposited on the sand grains, thus causing the characteristic blackness. A. R. POWELL.

Kaolins, clays. Formation of coal-bearing argillaceous schists. A. BIGOT (Compt. rend., 1926, **182**, 634—635).—Experiments on the compression of clays and the carbon tetrachloride extract of kaolin indicate that the pectisation of colloids in coal-bearing argillaceous schists proves the presence of organic matter and the existence of an elevation of temperature. The latter, apparently due to the enormous pressure, is probably sufficient to cause the partial pectisation of the colloids (cf. B., 1925, 318). S. K. TWEEDY.

Transformation of fibrolite. F. RAAZ (Tsch. Min. Petr. Mitt., 1925, **38**, 583—590).—A single crystal of fibrolite heated at 1100° and 1200° showed no change, but when heated at 1600—1700° it changed in density from 3·247 to 2·950. It then showed white porcellanous patches on the surface, and was found to consist of a mixture of mullite and silica-glass (cf. A., 1924, ii, 416). Preliminary experiments with fibrous fibrolite heated at 1330° showed a change in density from 3·01 to 2·65, and in another sample heated at 1100° from 3·1558 to 3·0875. The latter changes are, however, attributed to a mechanical loosening of the fibrous texture, rather than to any transformation of the material. This is supported by the fact that determinations of the electrical conductivity at temperatures up to 1350° fall on a continuous curve. L. J. SPENCER.

Alteration of spodumene in the Etta mine, Black Hills, South Dakota. G. M. SCHWARTZ and R. J. LEONARD (Amer. J. Sci., 1926, [v], **11**, 257—264).—The enormous crystals ("logs") of spodumene occurring in pegmatite at this locality measure up to 40 ft. long and 4 ft. across. The mineral weathers to a friable mass with a soapy feel; this consists of scaly and fibrous sericite, and corresponds with "killinite." Analysis I is of the fresh mineral, *d* 3·167; II—VII are of material in progressive stages of alteration, *d* 3·147—2·582. (In VI also FeO 0·18; in VII also FeO 0·37%.)

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	Li_2O.	H_2O.
I.	62·91	28·42	0·53	0·13	0·11	0·46	0·69	6·78	0·28
II.	62·73	28·29	0·62	0·14	0·06	0·70	0·11	6·61	0·54
III.	61·99	28·52	0·53	0·27	0·10	0·82	0·48	6·12	1·02
IV.	62·27	29·22	0·89	0·10	0·18	0·64	0·35	5·80	1·34
V.	60·61	29·29	0·58	0·31	0·23	0·48	0·59	5·76	2·48
VI.	49·25	31·39	0·96	1·24	0·79	0·67	7·25	0·60	8·46
VII.	47·29	31·31	1·19	2·38	0·69	0·88	4·07	0·28	11·80

Here there is a loss of silica and lithia and a gain of potash and water. L. J. SPENCER.

Leucitic rocks. Syenitic group. A. LACROIX (Compt. rend., 1926, **182**, 597—601).—Evidence is adduced for considering felspathic leucitic rocks as special phases of nephelitic rocks containing excess of potassium. They may then be classed into three groups, viz., syenitic, monzonitic, and theralitic, according as the ratio of the contents of orthoclase and plagioclase is greater than 1·6, between 1·6 and 0·6, or less than 0·6. It is proposed to reserve the name leucitites for those rocks which, because of a low silica content, cannot contain any appreciable quantity of plagioclase. S. K. TWEEDY.

Chemical equilibrium in the formation of the German potash deposits. E. FULDA (Kali, 1925, **19**, 333—337).—The composition of the salts crystallising from a given brine is affected by the degree of supersaturation of the brine at the time of formation of the deposit. An attempt is made to explain the origin of the various mixtures found in potassium salt deposits on this basis. CHEMICAL ABSTRACTS.

Pandermite. A. GUTBIER, G. F. HÜTTIG, and G. LINCK (Z. Elektrochem., 1926, **32**, 79—84).—The water content of pandermite obtained from natural and artificial sources is discussed in relation to different ways of combining water and the nature of the transition from the colloidal to the crystalline state. The composition of natural pandermite is represented by $4CaO,5B_2O_3,xH_2O$, where x may vary continuously, the water apparently being somewhat loosely bound. When the decomposition temperature of specimens (under a constant aqueous tension of 8 mm.) calculated from Nernst's formula is plotted against the number of mols. of water per mol. of calcium oxide, a two-stepped curve is obtained. Presumably water can be held in the space lattice in two different ways, corresponding with two different but not necessarily isolable chemical individuals, which may exist in equilibrium. The corresponding curve for colemanite, chemically similar to pandermite, but mineralogically different from it, indicates that the water is bound in a different way. Artificially prepared pandermite (see A., 1906, ii, 619) is at first colloidal, but after a few days becomes crystalline. The corresponding decomposition curves are traced experimentally, whereby it becomes necessary to distinguish between the colloidal and crystalloidal types of water combination. The transition is explained in terms of a continuous process occurring in a single phase, as distinct from crystal formation from saturated solutions, where two phases of definite composition coexist. C. H. D. CLARK.

Dewindtite: birefringence, chemical composition, and dehydration of the mineral. Comparison with dumontite. A. SCHOEP (Bull. Soc. chim. Belg., 1925, **34**, 347—354; cf. A., 1922, ii, 305).—Dewindtite is found in both micro- and macro-crystalline form, the crystals, probably orthorhombic, having low positive double refraction, α 1·762, β—α 0·004. Rejecting impurities, the air-dried mineral has the composition: P_2O_5, 10·37%; UO_3, 56·13%; PbO, 25·45%; H_2O, 8·12%, which agrees with the formula $3PbO,5UO_3,2P_2O_5,12H_2O$ (the figures previously announced were for material dried at 100°). About half the water is lost at 100°, the whole at 300—400°, the colour becoming orange.

Dewindtite is distinct from dumontite (see A., 1925, ii, 64), which occurs in large, deep yellow crystals having c/b 1·327. It is markedly pleochroic, the extinctions are straight, the double refraction being positive, but much larger than for dewindtite, β—α 0·010, the indices being above 1·78. In chemical

reactions, dumontite resembles dewindtite, but its composition is different:

P_2O_5.	UO_3.	PbO.	TeO_3.	H_2O.	Total.
8·65	56·49	27·19	1·01	5·78	99·12

which lead to the formula $2PbO,3UO_3,P_2O_5,5H_2O$. Dumontite loses half its water at 100° and the remainder at 300°, the colour becoming orange. The two minerals are best distinguished by means of their refractive index, double refraction, and content of water or phosphoric acid. G. M. BENNETT.

Hedyphane from Franklin Furnace, New Jersey. W. F. FOSHAG and R. B. GAGE (Amer. Mineral., 1925, **10**, 351—353).—The analysis: Cl 2·98, As_2O_3 29·94, PbO 52·77, (Mn,Fe)O 0·28, CaO 14·98, MgO 0·10, ZnO 0·23, H_2O 0·08% establishes hedyphane as a new species. It has $\omega=2·026$, $\epsilon=2·010$. CHEMICAL ABSTRACTS.

$FeSiO_3$–$CaSiO_3$–$MgSiO_3$–$NaFeSi_2O_6$ system of monoclinic amphiboles. A. N. WINCHELL (Amer. Mineral., 1925, **10**, 335—341).—By plotting the chemical composition of the minerals of the gruenerite–cummingtonite–kupferite series against the optical constants, the influence of each molecule on the optical properties is shown. $NaFeSi_2O_6$ produces the greatest effect. CHEMICAL ABSTRACTS.

Occurrence of zinc silicate ore of supposed primary origin. S. J. SPEAK (Inst. Min. Met., Feb., 1926; advance copy, 5 pp.).—The ore deposits at Broken Hill, Rhodesia, consist, below the weathered zone, of massive veins of zinc and lead sulphides in dolomite, but the sulphides are always separated from the dolomite walls by breccia consisting of angular fragments of dolomite cemented by a hard, yellow material consisting chiefly of zinc silicate. If this had been produced by weathering or by percolating solutions, it should gradually fade away into the dolomite and should also be found in fissures and cracks. Such is not the case, and all the available evidence at present is against the theory of metasomatic replacement. The author suggests that the deposit was formed either by dynamic or thermal action in such a way that the dolomite breccia was cemented by the injection of a viscous fluid containing zinc silicate probably during the last stages of the ore injection period, and that the presence of zinc silicate in the fluid mass was due to a deficiency of sulphur. A. R. POWELL.

Titanobiotite (wodanite). W. FREUDENBERG (Mitt. Bad. geol. Landes-Anst., 1921, **8**, 319—340; from Chem. Zentr., 1925, II, 2201).—Wodanite (titanobiotite), occurring in a nepheline mica porphyry, contains 11—12·5% of titanium oxide. G. W. ROBINSON.

Composition and age of uranium minerals. C. W. DAVIS (Amer. J. Sci., 1926, [v], **11**, 201—217).—Detailed analyses are given of: I, pitchblende from Katanga; this is penetrated by a network of various secondary minerals which were dissolved out by warm dilute hydrochloric acid; *d* 9·66. II, uraninite in pegmatite from Black Hills, South Dakota, *d* 9·182. III, asphaltite in sandstone from Temple Mtn., Utah, containing 92·35% of volatile matter; dilute nitric acid extracts all the uranium and lead, and analysis is given of the soluble portion.

	UO_3.	UO_2.	PbO.	ThO_2.	He.	$(Yt,Er)_2O_3$.	$(La,Di)_2O_3$.	CeO_2. etc.
I.	37·537	52·77	7·62	nil	0·159	0·35	0·155	0·22
II.	28·582	48·37	16·42	2·15	0·08	1·01	0·80	0·265
		3·28						
III.			0·008	nil	—		0·08	

The lead/uranium+thorium ratios give as ages 665, 1667, and 20·5 million years, respectively; whilst the helium/U+Th ratios give 104 (Katanga) and 58·6 (Black Hills) million years. These results are discussed: the former are the more trustworthy. L. J. SPENCER.

Radioactive manganiferous nodules from Tanokami, Japan. S. IIMORI (Sci. Papers Inst. Phys. Chem. Res., 1926, **4**, 79—83).—Nodules occurring in a river bed and in the adjacent hillside contain 68—90% of matter insoluble in acid, the black soluble constituent being mainly manganese dioxide (66—69% of MnO_2). Concretionary matter filling cracks of the surrounding rock consists of similar manganiferous material. The radioactive content of the nodules varies from 1·3% to 200%, referred to uranium oxide as 100%, the insoluble gangue containing only 0·25%. As the origin of the radioactivity, primary uraniferous minerals in the vicinity are suggested. W. A. CASPARI.

Microscopic structure of pit-coals. A. DUPARQUE (Compt. rend., 1926, **182**, 475—477; cf. Ann. Soc. Géol. Nord, 1925, **50**, 56, 97, 118).—The fundamental constituent of coal, vitrain, is assumed to be formed either by the conversion of structural matter into a gel, or by the precipitation of organic substances from solution, or pseudo-solution, in water. The pockets of clarain and vitrain in durain are formed by the former process, and the fine bands of vitrain in bright coal, and the structureless portions of clarain and durain, by the latter process. The two microscopic constituents of coal (structural substances such as spores, and the structureless colloidal material) appear to have an exclusively vegetable origin. In boghead, cannel, and bright coal, the content of volatile matter is inversely proportional to the development of the fundamental structureless constituent. F. G. TRYHORN.

Composition of natural gases from thermal sources in Madagascar and Réunion. C. MOUREU, A. LEPAPE, H. MOUREU, and M. GESLIN (Compt. rend., 1926, **182**, 602—605; cf. Moureu and Lepape, A., 1916, ii, 389, 481).—Ten samples of gas from different natural sources contained small quantities of oxygen and nitrogen and large amounts of carbon dioxide (about 98%) together with traces of a combustible gas (probably methane); an eleventh sample contained mainly nitrogen. The five inert gases were always present, argon preponderating; the latter sample contained much more helium than the others. The ratio of the argon, krypton, and xenon concentration to that of the nitrogen is of the same order as that for air (cf. *loc. cit.*); except for the

sample rich in nitrogen, it is always greater than the ratio for air. S. K. TWEEDY.

Photo-chemical disintegration of realgar. O. WEIGEL.—See this vol., 366.

Action of radium rays on rock-salt, fluorspar, and quartz. H. LEITMEIER.—See this vol., 367.

Coloration of minerals by radiation. C. DOELTER.—See this vol., 367.

Organic Chemistry.

Hydrogenation of organic substances at high temperature under increased pressure. A. KLING and D. FLORENTIN (Compt. rend., 1926, **182**, 389—391).—It is suggested that in the absence of a catalyst compounds are hydrogenated by thermal decomposition and addition of hydrogen to the products of scission at the moment of their formation. Formation of tarry products by polymerisation of the unsaturated scission products is precluded by the hydrogenation of such unsaturated compounds immediately they are formed. Coal is not readily hydrogenated, and yields benzene derivatives, which provides some evidence of the cyclic structure of the precursors of coal. French shale oil yields aliphatic and naphthalene derivatives together with about 10% of benzenoid compounds. The threshold temperatures for thermal decomposition, and thus hydrogenation, of some organic substances are as follow: *tert.*-butyl alcohol, 250°; *sec.*-butyl alcohol, 380°; colza oil, 430—440°; fish oil, 410°; paraffin hydrocarbons, 410—440°; naphthalene, 500° (approx.); anthracene, 475°; colophony, 460°; caoutchouc, 350—360°. L. F. HEWITT.

Hydrogenation of organic substances at high temperature and pressure using non-hydrogenating catalysts. A. KLING and D. FLORENTIN (Compt. rend., 1926, **182**, 526—527).—Complex organic substances, when heated with hydrogen under pressure, are more readily reduced in the presence of a catalyst such as aluminium chloride, which causes the intermediate formation of substances less stable than the original. Thus, *cyclo*hexanol, heated at 420—440° with hydrogen under pressure, in presence of aluminium chloride, gives an excellent yield of *cyclo*hexane and some normal hexane. Naphthalene under similar conditions yields chiefly benzene, toluene, xylenes, etc. The method is of general application. B. W. ANDERSON.

Methyl and ethyl iodides from the corresponding toluenesulphonates. D. H. PEACOCK and B. K. MENON (J. Indian Chem. Soc., 1925, **2**, 240).—Methyl and ethyl iodides are obtained in yields of 84·5% and 66·6%, respectively, when the corresponding *p*-toluenesulphonates are decomposed with aqueous potassium iodide solution.
R. W. WEST.

Organic molecular compounds. IX. The trichloromethyl group. G. WEISSENBERGER, F. SCHUSTER, and R. HENKE (Monatsh., 1925, **46**, 57—60).—The formation of molecular compounds between chloroform and phenol or phenyl acetate is indicated by the negative deviation of the vapour pressure of mixtures of these pairs of substances from that calculated. The necessary residual valency appears to reside in the trichloromethyl group, since trichloroethylene does not combine with *cyclo*hexanone, whilst chloroform combines with *cyclo*hexanone, benzaldehyde, and anisole. Viscosities and surface tensions of mixtures of chloroform and phenetole, and of trichloroethylene and *cyclo*hexanone, are recorded. F. G. WILLSON.

Preparation of ethylene bromohydrin. F. H. MCDOWALL (J.C.S., 1926, 499—500).—A modification of the method of Read and Brook (*ibid.*, 1920, **117**, 1214). By introducing a fine stream of liquid bromine in place of air saturated with bromine vapour, a considerable saving of ethylene is effected.
H. E. F. NOTTON.

α-Halogenated hydrocarbons of the acetylene series. V. GRIGNARD and H. PERRICHON (Ann. Chim., 1926, **5**, [x], 5—36).—An attempt to replace the halogen in α-halogenated acetylene derivatives by hydroxyl in the hope that a keten would be produced by subsequent intramolecular rearrangement was found to be impracticable, as the halogen is too strongly linked to carbon. The action of alcoholic potassium hydroxide on the bromine derivatives, CR:CBr, results in the formation of CR:CH, together with $CH_2R{\cdot}CO_2H$ (cf. Nef, A., 1900, i, 20), the proportion of acid being greater when R is aromatic and less when R is aliphatic. No acid is obtained from the iodine derivatives, and this difference is attributed to the greater facility with which iodine furnishes auxiliary valencies in the course of the reaction (cf. Nef, *loc. cit.*), so that no fixation of alcohol at the triple linking occurs. The preparation and properties of the α-halogenated derivatives of acetylene dealt with in the course of the work give rise to the following general conclusions. The action of cyanogen bromide on compounds of the type CR:C·MgBr appears to be the only general method of preparing α-bromoacetylenes. In the case of iodo-compounds, twice the theoretical amount of cyanogen iodide must be used, as a compound of this substance with magnesium bromocyanide appears to be formed in the course of the action. Free iodine may also be used in preparing the iodides, but if insufficient is present and the temperature is allowed to rise, a diacetylenic compound, CR:C·C:CR, is obtained. α-Bromo- and α-iodo-acetylenes appear to be divisible into two groups, those in which the triple linking is conjugated with the ring, and those in which this linking retains its aliphatic charac-

teristics. The former readily turn brown and appear to polymerise, the latter are stable. In the former group, the triple linking is more reactive, and derivatives of this group may be converted by sulphuric acid in presence of acetic acid into aromatic ketones with bromine or iodine in the nucleus. In the latter group, mercuric chloride acts on the bromine compounds, which are converted into bromomethyl ketones, whilst the iodine compounds undergo a similar change accompanied by the replacement of iodine by chlorine. When acid mercuric sulphate is used, the iodine compounds are reduced and form ketones. The monohalogenated acetylenes readily add 1 mol. of bromine or iodine; sodium replaces the halogen, yielding the sodio-derivative of the hydrocarbon.

The following are described: m-*xylyl*-4-*acetylene*, b. p. 85°/22 mm., 184—186°/756 mm., d_4^{12} 0·9258, n_D^{12} 1·5438; α-*chloro*-α-m-*xylyl*-4-*ethylene*, C_8H_9·CCl:CH_2, b. p. 104—105°/19 mm., d_4^{12} 1·044, n_D^{13} 1·5446; α-*bromopentinene*, b. p. 44—46°/52—54 mm., d_4^{13} 1·281, n_D^{13} 1·4579; α-*bromoheptinene*, b. p. 64°/19 mm., d_4^{17} 1·1969, n_D^{17} 1·4694; α-*bromoundecinene*, b. p. 125°/16 mm., d_4^{12} 1·1015, n_D^{13} 1·4714; α-*bromo*-β-cyclo*hexylacetylene*, b. p. 83—84°/20 mm., d_4^{12} 1·2989, n_D^{13} 1·5124; α-*bromo*-γ-*phenylpropinene*, b. p. 106—107°/15 mm., $d_4^{11\cdot5}$ 1·377, $n_D^{11\cdot5}$ 1·5693; α-*bromo*-δ-*phenylbutinene*, b. p. 110—111°/7 mm., $d_4^{11\cdot5}$ 1·3354, $n_D^{11\cdot5}$ 1·5636; α-*bromo*-β-p-*tolylacetylene*, b. p. 93—94°/6 mm., d_4^{13} 1·3326, n_D^{13} 1·5985; α-*bromo*-β-m-*xylyl*-4-*acetylene*, b. p. 100—101°/6 mm., d_4^{12} 1·2969, n_D^{13} 1·5927; α-*bromo*-β-p-*anisylacetylene*, b. p. 122—123°/10 mm., d_4^{12} 1·352, n_D^{13} 1·599; α-*iodopentinene*, b. p. 54°/23 mm., d_4^{19} 1·6127, n_D^{19} 1·5148; α-*iodoheptinene*, b. p. 90—92°/17 mm., d_4^{19} 1·4701, n_D^{19} 1·5123; α-*iodoundecinene*, b. p. 143°/14 mm., d_4^{19} 1·2725, n_D^{19} 1·4975; α-*iodo*-β-cyclo*hexylacetylene*, b. p. 85—86°/5 mm., 125—126°/35 mm., d_4^{11} 1·5779, n_D^{11} 1·559; α-*iodo*-γ-*phenylpropinene*, b. p. 139—140°/19 mm., $d_4^{11\cdot5}$ 1·6397, $n_D^{11\cdot5}$ 1·6129; α-*iodo*-δ-*phenylbutinene*, b. p. 142—143°/9 mm., 170—171°/28 mm., d_4^{13} 1·5814, n_D^{13} 1·601; α-*iodo*-β-p-*tolylacetylene*, b. p. 126—127°/14 mm., d_4^{14} 1·6249, n_D^{14} 1·6494; α-*iodo*-β-m-*xylyl*-4-*acetylene*, b. p. 122—123°/5 mm., d_4^{13} 1·5657, n_D^{13} 1·6396; *di*-m-*xylyldiacetylene*, m. p. 138°; m-*xylyl iodomethyl ketone*, m. p. 32—33°; b. p. 140—142°/4 mm., *semicarbazone*, m. p. 160° (decomp.); *bromomethyl amyl ketone*, b. p. 95—97°/17—18 mm., d_4^{13} 1·2507, n_D^{13} 1·4653 [*semicarbazone*, m. p. 245—248° (decomp.)]; *bromomethyl nonyl ketone*, m. p. 25—26°, b. p. 147—150°/19—20 mm., [*semicarbazone*, m. p. 235—238° (decomp.)]; *bromomethyl* cyclo*hexyl ketone*, b. p. 124—125°/24—25 mm., d_4^{12} 1·3616, n_D^{13} 1·5072 (*semicarbazone*, m. p. 181—182°); *bromoethyl benzyl ketone*, m. p. 58° (*semicarbazone*, m. p. 225—230°); *chloromethyl nonyl ketone*, m. p. 44—45° [*semicarbazone*, m. p. 155—157° (decomp.)]; αα*β-tri-iodo*-Δ$^{\alpha}$-*undecene*, b. p. 168—173°/3 mm.; *dibromoiodo*cyclo*hexylethylene*, b. p. 140—145°/4 mm.; *dibromoiodobenzylethylene*, b. p. 150—160°/3 mm.; *tri-iodo*-p-*tolylethylene*, m. p. 70—71°; Δ$^{\alpha}$-*dodecinenonitrile*, b. p. 121—122°/8 mm., $d_4^{11\cdot5}$ 0·8596, $n_D^{11\cdot5}$ 1·4631; (*amide*, m. p. 78—79°); cyclo*hexylpropinenonitrile*, b. p. 96°/21 mm., d_4^{11} 0·9468, n_D^{11} 1·4947; (*amide*, m. p. 103—104°); *phenylpentinenonitrile*, b. p. 125—126°/9 mm., $d_4^{11\cdot5}$ 1·0103, $n_D^{11\cdot5}$ 1·5487; p-*tolylpropinenonitrile*, m. p. 44—45°, b. p. 127°/20 mm., d_4^{16} 1·006, n_D^{16} 1·5755; *amide*, m. p. 91°; m-*xylylpropinenonitrile*, b. p. 140°/25 mm., d_4^{11} 1·0059, n_D^{11} 1·5910 (*amide*, m. p. 72°); *amyl* α-*undecinyl ketone*, b. p. 175—180°/7—8 mm., d_4^{12} 0·8585, n_D^{12} 1·4612; *di*-α-*undecinyl ketone*, b. p. 215—220°/6 mm., m. p. 14°, d_4^{12} 0·8660, n_D^{12} 1·4860.

H. J. Evans.

Manufacture of alcohols. C. B. Carter and A. E. Coxe.—See B., 1926, 217.

Manufacture of *n*-butyl alcohol. F. Boinot.—See B., 1926, 211.

Magnesium alkoxides and their application to the synthesis of alcohols. III. Condensations between dissimilar alcohols. A. P. Terentiev [with J. Gribkov and N. Titov] (Bull. Soc. chim., 1926, [iv], **39**, 44—47).—Dissimilar alcohols may be used in the conditions previously described (A., 1925, i, 110) for the synthesis of higher alcohols. Thus ethyl alcohol and magnesium propoxide at 400° give *n*-amyl alcohol (yield 7%); replacement of the magnesium by calcium gives the same yield. *iso*Propyl alcohol and magnesium propoxide at 375—380° give a 5% yield of *sec.*-hexyl alcohol, b. p. 136—138°, n_D^{20} 1·4193, d_4^{20} 0·8215. Ethyl alcohol and magnesium methoxide react at 370—390°, but evidence of the formation of propyl alcohol was inconclusive.

R. Brightman.

Chlorohydrins of some αβ-unsaturated acetone derivatives. Pastereau and Bader (Compt. rend., 1926, **182**, 527—529).—Aqueous hypochlorous acid, when mechanically stirred with methyl Δ$^{\alpha}$-propenyl ketone and acetic acid for 4 hrs., gives a 35% yield of the γ-*chloro*-β-*ketopentan*-δ-*ol*, b. p. 75—78°/15 mm., n_D^{22} 1·4548, d_4^{22} 1·1254. Similarly, but in poorer yields and after 2 days' reaction, γ-*chloro*-β-*ketohexan*-δ-*ol*, b. p. 94°/13 mm., n_D^{15} 1·4639, d_4^{15} 1·1396, and γ-*chloro*-β-*keto*-δ-*methylheptan*-δ-*ol*, b. p. 61°/5 mm., n_D^{22} 1·4690, d_4^{22} 1·099, are obtained. These liquids possess a camphor-like odour and darken on exposure to light with liberation of water and hydrogen chloride.

B. W. Anderson.

Aliphatic trisubstituted α-glycols. P. Nicolle (Bull. Soc. chim., 1926, [iv], **39**, 55—67).—Dimethylhexyl glycol and diphenylhexyl glycol on dehydration with sulphuric acid yield *iso*propyl hexyl ketone and αα-diphenyloctan-β-one, respectively. The results confirm the view previously adduced (Tiffeneau, A., 1923, i, 788; Lévy, A., 1921, i, 860; 1924, i, 283) that in the dehydration of glycols molecular transposition takes place only when a phenyl group is attached directly to the carbon of the secondary alcoholic group. With a view to examine their hypnotic power, a series of ααα′-trialkyl glycols has been prepared. All members of the series obtained are hypnotics, the magnitude of the effect depending on the number and mol. wt. of the substituent radicals (cf. Tiffeneau and Dorlencourt, A., 1923, i, 676). In the case of ethyl*iso*butylhexyl glycol, the two stereoisomerides required by theory have been isolated.

The following glycols, obtained by the action of Grignard reagents on the ethyl ester of the

appropriate α-hydroxy-fatty acid, are described. *γ-Ethylheptane-γδ-diol*, m. p. 45—46°; *βδ-dimethylpentane-βγ-diol*, m. p. 59° (from *ethyl α-hydroxyisovalerate*, b. p. 170°/760 mm.); *ε-methyl-γ-ethylhexane-γδ-diol*, m. p. 76°; *βε-dimethylhexane-βγ-diol*, b. p. 100—105°/20 mm., *d* 0·925; *γ-ethyl-ζ-methylheptane-γδ-diol*, m. p. 75—76°, and *η-methyl-δ-propyloctane-δε-diol*, m. p. 59—60°, are similarly obtained from ethyl *iso*butylglycollate (*amide*, m. p. 51—52°). The following glycols are similarly prepared from ethyl hexylglycollate: *β-methylnonane-βγ-diol*, *d* 0·9375, obtained in two fractions, b. p. 115—125°/21 mm., 125—139°/21 mm., yielding on dehydration *iso*propyl hexyl ketone, b. p. 200—202°, d^0 0·843. The ketone is also obtained from heptaldoxime, by conversion into the *nitrile*, b. p. 175—180°, and treating the latter with magnesium *iso*propyl bromide. *γ-Ethyldecane-γδ-diol*, m. p. 45—46°; *δ-propylundecane-δε-diol*, m. p. 57—58°; *ε-butyldodecane-εη-diol*, m. p. 73—74°; and *αα-diphenyloctane-αβ-diol*, m. p. 102—103°, yielding *αα-diphenyloctan-β-one*, b. p. 210—220°/12 mm., d^0 1·022 (*semicarbazone*, m. p. 121°), the structure of which is established by its oxidation to benzophenone and heptoic acid. Starting with α-hydroxyoctoamide, obtained in 70% of the theoretical yield by the action of hydrogen chloride on heptaldehyde cyanohydrin in ether, a further series of disubstituted glycol derivatives of heptaldehyde containing dissimilar alkyl groups has been similarly prepared. The following are described: *nonan-β-on-γ-ol*, b. p. 125—130°/31 mm., d^0 0·9513 (*semicarbazone*, m. p. 184°), and *decan-γ-on-δ-ol*, b. p. 126—131°/21 mm., d^0 0·9349 (*semicarbazone*, m. p. 121°), both of which yield the same *γ-methyldecane-γδ-diol*, b. p. 126—142°/19 mm. d^0 0·939; *undecan-δ-on-ε-ol*, b. p. 134—136°/18 mm., d^0 0·9243 (*semicarbazone*, decomp. 220°, m. p. 258—260°); *δ-methylundecane-δε-diol*, b. p. 150°/18 mm., *d* 0·9355; *α-phenyloctan-α-on-β-ol*, b. p. 200°/36 mm.; *β-phenylnonane-βγ-diol*, b. p. 160—180°/16 mm. *ε-Ethyldodecane-εη-diol* is obtained in two isomeric forms, m. p. 61° and 49°, according as propionylhexylcarbinol or *dodecan-ε-on-η-ol*, b. p. 145—146°/19 mm., d^{15} 0·904 (*semicarbazone*, m. p. 270°), respectively, serves as starting point (cf. Tiffeneau and Lévy, A., 1924, i, 825). R. Brightman.

Methylalkylglycerols. R. Delaby and G. Morel (Bull. Soc. chim., 1926, [iv], **39**, 220—230).—See A., 1925, i, 773.

Ethers derived from propylene chlorohydrin. A. Dewael (Bull. Soc. chim. Belg., 1925, **34**, 343—346).—A series of ethers has been prepared from β-chloro-*n*-propyl alcohol by the action of methyl sulphate at 100°, ethyl and allyl alcohols in presence of sulphuric acid, and *n*-propyl alcohol with sulphuryl chloride. The following *β-chloro*-n-*propyl ethers* are described: *methyl ether*, b. p. 98—99°/756 mm., d_4^{20} 0·9946, n_D^{20} 1·40754; *ethyl ether*, b. p. 116—117°/758 mm., d_4^{20} 0·9828, n_D^{20} 1·41285; n-*propyl ether*, b. p. 139°/756 mm., d_4^{20} 0·9399, n_D^{20} 1·41912; *allyl ether*, b. p. 142—143°/762 mm., d_4^{20} 0·9683, n_D^{20} 1·42887. *ββ'-Dichloro*-n-*propyl ether*, b. p. 188°/762 mm., d_4^{20} 1·109, n_D^{20} 1·44675, results from the action of sulphuryl chloride on β-chloropropyl alcohol at 130°. In this and some of the preceding preparations small amounts of β-chloropropylene, b. p. below 40° (dibromide, b. p. 189—190°), and αβ-dichloropropane are obtained. G. M. Bennett.

Isomerism of ethylene oxides and comparison of saturation capacities of cyclic and acyclic radicals. M. Tiffeneau and J. Lévy (Compt. rend., 1926, **182**, 391—393; cf. Orékhov and Roger, A., 1925, **i**, 261; Orékhov and Tiffeneau, *ibid.*, 378, 679; Tiffeneau, Orékhov, and Lévy, *ibid.*, 544).—Ethylene oxides on distillation undergo isomerisation according to the equation:

$$\text{(I.)}\ \begin{matrix}\text{CR'R''}\\ \text{CHR'''}\end{matrix}\!\!>\!\text{O} \longrightarrow \text{CHR'R''·CO·R'''}\ \text{(II.)}$$

The conclusion is reached that rupture of the C·O linking takes place from that carbon atom which is attached to the group or groups of highest saturation capacity. The *p*-anisyl group has a higher saturation capacity than the phenyl group, and the phenyl group greater than two benzyl radicals. *α-Phenyl-β-anisylethylene oxide*, m. p. 118—119°, prepared by the action of benzoyl peroxide on α-phenyl-β-anisylethylene, is transformed when distilled into phenyl *p*-methoxybenzyl ketone. *αα-Dibenzyl-β-phenylethylene oxide*, b. p. 240—245°/30 mm., prepared by the action of benzoyl peroxide on β-phenyl-αα-dibenzylethylene, when distilled at atmospheric pressure yields *αγδ*-triphenylbutan-β-one, the oxygen linking attached to the carbon atom to which the phenyl group is attached being ruptured. L. F. Hewitt.

Halogenated organic oxides. Oxidation of α-chloro-Δ$^{\alpha}$-heptene and β-chloro-Δ$^{\beta}$-octene by perbenzoic acid. N. Prileschajev (Ber., 1926, **59**, [*B*], 194—198).—α-Chloro-Δ$^{\alpha}$-heptene is slowly oxidised by perbenzoic acid in chloroform solution to *α-chloroheptene oxide*, $C_5H_4{\cdot}CH\!<\!\begin{matrix}\text{CHCl}\\ \text{O}\end{matrix}$, b. p. 93—95°/15 mm., d_4^{16} 0·9874, n_D 1·4370, which is converted by calcium carbonate into *β-hydroxyheptaldehyde*, m. p. 98·5—99·5°. Similarly, *β-chloro-Δ$^{\beta}$-octene*, b. p. 84—86°/50 mm., d_{16}^{16} 0·8923, n_D^{16} 1·4424, obtained by the successive action of phosphorus pentachloride and alkali hydroxide on methyl hexyl ketone, is oxidised to *β-chloro-octene oxide*, b. p. 81—82°/21 mm., $d_4^{?}$ 0·9755, d_4^{16} 0·9609, n_D 1·4359, which, with aqueous potassium carbonate solution, affords *γ-hydroxyoctan-β-one*, b. p. 120—122°/50 mm., d_4^{16} 0·9299, n_D^{16} 1·4378 (*semicarbazone*, m. p. 179·5—180°), and an acid (isolated as the calcium salt) which has not been examined completely. H. Wren.

Resolution of glycerol-α-phosphoric acid. P. Karrer and P. Benz (Helv. Chim. Acta, 1926, **9**, 23—25).—The quinine salt of synthetic *dl*-glycerol-α-phosphoric acid (A., 1920, i, 807), after fractional crystallisation from water, has m. p. 155°, $[\alpha]_D$ −144·7°. The barium salt prepared thence was optically inactive. It was converted into the silver salt and thence into the dimethyl ester of glycerol-α-phosphoric acid dimethyl ether, which gave $[\alpha]_D$ −1·76°. This rotation is lower than that (−3·2°) shown by the ester prepared from lecithin (following abstract), indicating that resolution was incomplete. M. Clark.

Glycerol-phosphoric acids from lecithin. P. KARRER and H. SALOMON (Helv. Chim. Acta, 1926, **9**, 3—23; cf. A., 1904, i, 1067; J.C.S., 1905, **87**, 249; 1906, **89**, 1749; A., 1912, ii, 1109; 1917, i, 2).—Hydrolysis of egg-lecithin with aqueous barium hydroxide solution yields a mixture of the barium salts of glycerol-α-phosphoric acid and glycerol-β-phosphoric acid. These are separated by precipitation from aqueous solution of the double salt of the latter with barium nitrate, $[C_3H_7O_6PBa]_2,Ba(NO_3)_2$, which, on treatment with sulphuric acid, gives the β-acid and thence the barium salt. The α-salt, more soluble in cold water than in hot, is precipitated from the filtrate by boiling. Absence of reaction with aqueous barium nitrate, after repeated solution and precipitation, indicates its complete homogeneity. One hundred parts of water at 18° take up only 0·8 part of the β-double salt, which can, therefore, be employed for quantitative separation of mixtures of the α- and β-compounds, due correction being made for the small percentage of double salt left in solution. For accurate determination of the glycerol-phosphoric acids obtained by hydrolysis of lecithin with barium hydroxide, these must be precipitated with alcohol in presence of excess of alkali, thus preventing partition of the acids between the choline and barium hydroxide present. The barium salt mixture from egg-lecithin contains up to 85% of the β-compound. Formation of the double salt from the β-acid only was confirmed by the behaviour of synthetically prepared specimens of the two barium salts.

The β-acid, its barium salt, and its derivatives, as their structure implies, are optically inactive. Methylation of the silver salt with methyl iodide and silver oxide gives the *dimethyl* ester of *glycerol-β-phosphoric acid dimethyl ether*, b. p. 126—128°/0·8 mm. The α-barium salt, inactive itself, gives certain lævorotatory derivatives. Optical activity of varying sign and degree observed for the mixture of barium salts by previous investigators is ascribed to admixture with other substances. For the preparation of the *dimethyl* ester of *glycerol-α-phosphoric acid dimethyl ether*, b. p. 125—126°/0·8 mm., b. p. 110—112°/0·4 mm., the crude mixture of barium salts is treated with silver nitrate in aqueous solution. The precipitate, consisting of α-silver salt and β-double salt with barium nitrate, contains only a trace of β-silver salt and is methylated with methyl iodide. Since freedom of the product from inactive β-ester is uncertain, the maximum observed specific rotation, −3·2°, may not be that of the optically pure compound. An attempt to elucidate the configuration of the glycerol-α-phosphoric acid obtained from lecithin, by fission of the phosphoric acid from this dimethyl ester, followed by conversion into αβ-dimethoxypropionic acid of known configuration, was frustrated by the unusual stability of the compound towards hydrolysing agents. Dilute acids split off only a trace of phosphoric acids. More concentrated acids and longer heating effect incomplete removal of phosphoric acid with accompanying hydrolysis of the methoxyl groups. The use of 20% sodium hydroxide solution is equally unsatisfactory. *Glycerol-α-phosphoric acid dimethyl ether*, isolated as the *barium* salt (+H_2O), was obtained when the compound was heated with 5% hydrochloric acid for 24 hrs. in a sealed tube. The anhydrous salt gave $[\alpha]_D^{20}$ +3·11°.

The proportions of glycerol-α-phosphoric acid and glycerol-β-phosphoric acid present in the hydrolytic products from egg- and ox-brain-lecithin, and from the phosphatides "kephalin" and "sphyngomyelin" (A., 1925, i, 1232), occurring with lecithin in egg-yolk, are tabulated. Both acids are also obtained from the phosphatide present in pea-meal, but quantitative determination of the β-acid present is untrustworthy.

M. CLARK.

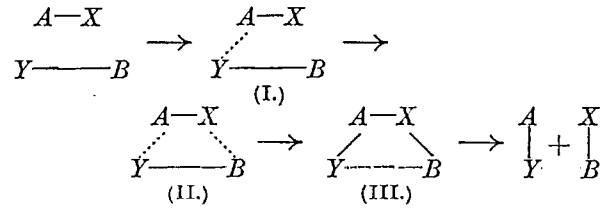
***iso*Oleic acid and other acids obtained by distilling ω-hydroxystearic acid.** V. VESELY and H. MAJTL (Bull. Soc. chim., 1926, [iv], **39**, 230—248).—See this vol., 47.

Preparation of triacetin. S. KAWAI.—See this vol., 281.

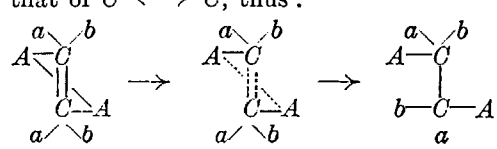
Preparation of trichloropyruvic acid. S. SKRAUP and F. WOLFSCHLAG.—See B., 1926, 216.

Ethyl β-hydroxybutyrate. A. DEWAEL (Bull. Soc. chim. Belg., 1925, **34**, 341—342).—β-Hydroxybutyronitrile (cf. A., 1925, i, 14) is converted by ethyl alcohol and hydrogen chloride into ethyl β-hydroxybutyrate, b. p. 184—185°/755 mm., d_4^{20} 1·017, n_D^{20} 1·4182. This agrees with the description of Tischtschenko (A., 1907, i, 182), but the preparation of Curtius and Müller (A., 1904, i, 481), b. p. 170°, was probably the α-isomeride. G. M. BENNETT.

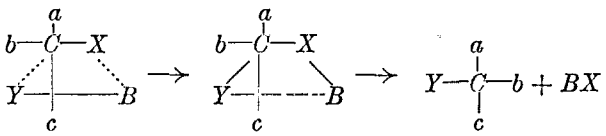
Stereochemical studies. XI. Reaction distances of anions. B. HOLMBERG (Ber., 1926, **59**, [*B*], 125—134).—To explain reactions involving a double exchange for the first phase of which dissociation into radicals or ions appears impossible, the author introduces the conception that the components of the individual molecules, at any rate at the moment of reaction, are separated by different intramolecular distances, termed "reaction distances." The following scheme is thus evolved:



If the change follows the bimolecular law, the intermediate phases are passed with unmeasurable rapidity and there is no possibility of isolating or detecting intermediate products: the formulæ I, II, and III represent merely arbitrary phases of a continuous process. A possibility of estimating reaction distances in certain cases appears to exist, since the addition of a molecule A_2 with *trans*-isomerisation at a double carbon linking is held to indicate that the reaction distance, $A \longleftrightarrow A$ is greater than that of $C \longleftrightarrow C$, thus:



Similar ideas are developed for the action of a base on a halogenated unsaturated ester or for the conversion of a chlorohydrin into an ethylene oxide. When a compound *CabcX* with an asymmetric carbon atom reacts with a compound *BY* in which the reaction distance, $B \longleftrightarrow Y$, is greater than $C \longleftrightarrow X$, the change proceeds according to the scheme:



and is therefore accompanied by a Walden inversion. Since the reactions between bases and unsaturated halogenated esters or chlorohydrins frequently proceed very readily, it appears that they, or possibly quite generally electrolytes or heteropolar compounds, have great reaction distances, and this must be true also for the ions. In general, therefore, steric inversion is to be expected when a bimolecular reaction occurs between an anion and a system containing an asymmetric carbon atom. An example of the replacement of halogen by hydroxyl cannot be given, but many examples are found in the author's work on the conversion of halogenosuccinic esters into thiol- and xantho-succinic esters (A., 1916, i, 307; 1917, i, 115). The previous observations have been made exclusively in aqueous solution, but they are now extended to both aqueous and absolute alcoholic solutions, whereby it is shown that active ethyl bromosuccinate invariably yields a strongly active ethyl xanthosuccinate of oppositive configuration and direction of rotation.

A further example is found in the racemisation of the active bromo- or iodo-succinic acids in the presence of the corresponding halide salts (A., 1913, i, 824; 1914, i, 139; 1917, i, 115; 1918, i, 523). Experimental evidence in favour of the scheme advanced previously in explanation of the change,

$CO_2H{\cdot}CHBr'{\cdot}CH_2{\cdot}CO_2H + Br'' = CO_2H{\cdot}CHBr''{\cdot}CH_2{\cdot}CO_2H + Br'$,

is afforded by the observation that *d*(−)-bromosuccinic acid is converted by chlorides into *l*(+)-chlorosuccinic acid. Previous failures are ascribed to the intermediate conversion of the acid into the lactone. The conversion of *d*(−)-bromosuccinamic acid into *l*(+)-chlorosuccinamic acid is also realisable, but the isolation of the latter acid has not been effected owing to the non-uniformity of the product due to partial hydrolysis of the amido-group during the reaction. H. WREN.

Tartaric acids. L. LONGCHAMBON (Compt. rend., 1926, **182**, 473—474).—*meso*Tartaric acid crystallises from water as the triclinic *monohydrate*, m. p. above 120°, *d* 1·668, $a : b : c = 0{\cdot}6424 : 1 : 0{\cdot}7925$, and from water above 50°, or from sulphuric acid solution, in the anhydrous orthorhombic form, m. p. 159—160°, *d* 1·737, $a : b : c = 0{\cdot}9467 : 1 : 1{\cdot}2265$. d-*Tartaric acid monohydrate*, orthorhombic, *d* 1·582, $a : b : c = 0{\cdot}4716 : 1 : 0{\cdot}5304$, is obtained by crystallisation of the acid below −5°, or by crystallisation at 0°, and inoculating the solution with a trace of the hydrate, or by inoculation at 0° with the isomorphous lithium hydrogen tartrate monohydrate. *d*-Tartaric acid monohydrate is readily dehydrated at the ordinary temperature, and is dextrorotatory. L. F. HEWITT.

Producing methylals. C. B. CARTER.—See B., 1926, 217.

Preparation of dibromoacetal by direct bromination of paracetaldehyde. R. DWORZAK (Monatsh., 1925, **46**, 253—259; cf. Freundler and Ledru, A., 1905, i, 326; Späth, Monatsh., 1915, **36**, 4).—By the action of bromine (2 mols.) on paracetaldehyde below 0° a 40% yield of the *dibromoacetal*, $CHBr_2{\cdot}CH(OEt)_2$, b. p. 96—96·5°/10 mm., is obtained, together with tetrabromobutaldehyde. With 3 mols. of bromine, there is also formed an impure tribromoacetal, b. p. 120·5—122·5°/10 mm. C. HOLLINS.

Effect of heat on chloral hydrate. J. D. MOUNFIELD and J. K. WOOD (J.C.S., 1926, 498—499).—The absence of a break in the vapour-pressure curve of chloral hydrate at 32° indicates that the change in density observed at this temperature is due to the commencement of dissociation, and not to the existence of two modifications (cf., A., 1908, i, 501). H. E. F. NOTTON.

Conversion of ligneous plant substances into coal. III. Formation of sugars as an intermediate phase of the production of coal. C. G. SCHWALBE and R. SCHEPP.—See B., 1926, 145.

Preparation of *l*-arabinose from mesquite gum. E. ANDERSON and L. SANDS.—See B., 1926, 169.

Sugars obtained from gein. H. HÉRISSEY and J. CHEYMOL (Bull. Soc. Chim. biol., 1926, **8**, 50—55).—See A., 1925, i, 1383.

Structure of normal monosaccharides. IV. Glucose. E. L. HIRST (J.C.S., 1926, 350—357).—Oxidation of tetramethylglucose yields, first, tetramethylgluconic acid and then, usually, *d*-dimethoxysuccinic and oxalic acids. Under special conditions (rapid oxidation with nitric acid of *d* 1·42), however, the product contains 40% of xylotrimethoxyglutaric acid, isolated as the crystalline diamide. As in the case of xylose (*ibid.*, 1923, **123**, 1352), the formation of the latter substance indicates that tetramethylglucose, and consequently other normal dextrose derivatives, possess the amylene-oxide structure. H. E. F. NOTTON.

Atmospheric oxidation. I. Oxidation of dextrose and related substances in the presence of sodium ferropyrophosphate. H. A. SPOEHR and J. H. C. SMITH (J. Amer. Chem. Soc., 1926, **48**, 236—248; cf. A., 1924, i, 836).—Sodium ferropyrophosphate is rapidly oxidised to ferripyrophosphate when shaken with air, in aqueous solution. Neither of these compounds could be isolated in crystalline form. The solution contains no iron ions, but the iron is present as part of a complex ion which passes through a semipermeable membrane, indicating that its catalysis of the oxidation of carbohydrates is not a case of surface catalysis. Measurement of the *E.M.F.* of a cell consisting of a platinum electrode

immersed in a solution of the partly-oxidised catalyst, connected, through 0·1*N*-potassium chloride solution, to a standard calomel electrode, indicated that the catalyst is electronically reversible in the sense $FeP_2O_7'' \rightleftharpoons FeP_2O_7' + e$, confirming Rosenheim's structure for similar complex pyrophosphates (A., 1915, ii, 463). The initial, relatively low rate of formation of carbon dioxide in the oxidation of dextrose in presence of the pyrophosphate catalyst (A., 1924, i, 836) is probably due to the formation, during the early stages of the reaction, of intermediate products which subsequently lose carbon dioxide, as the corresponding induction period for *d*-gluconic and *l*-arabonic acids is much shorter, indicating that in the case of dextrose the aldehydic group is first attacked. Whilst carbohydrates are oxidised whether the ferro- or ferri-pyrophosphate is originally present, formic acid is not oxidised in presence of the oxidised catalyst only, so that the catalytic oxidation takes place only with such compounds as can reduce the ferripyrophosphate. The reduction of the ferripyrophosphate by dextrose is preceded by an induction period which is decreased by increased concentration of the carbohydrate or of sodium pyrophosphate, indicating that it is due to a change in the structure of the dextrose molecule, and probably connected with the formation of *d*-fructose. The latter reduces ferripyrophosphate about 20 times as rapidly as does dextrose, which in turn acts about 25 times as fast as mannitol. Potassium cyanide in a concentration of 0·0025*M* increases the rate of oxidation of dextrose in these mixtures, the colour of which changes at the same time from bluish-green to orange. Neither platinum (gauze) nor insulin affects the rate of oxidation. F. G. Willson.

Synthesis and properties of γ-chlorodiacetone-glucose [γ-chloroglucose di*iso*propylidene ether]. J. B. Allison and R. M. Hixon (J. Amer. Chem. Soc., 1926, **48**, 406—410).—Phosphorus pentachloride (4 g.) is added to light petroleum, b. p. 60—70° (150 c.c.), and anhydrous sodium carbonate. When the latter has ceased to react with the phosphorus pentachloride, dry di*iso*propylidene ether (4 g.) is added and the mixture stirred until reaction is complete, whereby *γ-chloroglucose di*iso*propylidene ether*, b. p. 127°/0·5—0·005 mm., is obtained in 25% yield. It is unaffected by boiling 6*N*-sodium hydroxide, but is hydrolysed by boiling, concentrated, methyl-alcoholic sodium methoxide with formation of glucose di*iso*propylidene ether. Treatment of glucose di*iso*propylidene ether or its sodium salt with thionyl chloride in anhydrous light petroleum affords the corresponding *sulphite*. When the reaction with thionyl chloride is carried out at the b. p. of the solvent, a small proportion of the liquid *sulphonate* is also obtained. Glucose di*iso*propylidene ether toluenesulphonate does not react with magnesium phenyl bromide in ether. In boiling toluene, *p*-phenyltolylsulphone is obtained, this behaviour being characteristic of "aryl" compounds (cf. Gilman and Beaber, A., 1925, i, 803, 1057) and substantiating other reactions which indicate negative properties for the third carbon atom in glucose di*iso*propylidene ether. The by-products of the action of phosphorus chlorides on glucose di*iso*propylidene ether are phosphoric esters (readily hydrolysed) and probably a phosphinic acid (cf. Boyd and Smith, A., 1924, i, 1121), the latter predominating when phosphorus trichloride is used. F. G. Willson.

Occurrence of crystallised lævulose. E. O. von Lippmann (Ber., 1926, **59**, [*B*], 348—349).—Crystals of lævulose embedded in a gelatinous medium were observed on some half-ripe tomatoes which had been exposed to a sudden frost after an unusually warm autumn. The gelatinous medium possibly consists of lævulose anhydrides. H. Wren.

Synthesis of gentiobiose. B. Helferich, K. Bäuerlein, and F. Wiegand (Annalen, 1926, **447**, 27—37).—When treated with methyl-alcoholic sodium methoxide, fluorotetra-acetylglucose (cf. Brauns, A., 1923, i, 441) affords d-*glucosyl fluoride*, decomp. 118—125°, $[\alpha]_D^{18}$ +96·7° in water. This yields a *tetrabenzoyl* derivative, m. p. 110—112°, $[\alpha]_D^{22}$ +110·0° in pyridine, and is converted, on treatment with aqueous barium phenoxide, into β-phenolglucoside, together with a syrup, probably the α-isomeride. The action of triphenylmethyl chloride in pyridine yields *ζ-triphenylmethylglucosyl fluoride*, m. p. 140° (decomp.) after softening at 135°, $[\alpha]_D^{15}$ +58·4° in pyridine. The latter yields a *triacetate*, m. p. 147—148°, $[\alpha]_D^{20}$ +119·6°, and a *tribenzoate*, amorphous, m. p. about 95° after softening, $[\alpha]_D^{18}$ +75·1° in pyridine, which, when treated with hydrogen chloride in chloroform, yields *βγε-tribenzoylglucosyl fluoride*, complete separation of which from the accompanying triphenylmethyl derivatives was not effected. Condensation of the above βγε-tribenzoylglucosyl fluoride in carbon tetrachloride solution with acetobromoglucose and silver oxide yields 6-(*tetra-acetyl-β-glucosido*)-2 : 3 : 5-*tribenzoylglucosyl fluoride*, m. p. 195—196°, $[\alpha]_D^{20}$ +15° in chloroform, and this, when treated with methyl-alcoholic ammonia, yields *gentiobiosyl fluoride*, decomp. 215—220° after softening from about 180°, $[\alpha]_D^{20}$ +33·47° in water (*hepta-acetate*, m. p. 162—163°). When boiled in aqueous solution with calcium carbonate, the fluoride affords gentiobiose, identified by conversion into the octa-acetate, m. p. 189—191° (cf. Zemplén, A., 1913, i, 707), and the osazone, m. p. 170—173° (cf. Haworth and Wylam, J.C.S., 1923, **123**, 3123). F. G. Willson.

Synthesis of a disaccharide-glucoside. II. B. Helferich, W. Klein, and W. Schäfer (Annalen, 1926, **447**, 19—26; cf. A., 1925, i, 9).—Treatment of the triphenylmethyltriacetyl-α-methylglucoside, previously described, with 4 mols. of phosphorus pentabromide at 100° affords acetyldibromoglucose, m. p. 172°, $[\alpha]_D^{20}$ +189·1° (cf. Wrede, A., 1922, i, 226; Karrer and Smirnoff, *ibid.*, 228). When the proportion of phosphorus pentabromide is limited to 1 mol., triphenylmethyl bromide and *triacetyl-α-methylglucoside-6-bromohydrin* are obtained. Separation is effected by treatment in the cold with methyl-alcoholic ammonia, removal of excess of the latter under reduced pressure, and extraction with water, when triphenylmethyl methyl ether remains undissolved, and *α-methylglucoside-6-bromohydrin*, derived by hydrolysis of the above acetyl derivative, passes into solution. On evaporation of the aqueous

solution under reduced pressure, and treatment of the syrupy residue with benzoyl chloride in pyridine, *tribenzoyl-α-methylglucoside-6-bromohydrin*, m. p. 122°, $[\alpha]_D^{13}$ +90·9° in pyridine, is obtained. The latter can also be obtained similarly from the corresponding triphenylmethyltribenzoyl-α-methylglucoside, and by the action of 1 mol. of phosphorus pentabromide in carbon tetrachloride solution on 2 : 3 : 5-tribenzoyl-α-methylglucoside, the mild conditions of this last procedure excluding the probability of isomerisation. Reduction of the tribenzoylbromohydrin with zinc dust and acetic acid in presence of a trace of platinum chloride (cf. Bergmann, A., 1921, i, 648) affords *tribenzoyl-α-methyl*-d-iso*rhamnoside*, m. p. 139—140°, $[\alpha]_D^{19}$ +106·7° in pyridine. Treatment of the latter with methyl-alcoholic ammonia yields *α-methyl*-d-iso*rhamnoside*, m. p. 98—99°, b. p. 162°/1 mm., from which, on hydrolysis with 10% hydrochloric acid, *d-iso*rhamnose, $[\alpha]_D^{19}$ +29·2° in water (cf. Fischer and Zach, A., 1913, i, 164), is obtained. These reactions fix the constitution of the new methyl-*d*-glucose (A., 1925, i, 9) as a ζ-derivative.

2 : 3 : 5-Tribenzoyl-α-methyl-*d*-glucoside has m. p. 143°, and the 6-(tetra-acetyl-β-glucosido)-tribenzoyl-α-methyl-*d*-glucoside obtained from it by condensation with acetobromoglucose has m. p. 173°, $[\alpha]_D^{19}$ +53·2° in pyridine. The α-methylgentiobioside obtained from the latter on hydrolysis has $[\alpha]_D^{18}$ +58·5° and +65·5°, for the alcoholate and dried substance, respectively, in water. On treatment with cold acetic anhydride in pyridine, it yields a *hepta-acetate*, m. p. 96° after softening at 93°, $[\alpha]_D^{20}$ +64·5° in chloroform. F. G. Willson.

Molecular weight of soluble starch. A. Pictet (Helv. Chim. Acta, 1926, **9**, 33—37; cf. A., 1924, i, 1288; this vol., 52).—An attempt has been made to arrive at the mol. wt. of "soluble starch" by extrapolation of the straight-line graph obtained by plotting the molecular rotatory powers of the di-, tri-, tetra-, and hexa-hexosan depolymerisation products of potato starch against their "coefficients of polymerisation" or number of constituent molecules of hypothetical monohexosan ($C_6H_{10}O_5$). The literature dealing with the specific rotatory power of soluble starch gives, over a range of values lying between +186° and +202°, a large proportion of observations in the neighbourhood of 189°. This value may be taken as corresponding with the simplest and predominating member of a series of starch depolymerisation products, occurring simultaneously in the mixture known as "soluble starch." The extrapolated curve shows for $(C_6H_{10}O_5)_{18}$, mol. wt. 2916, a molecular rotatory power 5600 and thence a specific rotatory power +192°. The formula mol. wt.$=32{,}724/(317-1{\cdot}62\ [\alpha]_D)$, deduced from the di- and trihexosan figures, gives 2975 for the specific rotatory power +189°. This continued relationship between mol. wt. and molecular rotatory power suggests that, by analogy with the simpler hexosans, the atoms in the compound are bound chemically by their ordinary valencies. For values greater than +192°, the mathematical formula fails as the denominator becomes negative in sign. Thus it seems probable that "soluble starch" contains, besides the hexosan, $(C_6H_{10}O_5)_{18}$, not higher members of the hexosan series, but other more complicated depolymerisation products represented by associated molecules resembling those of starch itself. M. Clark.

***X*-Ray investigation of cellulose and lichenin.** E. Ott (Helv. Chim. Acta, 1926, **9**, 31—32; cf. A., 1923, i, 541, 1182; 1925, i, 371).—Cellulose hydrate, obtained by reprecipitation of cellulose from phosphoric acid, oxycellulose, obtained from viscose by the action of potassium permanganate (completely soluble in 10% alkali, copper value 3, acid value 0·46), and hydrocellulose, obtained from viscose by the action of sodium amalgam (completely soluble in 10% alkali), give Röntgen diagrams identical with that of lichenin, showing that the crystalline constituents of these substances are identical. The conversion of cellulose into reserve-cellulose (lichenin) is regarded as change of modification only. The variety of chemical agents bringing about a common result makes chemical change improbable. M. Clark.

Lignin. W. Küster and E. Schnitzler.—See B., 1926, 151.

Lignin. I. Spruce lignin. A. Friedrich and J. Diwald.—See B., 1926, 151.

γγ′γ″-Triaminotripropylamine and its complex compounds with nickel. F. G. Mann and (Sir) W. J. Pope (J.C.S., 1926, 489—493).—Phthal-γ-bromopropylimide is converted by ammonia into *γγ′γ″-triphthalimidotripropylamine hydrobromide*, $(C_8H_4O_2{\cdot}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2)_3N,HBr$, m. p. 243—244°, which crystallises with 1 mol. of acetic acid. *Triphthalimidotripropylamine* has m. p. 150—151°. Hydrolysis yields *γγ′γ″-triaminotripropylamine tetrahydrochloride*, $N(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2)_3,4HCl,0{\cdot}5H_2O$, m. p. 227—229° with foaming. The new base forms tetra-acidic salts only, of which the *chloroplatinate*, $C_9H_{24}N_4,4HCl,2PtCl_4,3H_2O$, m. p. 257—258° (decomp.), *chloroaurate*, $C_9H_{24}N_4,4HCl,4AuCl_3,3H_2O$, m. p. 191—192° (decomp.), and *picrate*, $C_9H_{24}N_4,4C_6H_4O_7N_3,H_2O$, m. p. 222° after softening at 190°, are described. *Tribenzamidotripropylamine* has m. p. 129—131°. The complex ion (Ni trpn) [trpn$=N(C_3H_6{\cdot}NH_2)_3$] is much less stable and less electropositive than the corresponding ethyl complex ion (see following abstract). The following *triaminotripropylamine-nickelous* salts are described: the *thiocyanate*, [Ni trpn](SCN)$_2$, m. p. 260—261° (decomp.); *iodide*, [Ni trpn]I_2,1·5H_2O; *hydroxyiodide*, [Ni trpn]I(OH),2H_2O, and its *compound* with potassium iodide, 2[Ni trpn]I(OH),KI,2H_2O. No co-ordinated complex compounds of the tetramine with nickel or platinum in which the metal showed a co-ordination number of six could be isolated. H. E. F. Notton.

Complex salts of ββ′β″-triaminotriethylamine with nickel and palladium. F. G. Mann and (Sir) W. J. Pope (J.C.S., 1926, 482—489; cf. this vol., 53).—Complex salts of ββ′β″-triaminotriethylamine (=tren) with bivalent nickel, of the types [Ni tren]SO_4 and [Ni_2 $tren_3$]I_4, in which the nickel shows co-

ordination numbers of four and six, respectively, have been prepared. Although, for obvious steric reasons, the sulphate might be expected to possess the double formula, $[Ni_2\,tren_2](SO_4)_2$, mol. wt. and conductivity determinations show that the unimolecular formula is correct. All attempts to resolve tristriaminotriethylaminebisnickelous iodide were unsuccessful. Bivalent palladium yields salts of the complex ion [Pd tren]$^{\cdot\cdot}$. The following compounds are described: (I) *Triaminotriethylaminenickelous* salts: the *thiocyanate*, [Ni tren]$(SCN)_2$, m. p. 285° (decomp.), after darkening at 260°; the *platinic tetrachloride dithiocyanate*, [Ni tren]$PtCl_4(SCN)_2$, m. p. above 280°, shrinking at 211—213°; the *sulphate*, [Ni tren]SO_4, m. p. above 300°, also the *dihydrate* and *heptahydrate*; and the d-α-*bromocamphor*-π-*sulphonate*, m. p. 263—266°, which forms a *dihydrate*, probably $[Ni\,tren(H_2O)_2](C_{10}H_{14}O_4BrS)_2$. (II) *Tristriaminotriethylaminebisnickelous* salts: the *iodide*,

$$[Ni_2\,tren_3]I_4,3\tfrac{1}{2}H_2O,$$

also with $2H_2O$, m. p. (anhydrous) 307—309° (decomp.); the *bromide*, $[Ni_2\,tren_3]Br_4$, m. p. above 290°; the d-α-*bromocamphor*-π-*sulphonate*, m. p. 183—185°, after shrinking at 180°; the *picrate*, $[Ni_2\,tren_3](C_6H_4O_7N_3)_4,3H_2O$, m. p. 205—206° (decomp.); and the d-*camphor*-β-*sulphonate*, m. p. 233—235°, after shrinking at 230°. (III) *Triaminotriethylaminepalladous iodide*, [Pd tren]I_2, m. p. 224—226°, darkening at 220°, and the *palladochloride*,

$$[Pd\,tren]PdCl_6,H_2O.$$

H. E. F. Notton.

Resolution of *dl*-alanine and formation of *trans*-2 : 5-dimethylpiperazine. F. B. Kipping and (Sir) W. J. Pope (J.C.S., 1926, 494—497).—*dl*-Alanine is conveniently resolved by condensing its ethyl ester with *d*-hydroxymethylenecamphor, when d-*methylenecamphor*-l-*alanine ethyl* ester, m. p. 108—109°, $[\alpha]_{Hg\ green}$ +256°, can readily be separated from the product. Hydrolysis with hydrochloric acid gives *l*-alanine hydrochloride, $[\alpha]_{Hg\ green}$ −12·2°. *l*-Alanine ethyl ester passes on keeping into *l*-lactimide (*l-cis*-2 : 5-dimethyl-3 : 6-diketopiperazine; cf. Fischer, A., 1906, i, 145). Reduction of the latter yields, however, *trans*-2 : 5-dimethylpiperazine (J.C.S., 1914, **105**, 219), instead of the expected *cis*-compound, and it is concluded that the lactimide must undergo enolisation during the reaction. H. E. F. Notton.

Enzymic fission of dipeptides. I. H. von Euler and K. Josephson (Ber., 1926, **59**, [*B*], 226—233).—Active preparations of erepsin are obtained by extracting the lining of the small intestine of the pig with glycerol and precipitation of the extract by alcohol; dialysis of the glycerol extract is accompanied by great loss in activity. The hydrolytic action of the enzyme preparations towards glycylglycine has been investigated, the activity being calculated by the expression, $Gl.f.=k/g.$ of enzyme preparation, in which k is the constant for the unimolecular change. The course of the change is followed by Sörensen's "formol" titration method. Other factors being constant, a proportionality exists between the quantity of enzyme and the constant for a reaction of the first order. The optimal hydrogen-ion concentration is p_H 8·0, in good agreement with the observations of Dernby (A., 1917, i, 234). The reaction constant diminishes when the concentration of glycylglycine exceeds about 0·05*N*. H. Wren.

Inorganic magnesyl compounds. Q. Mingoia (Gazzetta, 1925, **55**, 713—721).—When pure, dry hydrogen sulphide is passed into an ethereal solution of magnesium ethyl bromide, *magnesium bromohydrosulphide* is formed. This is proved, not only by measuring the volume of evolved ethane, but also by the preparation of the additive *compound* with quinoline, $C_{18}H_{15}N_2MgBrS$ (cf. Oddo, A., 1904, i, 920; 1907, i, 549). The new magnesium compound is successfully employed in the preparation of the following compounds: dibenzoyl disulphide from benzoyl chloride; thioacetic anhydride from acetyl chloride; monoethyl thiocarbonate, $OEt{\cdot}CO{\cdot}SH$, from ethyl chloroformate; ethyl mercaptan from ethyl iodide; trithioacetaldehyde, $(CHMeS)_3$, and the quinoline derivative, $C_{20}H_{14}ON_2MgBr$, from acetaldehyde; thio*iso*valeraldehyde from *iso*valeraldehyde.

W. E. Ellis.

Organo-lead compounds. R. Danzer (Monatsh., 1925, **46**, 241—244).—The organo-lead compounds, obtained by the action of magnesium *n*-butyl chloride on lead chloride, are brominated in ether at −75° to −85°, and converted by treatment with excess of magnesium *n*-butyl chloride into *lead tetra-n-butyl*, b. p. 156°/10 mm. By addition of more bromine to the brominated solution or to lead tetra-*n*-butyl, there is formed *lead di-n-butyl dibromide*. *Lead n-butyltriisobutyl*, b. p. 145—146°/10 mm., is prepared from magnesium *n*-butyl chloride and lead tri*iso*butyl bromide. C. Hollins.

***cyclo*Hexane*spirocyclo*hexane.** W. S. G. P. Norris (J.C.S., 1926, 245—253).—cyclo*Hexane*spirocyclo*hexane*, the first known spiran hydrocarbon, is a liquid of geranium-like odour. It is stable towards oxidising agents and bromine, and its molecular refraction and dispersion, and that of cyclo*hexane*spirocyclo*hexan*-3-*one*, do not show the exaltation characteristic of strained rings (cf. Kon, *ibid.*, 1922, **121**, 515). cyclo*Hexane*spiroeyclo*hexane*-3 : 5-*dione* (Norris and Thorpe, *ibid.*, 1921, **119**, 1199) gives, on hydrolysis with barium hydroxide, cyclo*hexane*-1-*acetone*-1-*acetic acid*, m. p. 67° (*semicarbazone*, m. p. 183·5°, decomp.). The diketone is converted by phosphorus trichloride in chloroform solution into cyclo*hexane*spiro-5-*chloro*-Δ^4-cyclo*hexen*-3-*one*, b. p. 167°/30 mm., 160°/17 mm., 157°/12 mm., m. p. 47° (*semicarbazone*, m. p. 219°). The chloroketone is reduced by zinc and glacial acetic acid to cyclo*hexane*spirocyclo*hexan*-3-*one*, b. p. 225°/772 mm., 130°/15 mm., $d^{21\cdot7}$ 0·98417, n_C 1·48432, n_D 1·48685, n_F 1·49322, $[R_L]_D$ 48·55, $[R_L]_{F-C}$ 0·76, calculated values being 48·61 and 0·75, respectively [*semicarbazone*, m. p. 224·5° (decomp.), *oxime*, m. p. 128°]. It is reduced by sodium in moist ether to cyclo*hexane*spirocyclo*hexan*-3-*ol*, b. p. 127—128°/15 mm., m. p. 58° (p-*nitrobenzoate*, m. p. 102°). Nitric acid converts the alcohol into cyclo*hexane*-1-*acetic*-1-*propionic acid*, which after purification through the *ethyl* ester, b. p. 179—183°/14 mm., or the calcium salt, melts

at 142·5°. Fuming hydrobromic acid gave a product, from which pure cyclo*hexane*spiro-3-*bromo*cyclo*hexane* could not be isolated; a fraction, b. p. 133°/12 mm., contained 84% of bromo-derivative. Similarly, hydrochloric acid gave a fraction, b. p. 142—148°/33 mm., containing 72% of chloro-derivative. Zinc dust and alcohol convert the bromo-derivative into a mixture of hydrocarbons which on reduction with hydrogen and colloidal palladium gives cyclo*hexane*spirocyclo*hexane*, b. p. 208°/777 mm., $d^{20\cdot6}$ 0·87833, n_C 1·47048, n_D 1·47313, n_F 1·47902, n_G 1·48398, $[R_L]_D$ 48·61, $[R_L]_{F-C}$ 0·75, $[R_L]_{G-C}$ 1·19, calculated values being 48·60, 0·74, and 1·19, respectively. cyclo*Hexane*spiro-3 : 5-*dichloro*-$\Delta^{2:4}$-cyclo*hexadiene*, a pale yellow oil, b. p. 152°/21 mm., is obtained by the action of phosphorus pentachloride on cyclo*hexane*spirocyclo*hexane*-3 : 5-*dione*, but it has not been possible to obtain a product free from halogen from this by reduction. H. E. F. Notton.

Decahydronaphthalene and its substitution products. E. Gysin (Helv. Chim. Acta, 1926, **9**, 59—67).—When a current of chlorine is passed through decahydronaphthalene, chlorination is very slow and is accompanied by much resin formation (cf. A., 1924, i, 32). An apparatus is devised whereby the decahydronaphthalene is atomised by means of compressed air or chlorine (for details cf. Diss., Geneva, 1925). In the former case, dilution with air prevents rapid chlorination, but only the monochloro-derivative is obtained and resin-formation is almost excluded. In the latter case, where further chlorination is desired, the monochloro-derivative, still the main product, is accompanied by dichloro-derivative and more highly chlorinated products. The general applicability of the apparatus is illustrated by the results obtained in the chlorination of *p*-cymene, where excellent yields of the 2- and 3-monochloro- and 2 : 5-dichloro-derivatives are obtained.

The action of alcoholic potassium or silver cyanide on the chlorodecahydronaphthalene gives octahydronaphthalene instead of a cyano-derivative. The following condensation products are obtained by the Friedel–Crafts reaction from chlorodecahydronaphthalene: 2-*phenyldecahydronaphthalene*, b. p. 170—180°/18 mm.; 2-*p*-*tolyldecahydronaphthalene*, b. p. 180—190°/18 mm. with violet fluorescence; 2-3′ : 5′-dimethylphenyldecahydronaphthalene, b. p. 182—192°/18 mm.; 2 : 2′-*methyl*-5-iso*propylphenyldecahydronaphthalene*, b. p. 192—212°/18 mm.; 2-4′(?3′)-*methoxylphenyldecahydronaphthalene*, b. p. 185—195°/18 mm.; 2-3′ : 5′-*dimethoxyphenyldecahydronaphthalene*, b. p. 225—235°/18 mm.; 2-2′ : 5′-*dimethoxyphenyldecahydronaphthalene*, b. p. 208—225°/18 mm.; 2-β-*naphthyldecahydronaphthalene*, b. p. 240—280°/18 mm., giving two crystalline *isomerides*, white leaflets, m. p. 62°, greenish-yellow leaflets, m. p. 68°. M. Clark.

Cuprene tar. Pyrogenic condensation of acetylene. P. Schläpfer and O. Stadler (Helv. Chim. Acta, 1926, **9**, 185—199).—The composition of cuprene tar (cf. Sabatier and Senderens, A., 1900, i, 197), obtained by the pyrogenic condensation of acetylene when it is passed over copper at 300°, has been investigated. The tar was fractionally distilled, first at atmospheric pressure, then at 12 mm., and finally at 0·3—0·5 mm. It consists mainly of aromatic and unsaturated (olefine) hydrocarbons, the following substances being detected: benzene, naphthalene, and a small amount of anthracene, and their methyl-, ethyl-, and propyl-substituted derivatives; hexylene, heptylene, octylene, and styrene; a small amount of paraffins of low b. p.; and, in the fractions b. p. 85—125°/0·5 mm., a blue *hydrocarbon*, b. p. 95—100°/0·7 mm., d^{15} 0·9889 (*picrate*, m. p. 118°), which was isolated by means of its phosphoric acid compound (cf. Ruzicka and Rudolph, this vol., 299), and is similar in nature and characteristics to the azulenes, but has one methyl group less, having the composition $C_{14}H_{16}$. Oxidation either with potassium permanganate or ozone gave no recognisable products, except, possibly, lower fatty acids.

On treatment of the various aromatic hydrocarbon fractions with concentrated sulphuric acid to remove olefines, condensation products of the two hydrocarbons are formed in accordance with the scheme: $CHR{:}CH_2+C_6H_6 \longrightarrow CHRPhMe$, and fractions of compositions approximating to the *compounds*, $C_{12}H_{18}$, $C_{14}H_{22}$, $C_{16}H_{26}$, $C_{16}H_{18}$, $C_{18}H_{22}$, $C_{18}H_{30}$, derived in this manner from benzene, toluene, xylene, and mesitylene with various olefines, were isolated.

J. W. Baker.

Rate of chlorination of toluene. F. Bergel (Ber., 1926, **59**, [*B*], 153—155; cf. Book and Eggert, A., 1924, ii, 10).—The chlorination of boiling toluene is very considerably accelerated by sunlight. Addition of phosphorus pentachloride does not appear to be advantageous in so far as the preparation of benzyl chloride is concerned. H. Wren.

Preparation, hydrolysis, and reduction of the fluoro-, chloro-, and bromo-benzyl bromides. J. B. Shoesmith and R. H. Slater (J.C.S., 1926, 214—222; cf. *ibid.*, 1922, **121**, 1392; 1923, **123**, 2828; A., 1924, i, 842; 1925, i, 16).—Previous work on substituted benzyl bromides has been extended to the fluoro-, chloro-, and bromo-derivatives. The orders of ease of hydrolysis in aqueous alcohol are: (1) fluoro-derivatives, $p>\omega>o>m$; (2) chloro-derivatives, $\omega>p>o>m$; (3) bromo-derivatives, $\omega>p>o>m$. The orders of ease of reduction are: (1) $o>m>\omega>p$, (2) $o>p>m>\omega$, (3) $o>p>m>\omega$ (ω= benzyl halide). The fact that *p*-chloro- and *p*-bromo-benzyl bromides are more reactive to both reagents than the *m*-isomerides is at present unexplained. Formulæ have been evolved by which all the investigations may be summarised, and separate values obtained for the general, alternating, and steric influences of substituents (cf. Flürscheim, J.C.S., 1909, **95**, 726). The order of the general effect of substituents is (*a*) on ease of hydrolysis, $OMe>Me>F>Cl>Br>CO_2H>NO_2$; (*b*) on ease of reduction, OMe and $Me>Cl>Br>CO_2H$ and F. The order of the alternating effect is (*a*) on ease of hydrolysis, $OMe>F>Me>Cl>Br>CO_2H>F$; (*b*) on ease of reduction, $OMe>Me>CO_2H>F$, Cl, and Br. In general, the steric effect diminishes the ease of hydrolysis and increases the ease of reduction. The

order in which the three groups having the same electronic shell affect reactivity is OMe>Me>F. *o-Chlorobenzyl bromide*, b. p. 102°/9 mm., *m-chlorobenzyl bromide*, b. p. 102°/10 mm., and *p*-chlorobenzyl bromide, m. p. 51° (cf. Jackson, A., 1879, 62), are best prepared from the chlorobenzaldehydes. *m*-Chlorobenzyl alcohol has b. p. 242° (Mettler, A., 1905, i, 790, gives 234°). The bromobenzyl bromides, m. p. (*o*) 31°, (*m*) 40°, (*p*) 63° (cf. Jackson, A., 1876, ii, 512), are converted by boiling with potassium iodide into *o-bromobenzyl iodide*, m. p. 47°, *m-bromobenzyl iodide*, m. p. 42°, and *p*-bromobenzyl iodide, m. p. 73° (cf. Hantzsch, A., 1896, i, 672), respectively. The fluorotoluenes give, on bromination at the b. p., *o-fluorobenzyl bromide*, b. p. 84—85°/15 mm.; *m-fluorobenzyl bromide*, b. p. 77°/12 mm.; and *p-fluorobenzyl bromide*, b. p. 85°/15 mm. H. E. F. Notton.

Nitration of aromatic compounds with bismuth nitrate. L. Spiegel and H. Haymann (Ber., 1926, **59**, [*B*], 202—204).—Benzene and toluene are little affected by protracted boiling with bismuth nitrate; *p*- and *m*-xylene are transformed mainly into the corresponding toluic acids. Naphthalene gives α-nitronaphthalene in small yield, whereas anthracene affords anthraquinone. Phenol and bismuth nitrate at the atmospheric temperature (also in acetic acid solution) yield *o*- and *p*-nitrophenol or, with a greater proportion of nitrate, resinous products containing picric acid. Anisole at 100° affords *o*- and *p*-nitroanisole. β-Naphthol under varied conditions gives non-crystalline products, whereas β-naphthyl ethyl ether yields 1-nitro-β-naphthyl ethyl ether. Methyl salicylate affords methyl 3-nitrosalicylate. *p*-Benzoquinone is converted to a small extent into nitranilic acid; anthraquinone at 200° affords *o*-nitroanthraquinone. Further nitration of nitrobenzene or *o*-nitrotoluene could not be effected by bismuth nitrate; 1-nitro-β-naphthyl ethyl ether gives the 1 : 8-dinitro-compound. Benzoic, phthalic, benzene- or naphthalene-sulphonic acids or their esters do not react with bismuth nitrate; ethyl phthalate is hydrolysed by protracted boiling. Aniline is not affected by bismuth nitrate, whereas acetanilide affords a mixture of *o*- and *p*-nitroacetanilide in the presence of acetic anhydride (whereby nitric acid is liberated); *p*-toluidine in glacial acetic acid gives an additive compound.

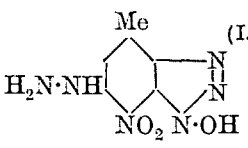
Bismuth nitrate pentahydrate is converted into the stable basic salt at 120° if the liberated nitric acid is continuously removed. H. Wren.

Dinitro-s-trihydrazinobenzene and some other derivatives of s-trichlorodinitrobenzene. W. Borsche and W. Trautner (Annalen, 1926, **447**, 1—18).—When alcoholic hydrazine hydrate is added gradually to a hot alcoholic solution of 2 : 4 : 6-trichloro-1 : 3-dinitrobenzene (m. p. 131·5°), the *hydrazine* salt of 5 : 7-*dichloro*-6-*nitro*-1-*hydroxybenzotriazole*, decomp. 169°, separates. When decomposed with dilute aqueous nitric acid, the latter yields the free 5 : 7-*dichloro*-6-*nitro*-1-*hydroxybenzotriazole*, decomp. 196°. The action of excess of hydrazine hydrate on the above trichlorodinitrobenzene affords, in addition, a *compound*, $C_6H_{11}O_2N_{10}Cl$, exploding above 200°. Condensation of *dinitrophloroglucinol triphenyl ether*, m. p. 110—111°, obtained by heating sodium phenoxide with trichlorodinitrobenzene for 2 hrs. at 100° and then for 4 hrs. at 125°, with hydrazine hydrate as above, affords 1 : 3-*dinitro*-2 : 4 : 6-*trihydrazinobenzene*, exploding when heated. When heated with alcoholic ammonia for 3 hrs. at 100°, *s*-trichlorodinitrobenzene yields (?) 5-*chloro*-4 : 6-*dinitro*-1 : 3-*diaminobenzene*, yellow, m. p. 206° (decomp.) after becoming brown at 185° (cf. Hüffer, A., 1921, i, 549), and dinitro-*s*-triaminobenzene, decomp. 298° (cf. Jackson and Robinson, A., 1890, 247). By the action of piperidine in boiling alcoholic solution, in presence of sodium acetate, trichlorodinitrobenzene can be converted into 3 : 5-*dichloro*-4 : 6-*dinitro*-1-*piperidinobenzene*, m. p. 108°, and 4 : 6-*dinitro*-1 : 3 : 5-*tripiperidinobenzene*, m. p. 147—148°. Aniline affords similarly 2 : 4-dinitro-1 : 3 : 5-trianilinobenzene, m. p. 179—180°, whilst *p*-toluidine yields a *chlorodinitrodi*-p-*toluidinobenzene*, m. p. 231°, and β-naphthylamine affords a *chlorodinitrodi*-β-*naphthylaminobenzene*, m. p. 225° (decomp.). When heated with acetamide and sodium acetate at 160°, trichlorodinitrobenzene yields 3 : 5-*dichloro*-2 : 4-*dinitrophenol*, m. p. 120° (p-*anisidine* salt, decomp. 195°), whilst sodium phenoxide yields, similarly, in boiling ethereal suspension, the corresponding *phenyl ether*, m. p. 108°. When boiled with an ethereal suspension of methyl sodiomalonate, trichlorodinitrobenzene yields *methyl* 3 : 5-*dichloro*-2 : 4-*dinitrophenylmalonate*, m. p. 132°, together with a *methyl chlorodinitrophenylmalonate*, m. p. 105° after softening (cf. Jackson and Koch, A., 1899, i, 677; Jackson and Robinson, A., 1890, 377). *Methyl* 5-*chloro*-2 : 4-*dinitrophenylmalonate*, obtained similarly from 1 : 3-dichloro-4 : 6-dinitrobenzene, has m. p. 70·5—71·5°. Hydrolysis of the above methyl 3 : 5-dichloro-2 : 4-dinitrophenylmalonate affords 3 5-dichloro-2 : 4-dinitrophenylacetic acid, m. p. 140° (cf. Jackson and Lamer, A., 1897, i, 29), the *methyl* ester of which, m. p. 87·5°, is converted into 3 : 5-dichloro-2 : 4-dinitrotoluene when heated in aqueous solution at 140°, and into 2 : 4-dinitro-3 : 5-diaminotoluene by the action of alcoholic ammonia. When treated with ethyl sodioacetoacetate in ethereal suspension, trichlorodinitrobenzene yields *ethyl* 3 : 5-*dichloro*-2 : 4-*dinitrophenylacetoacetate*, m. p. 124°, together with a substance of m. p. 94°.

When 3 : 5-dibromo-4-nitro-*o*-toluidine is diazotised in strong hydrochloric acid solution, the diazonium salt is spontaneously transformed into the corresponding dichloronitrotoluenediazonium bromide (cf. Hantzsch, A., 1898, i, 19). When boiled with alcohol, this yields 3 : 5-dichloro-4-nitrotoluene, which, when treated with nitric acid (*d* 1·5), affords 3 : 5-*dichloro*-2 : 4-*dinitrotoluene*, m. p. 127°. Treatment of 3 : 5-dichlorotoluene with cold nitric acid (*d* 1·52) affords 3 : 5-dichloro-2-nitrotoluene, which on further nitration yields a mixture of the 2 : 4- and 2 : 6-dinitro-derivatives. When this mixture is treated with alcoholic ammonia or aniline, the 2 : 4-dinitro-derivative reacts first, yielding 2 : 4-*dinitro*-3 : 5-*diaminotoluene*, m. p. 210°, and 2 : 4-*dinitro*-3 : 5-*dianilinotoluene*, m. p. 163—164°, respectively.

3 : 5-Dibromo-2 : 4-dinitrotoluene, m. p. 159—160°

(cf. Blanksma, A., 1909, i, 779), is converted, when heated with alcoholic ammonia at 125°, into 2 : 4-*dinitro*-3 : 5-*diaminotoluene*, m. p. 210°; aniline affords similarly 2 : 4-*dinitro*-3 : 5-*dianilinotoluene*, m. p. 163—164°. The controlled action of hydrazine on the above dibromodinitrotoluene in warm, alcoholic solution yields 2 : 4-*dinitro*-3 : 5-*dihydrazinotoluene* (+2H_2O), decomp. 173°, whilst excess of hydrazine in boiling alcohol affords similarly the *hydrazine* salt of the *benzotriazole*, presumably (I), decomp. 176°, from aqueous solutions of which the *triazole* (or its nitrate) is precipitated by nitric acid as a yellow powder.



(I.)

When boiled with acetic anhydride and anhydrous sodium acetate, 3 : 5-dibromo-2-nitro-*p*-toluidine yields a *diacetyl* derivative, m. p. 170°. Nitration of the monoacetyl derivative, with subsequent hydrolysis and elimination of the amino-group by Staedel's method (cf. A., 1883, 864), affords 3 : 5-dibromo-2 : 6-dinitrotoluene, m. p. 119—120° (cf. Blanksma, *loc. cit.*). When heated with alcoholic ammonia at 160°, the latter affords impure 2 : 6-dinitro-3 : 5-diaminotoluene, m. p. about 140°. Aniline affords similarly only mixtures, whilst *p*-toluidine yields 2 : 6-*dinitro*-3 : 5-*di*-p-*toluidinotoluene*, m. p. 191°. Hydrazine hydrate affords analogously 5-*bromo*-6-*nitro*-1-*hydroxy*-7-*methylbenzotriazole*, decomp. 236°, whilst sodium ethoxide affords, in the same way, 5-*bromo*-2 : 4-*dinitro*-m-*tolyl ethyl ether*, m. p. 133°. *Chloro*-2 : 4-*dinitroresorcinol diphenyl ether*, m. p. 129—130°, obtained from sodium phenoxide and trichlorodinitrobenzene, is described.

F. G. Willson.

Influence of sunlight on trinitrotoluene. D. Lodati.—See B., 1926, 220.

Orientation effects in the diphenyl series. I. H. G. Dennett and E. E. Turner (J.C.S., 1926, 476—481).—4 : 4′-Dibromodiphenyl, on nitration, yields first the 2-nitro- and then the 2 : 3′-dinitro-derivatives; the former, accompanied by benzerythrene derivatives, is also obtained from 2-nitrobenzidine by the Sandmeyer reaction; the latter, which is quantitatively formed by the further nitration of the 2-nitro-compound, contains a reactive bromine atom, which is readily replaced by the piperidino-group, forming 4-*bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*, m. p. 136—137°; this reactivity is not shown by the 2-nitro- or 2 : 2′-dinitro-compounds. 4 : 4′-Dibromo-2 : 3′-diaminodiphenyl furnishes a *disalicylidene*-derivative, m. p. 195°. 4 : 4′-Dichlorodiphenyl similarly affords a 2 : 3′-*dinitro*-derivative, m. p. 140°. These are the first examples known of unsymmetrical nitration in the diphenyl series. The 2 : 3′-dinitro-compound yields 4-*chloro*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*, m. p. 132°, whilst the 2 : 2′-dinitro-compound is unaffected by piperidine. The nitration of 4 : 4′-ditolyl yields first *mononitro*-4 : 4′-*ditolyl*, m. p. 91—92°, and then a *dinitro*-derivative, m. p. 119°, probably the 2 : 3′-dinitro-compound. 3 : 3′(3 : 5′ ?)-Dinitro-4 : 4′-ditolyl (cf. Ullmann and Frentzel, A., 1905, i, 308) was prepared from 4-iodo-2-nitrotoluene by treatment with copper-bronze. The instructions of these authors for the preparation of 3 : 5′-dinitrodiphenyl led generally to the formation of *m*-chloronitrobenzene, but treatment of *m*-iodonitrobenzene with copper-bronze furnished the desired product, which, after reduction, gave a *disalicylidene*-derivative, m. p. 176—177°. *p*-Nitrobenzylidenebenzidine (cf. Barzilowski, J. Russ. Phys. Chem. Soc., 1891, **23**, 69) combines with salicylaldehyde to form p-*nitrobenzylidenesalicylidenebenzidine*, m. p. 210°, and with acetylacetone to form p-*nitrobenzylideneacetylisopropylidenebenzidine*, m. p. 185°.

J. S. H. Davies.

True α-naphthylpropinene. L. Bert and P. C. Dorier (Bull. Soc. chim., 1925, [iv], **37**, 1600—1602).—Application of methods previously described (Bert, A., 1925, i, 803; Bert, Dorier, and Lamy, *ibid.*, 1373) to αγ-dichloropropylene and α-bromonaphthalene, with subsequent treatment of the product by means of sodamide, yielded *α-naphthylpropinene*, b. p. 154°/15 mm., d_4^0 1·066, n_D^{15} 1·630.

H. J. Evans.

Acetylene derivatives. V. Phenyl-β-naphthylacetylene. P. Ruggli and M. Reinert (Helv. Chim. Acta, 1926, **9**, 67—79; cf. A., 1920, i, 599).—Phenylacetyl chloride condenses with naphthalene in presence of aluminium chloride and carbon disulphide (cf. A., 1879, 897), giving, in good yield, a mixture of α-naphthyl benzyl and β-naphthyl benzyl ketones, separated by fractional crystallisation of the picrates from benzene. *α-Naphthyl benzyl ketone*, m. p. 66—67° [*picrate*, m. p. 101—102°; *phenylhydrazone*, m. p. 101—101·5°; *oxime*, m. p. 148—152° (decomp.)], is oxidised by potassium permanganate in hot aqueous pyridine to α-naphthoic acid and *phenyl-α-naphthylglyoxal*, m. p. 101·5—102°, which gives with *o*-phenylenediamine *phenyl-α-naphthylquinoxaline*, m. p. 137—139°. The ketone reacts with phosphorus pentachloride at 100°, giving *β-chloro-α-phenyl-β-1-naphthylethylene*, b. p. 228—233°/11 mm. Treatment with alkali failed to give phenyl-α-naphthylacetylene. In chloroform solution, the ketone reacts differently with phosphorus pentachloride, giving *ββ-dichloro-α-phenyl-β-1-naphthylethane*, m. p. 102° (decomp.). With phosphorus pentabromide at 180° *β-bromo-α-phenyl-β-dibromo-1-naphthylethylene*, m. p. 170—171°, is obtained. With phosphorus pentabromide at the ordinary temperature, the ketone gives *ω-bromobenzyl 1-naphthyl ketone*, m. p. 63—64°, converted by alcoholic potassium hydroxide into *ω-hydroxybenzyl 1-naphthyl ketone*, m. p. 105—105·5° giving a solution in dilute sodium hydroxide which, on acidification, yields α-naphthoic acid.

β-Naphthyl benzyl ketone, m. p. 99—99·5° [*picrate*, m. p. 142·5—143·5°; *phenylhydrazone*, m. p. 165—167° after darkening at 161° (170—171° from aqueous pyridine); *oxime*, m. p. 128—129·5°], is oxidised by potassium permanganate in hot aqueous pyridine, giving β-naphthoic acid and *phenyl-β-naphthylglyoxal*, m. p. 86·5—87·5°, which reacts with *o*-phenylenediamine to give *phenyl-β-naphthylquinoxaline*, m. p. 108—110°. The ketone reacts in chloroform solution

with phosphorus pentachloride, giving β-*chloro*-α-*phenyl*-β-2-*naphthylethylene*, m. p. 116—117°, which yields, on vacuum distillation, a substance of the same m. p. (slight decomp.), decolorising aqueous permanganate only after 2 min. On boiling with potassium hydroxide in pyridine solution, the ethylene derivative is converted into *phenyl*-β-*naphthylacetylene*, m. p. 115—116°, decolorising permanganate after 1 min. When the acetylenic compound is preserved in concentrated sulphuric acid solution, it is converted into β-naphthyl benzyl ketone. Its constitution is established by synthesis from the dihydrazone of phenyl-β-naphthylglyoxal, oxidised by yellow mercuric oxide to an unstable diazide, which loses nitrogen giving the desired compound. β-Naphthyl benzyl ketone reacts in benzene solution at the ordinary temperature, more rapidly in hot chloroform solution, with phosphorus pentabromide, giving ω-*bromobenzyl* 2-*naphthyl ketone*, m. p. 111—111·5°, converted by alcoholic potassium hydroxide into ω-*hydroxybenzyl* 2-*naphthyl ketone*, m. p. 151—152°, reconverted by oxidation with chromic acid in pyridine into phenyl-β-naphthylglyoxal.

M. CLARK.

Polynitrostilbenes. I. A. PASTAK (Bull. Soc. chim., 1926, [iv], **39**, 72—77).—Using piperidine as catalyst, a series of nitrated stilbenes has been readily obtained by the action of 2 : 4-dinitrotoluene, 2 : 4 : 6-trinitrotoluene, or 2 : 4-dinitro-1-methylnaphthalene on aldehydes in pyridine solution at the ordinary temperature (cf. Ullmann, A., 1908, i, 622). The following are described: 2 : 4-dinitro-*s*-diphenylethylene, m. p. 143—145°; α-*phenyl*-β-2 : 4-*dinitro*-1-*naphthylethylene*, m. p. 166°; *s*-2 : 4-dinitro-4′-methoxydiphenylethylene, m. p. 162—163°; *s*-2 : 4 : 6-trinitro-4′-methoxydiphenylethylene; s-*furyl*-2 : 4 : 6-*trinitrophenylethylene*, m. p. 128°; s-2 : 4-*dinitro*-4′-*hydroxy*-3′-*methoxydiphenylethylene*, m. p. 191—192°; s-2 : 4-*dinitro*-3′ : 4′-*methylenedioxydiphenylethylene*, m. p. 183—184°. s-3 : 4-*Methylenedioxyphenyl*-2′ : 4′-*dinitronaphthylethylene*, m. p. 197—198°; s-2 : 4 : 6-*trinitro*-4′-*methyldiphenylethylene*, m. p. 162—163°; s-2 : 4 : 6-*trinitro*-4′-*hydroxy*-3′-*methoxydiphenylethylene*, m. p. 197°, and s-2 : 4 : 6-*trinitro*-3′ : 4′-*methylenedioxydiphenylethylene*, m. p. 159°, were obtained by reaction of the fused aldehyde and nitro-compound in the presence of piperazine. Reaction in the first two cases did not take place in cold pyridine; in the last case, a triphenylpropane derivative was formed in cold pyridine.

R. BRIGHTMAN.

2 : 2′ : 4 : 4′ : 6 : 6′-Hexanitro-αβγ-triphenylpropane and its derivatives. I. A. PASTAK (Bull. Soc. chim., 1926, [iv], **39**, 77—82).—2 : 4 : 6-Trinitrotoluene and benzaldehyde when condensed in cold pyridine solution in the presence of piperidine or piperazine yield 2 : 2′ : 4 : 4′ : 6 : 6′-*hexanitro*-αβγ-*triphenylpropane*, m. p. 183—185°, with a little trinitrostilbene. It is suggested that the hydrol

$$CHPh(OH)\cdot CH_2\cdot C_6H_2(NO_2)_3$$

is first formed and that this reacts with a second molecule of trinitrotoluene. Since *s*-2 : 4 : 6-trinitro-3′ : 4′-methylenedioxydiphenylethylene could not be nitrated with tetranitromethane, the possibility of α- or β-nitration to a tetranitrostilbene in the reaction is excluded. Similarly, *p*-tolualdehyde yields 2 : 2′ : 4 : 4′ : 6 : 6′-*hexanitro*-αγ-*diphenyl*-β-*p*-*tolylpropane*, m. p. 183—186°; cumaldehyde, 2 : 2″ : 4 : 4″ : 6 : 6″-*hexanitro*-4′-isopropyl-αβγ-*triphenylpropane*, m. p. 202—203°; *m*-nitrobenzaldehyde, 2 : 2″ : 3′ : 4 : 4″ : 6 : 6″-*heptanitro*-αβγ-*triphenylpropane*, m. p. 207—208°, the main product being the tetranitrostilbene. Anisaldehyde gives exclusively the stilbene derivative, but piperonal gives mainly 2 : 2″ : 4 : 4″ : 6 : 6″-hexanitro-3′ : 4′-methylenedioxy-αβγ-triphenylpropane, m. p. 137—140°. The hexanitrotriphenylpropanes containing a methoxy- or methylenedioxy-group are yellow, whilst the analogous stilbene compounds are orange-red.

R. BRIGHTMAN.

Fission of azimethines by means of mercuric chloride. G. SACHS [with W. DRESSLER and R. SMIRZITZ] (Monatsh., 1925, **46**, 137—142).—When benzylidene-ethylamine is added to a solution of mercuric chloride in absolute ether, an additive *compound*, $2CHPh{:}NEt,3HgCl_2$, decomp. 150°, separates after some time. The presence of traces of moisture leads to complete fission of the azimethine and formation of ethylamine mercurichloride, which is also obtained when alcoholic solutions of benzylidene-ethylamine and mercuric chloride are mixed. Benzylidenebenzylamine behaves similarly, giving in the complete absence of water the additive *compound* $2CHPh{:}NCH_2Ph,3HgCl_2$. Azimethines derived from arylamines do not react with mercuric chloride in dry ether. In moist ether benzylideneaniline yields aniline mercurichloride, $NH_2Ph,HgCl_2$. Both this and the dianiline compound, $2NH_2Ph,HgCl_2$, are obtained readily from aniline and mercuric chloride in alcoholic solution. Mercuric acetate dissolves readily in benzylidene-ethylamine, but an additive compound cannot be isolated; with benzylideneaniline in hot alcohol a true mercuration occurs, and from the mixture of products a *compound*, $C_{15}H_{13}O_2NHg$, m. p. 155—157°, is extracted with light petroleum.

C. HOLLINS.

Introduction of the thiocyano-group into organic compounds. H. P. KAUFMANN and W. OEHRING (Ber., 1926, **59**, [*B*], 187—194).—The introduction of the thiocyano-group into suitable organic compounds and the addition of thiocyanogen to unsaturated substances can frequently be effected by the cautious addition of bromine to or passage of chlorine through a solution of the substance and sodium thiocyanate in formic or acetic acid. In certain cases, hydrochloric or sulphuric acid may be used. Thiocyanogen generated in this manner appears more active than that prepared in indifferent solvents from lead thiocyanate and bromine. Reaction is usually effected at the atmospheric temperature, since increase in temperature involves increased risk of polymerisation of thiocyanogen. The following compounds have been prepared: *p*-thiocyanoaniline, m. p. 57—58° (yield 80%); 2 : 4-*dithiocyanoaniline*, m. p. 198°; 2 : 4(?)-*dithiocyano*-α-*naphthylamine*, m. p. 204°; 4-*thiocyano*-α-*naphthylamine*, m. p. 146—147°, converted by oxidation in alkaline solution

into di-α-aminonaphthyl 4 : 4′-disulphide, m. p. 168° (cf. Zincke and Schütz, A., 1912, i, 257); 1-*thiocyano*-β-*naphthylamine*, m. p. about 261° (decomp.) after softening at 150—154° and subsequently re-solidifying, transformed by ethyl-alcoholic sodium hydroxide into di-β-aminonaphthyl 1 : 1′-disulphide; *pp′*-dithiocyanodiphenylamine, m. p. 120°; 4-thiocyano-α-naphthol, m. p. 113° (cf. Kaufmann and Kögler, A., 1925, i, 1252); 2 : 4(?)-*dithiocyano*-α-*naphthol*, m. p. 118—119° (decomp.); 5-thiocyanosalicylic acid, m. p. 167°; αβ-dithiocyanoethane, m. p. 90°; αβ-*dithiocyano*-α-*phenylethane*, m. p. 101°; αβ-dithiocyano-α-*p*-methoxyphenylpropane, m. p. 87° (cf. Kaufmann and Liepe, A., 1923, i, 766); di-1-phenyl-2 : 3-dimethyl-5-pyrazolonyl 4 : 4′-disulphide, m. p. 256°.

H. Wren.

Isatin and related compounds. VII. Oximinoacetanilide. W. Borsche and A. Fritzsche (Ber., 1926, **59**, [*B*], 272—276; cf. A., 1924, i, 986, 1342).—*Oximinoacet*-2 : 4-*dinitroanilide*, m. p. 184°, is obtained by the action of nitric acid (*d* 1·5) at 0° on oximinoacetanilide or oximinoacet-*p*-nitroanilide; its constitution is established by its conversion by acetic anhydride into acet-2 : 4-dinitroanilide, m. p. 120°. Similarly, oximinoacet-4-nitroanilide, oximinoacet-3-nitroanilide, and 5-oximinoacetamidoisatin are converted into acet-4-nitroanilide, m. p. 107°, acet-3-nitroanilide, m. p. 151°, and 5-*acetamidoisatin*, m. p. 282—283° after softening at 270°. Oximinoacetanilide is transformed by benzoyl chloride and pyridine into *s*-diphenylcarbamide, m. p. 236°, cyanoformanilide and phenylcarbimide being successively formed intermediately. Similarly, oximinoacet-3-nitroanilide affords a mixture of *s*-di-*m*-nitrophenylcarbamide and, apparently, *tri*-m-*nitrophenyl* isocyanurate, m. p. about 260° after softening at 225°. Oximinoacetanilide is converted by benzenediazonium chloride in alkaline solution into the *oxime* of *phenylglyoxylanilide*, m. p. 154—155°, which is hydrolysed by 2*N*-sulphuric acid to *phenylglyoxylanilide*, m. p. 63°. Similarly, oximinoacetanilide and diazotised *p*-toluidine afford the *oxime* of p-*tolylglyoxylanilide*, m. p. 164—165°, from which p-*tolylglyoxylanilide*, m. p. 124°, is prepared. *p*-Anisylglyoxylanilide, m. p. 107°, and its *oxime*, m. p. 163—164°, are also described.

H. Wren.

Hydrazides and azides of acetylsulphanilic and sulphanilic acids. T. Curtius and W. Stoll (J. pr. Chem., 1926, [ii], **112**, 117—137).—When acetylsulphanilic chloride is treated with excess of hydrazine hydrate it yields p-*acetamidobenzenesulphonhydrazide*, m. p. 177—178° (decomp.) [*hydrochloride*, m. p. 163—165° (decomp.); *sodium* and *silver nitrate* salts described; *benzylidene* compound, m. p. 182°; *acetonyl* compound, m. p. 174°]. When treated with nitrous acid, the hydrazide yields p-*acetamidobenzenesulphonazide*, m. p. 107°, which reacts with ethyl sodiomalonate to give *ethyl* 5-*hydroxy*-1-p-*acetamidobenzenesulphonyl*-1 : 2 : 3-*triazole*-4-*carboxylate* as an oil which rapidly isomerises to *ethyl diazomalon*-p-*acetamidobenzenesulphonylamate*, m. p. 146°. When hydrolysed with hydrochloric acid, the hydrazide yields p-*aminobenzenesulphonhydrazide*, m. p. 131° (*benzylidene* compound, m. p. 172°; *acetonyl* compound, m. p. 136°), which on treatment with nitrous acid and subsequent coupling with dimethylaniline yields p-*dimethylaminoazobenzene*-p-*sulphonazide*, m. p. 158°. Hydrolysis with hydrochloric acid converts *p*-acetamidobenzenesulphonazide into p-*aminobenzenesulphonazide*, m. p. 36° (decomp.), which yields p-*diazobenzenesulphonazide*, very explosive, on treatment with sodium nitrite solution. When treated with an alcoholic solution of ethyl sodiomalonate, *p*-aminobenzenesulphonazide yields *ethyl diazomalon*-p-*aminobenzenesulphonylamate* as final product, and on diazotisation and coupling with β-naphthol it yields p-*sulphonazidobenzeneazo*-β-*naphthol*, orange, m. p. 161°.

R. W. West.

Influence of substitution in the components of binary solution equilibria. L. Binary systems of acids and amines. R. Kremann, G. Weber, and K. Zechner (Monatsh., 1925, **46**, 193—224; cf. this vol., 394, 396).—Setting-point curves for mixtures of organic acids with arylamines and with carbamide are investigated. Where the method gives positive evidence of the existence of compounds it is trustworthy, but absence of indications may be due to great solubility or high degree of dissociation of the compounds. Benzoic acid forms no solid compound with α- or β-naphthylamine or aniline; with *p*-toluidine and *m*- and *p*-phenylenediamines it gives equimolecular compounds, whilst with *o*-phenylenediamine the compound 2 acid : 1 base is formed. Salicylic acid forms equimolecular compounds with *p*-toluidine, α- and β-naphthylamines, *o*-, *m*-, and *p*-phenylenediamines. Cinnamic acid gives eutectics only with α- and β-naphthylamines, *p*-toluidine, and *m*-phenylenediamine; with *o*-phenylenediamine an equimolecular compound is formed, whilst the mixture with *p*-phenylenediamine undergoes further chemical change. Succinic acid gives an equimolecular compound with β-naphthylamine, but only a simple eutectic with the α-base. No solid compound is observed with acetic acid and α- or β-naphthylamine or *p*-phenylenediamine, with propionic acid and β-naphthylamine, or with butyric acid and *o*-phenylenediamine. Acetic acid forms compounds, however, with *o*-phenylenediamine (2 acid : 1 base) and *m*-phenylenediamine (4 acid : 1 base). The curves for carbamide in admixture with cinnamic, benzoic, acetic, and salicylic acids show the formation of compounds with 2 mols. of acetic acid or 1 mol. of salicylic acid; in the case of succinic acid, chemical change occurs at 100°.

C. Hollins.

Preparation of primary aromatic amines. Finow-G.m.b.H., and H. Müller.—See B., 1926, 149.

Preparation of secondary bases of the naphthalene series [dinaphthylmethylamines]. H. Rupe.—See B., 1926, 185.

Influence of chemical constitution on the odour of mustard oils. G. M. Dyson.—See B., 1926, 215.

4-Nitro-1-acetnaphthalide-6(or 7)-sulphonic acid. W. M. Ralph.—See B., 1926, 185.

Preparation and separation of 1-naphthylamine-8- and -5-sulphonic acids. G. POMA.—See B., 1926, 185.

Greenish-blue dyes [from 8-chloro-1 : 2-naphthylenediamine-5-sulphonic acid]. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 149.

Azoxy-compounds. W. M. CUMMING and G. S. FERRIER (J. Royal Tech. Coll., 1925, [2], 34—41).—See A., 1924, i, 774; this vol., 162.

Influence of substitution in the components of binary solution equilibria. XLVIII. Binary systems of azobenzene with acids. R. KREMANN and K. ZECHNER (Monatsh., 1925, **46**, 171—176; cf. A., 1925, ii, 650).—Setting-point curves for mixtures of azobenzene with some organic acids are given. In no case is a molecular compound formed. The eutectics are: benzoic acid, 58° (83% azobenzene); cinnamic acid, 62° (90%); salicylic acid, 63·5° (95%); succinic acid, 65° (nearly 100%); acetic acid, 16° (about 1%); dichloroacetic acid, 9° (15%); trichloroacetic acid, 10° (27%).

C. HOLLINS.

Monoazo dye. CHEM. FABR. ROHNER A.-G. PRATTELN.—See B., 1926, 149.

Brown trisazo dyes. B. VOSSEN.—See B., 1926, 185.

***p*-Nitrophenylhydrazine, its preparation and gravimetric utility.** H. H. HODGSON and H. G. BEARD (J.S.C.I., 1926, **45**, 56T).—The gravimetric determination of *m*-hydroxybenzaldehyde by means of *p*-nitrophenylhydrazine hydrochloride in aqueous acetic acid is described. *p*-Nitrophenylhydrazine hydrochloride is obtained in 90% of the theoretical yield by the reduction of diazotised *p*-nitroaniline with neutral sodium sulphite.

2 : 4-Dinitrophenylhydrazine as a reagent for aldehydes and ketones. O. L. BRADY and G. V. ELSMIE (Analyst, 1926, **51**, 77—78).—Aldehydes and ketones yield characteristic, stable, crystalline derivatives having sharp m. p. when treated with a solution of 2 : 4-dinitrophenylhydrazine in 2*N*-hydrochloric or, in the case of aldehydes and ketones insoluble in water, when boiled with an alcoholic suspension of the reagent. The compounds may be purified by recrystallisation from absolute alcohol. 2 : 4-*Dinitrophenylhydrazones* of the following have been prepared: n-*propaldehyde*, tangerine-red, m. p. 155°; n-*butaldehyde*, pale orange, m. p. 122°; iso*butaldehyde*, orange, m. p. 182°; iso*valeraldehyde*, orange-red, m. p. 123°; n-*hexaldehyde*, orange-yellow, m. p. 104°; n-*heptaldehyde*, pale orange, m. p. 106°; n-*nonaldehyde*, bright yellow, m. p. 96°; *methyl ethyl ketone*, orange, m. p. 115°.

A. R. POWELL.

3 : 4- and 2 : 5-Dimethoxyphenylhydrazine. W. H. PERKIN, jun., and L. RUBENSTEIN (J.C.S., 1926, 357—362).—3 : 4-Dimethoxyaniline hydrochloride, on diazotisation with methyl nitrite in acetic acid followed by treatment with ammonium sulphite and ammonia, gives *ammonium* 3 : 4-*dimethoxydiazobenzenesulphonate*, which is reduced by zinc and acetic acid to *ammonium* 3 : 4-*dimethoxyphenylhydrazinosulphonate*. This, on successive treatment with alcoholic hydrochloric acid and sodium acetate, yields 3 : 4-*dimethoxyphenylhydrazine*, m. p. 81° (*hydrochloride*, m. p. 162° with decomposition), which, on condensing with *cyclo*hexanone and treating the syrupy *hydrazone* with alcoholic hydrochloric acid, forms 6 : 7-*dimethoxy*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 98°. A similar condensation with ethyl pyruvate furnishes an oily *hydrazone*, from which *ethyl* 5 : 6-*dimethoxyindole*-2-*carboxylate*, m. p. 172°, is obtained on treatment with alcoholic hydrochloric acid. 2 : 5-*Dimethoxyphenylhydrazine*, m. p. 84°, (*hydrochloride* darkens above 250°), prepared in a similar manner (intermediate products described) from 2 : 5-dimethoxyaniline hydrochloride, resists condensation with ketones. α-Ketoglutaric acid, on condensation with *o*-methoxyphenylhydrazine, yields the corresponding *hydrazone*, m. p. 168° (decomp.), which with alcoholic hydrochloric acid furnishes *ethyl* 2-*carbethoxy*-7-*methoxyindole*-3-*acetate*, m. p. 106°, b. p. 245—255°/11 mm., from which the *acid*, m. p. 253° (decomp.), is obtained on hydrolysis with sodium hydroxide. *p*-Methoxyphenylhydrazine and α-ketoglutaric acid under similar conditions give an oily *hydrazone* and a syrupy *ester*, which with aqueous sodium hydroxide forms 2-*carboxy*-5-*methoxyindole*-3-*acetic acid*, m. p. 265°. The various methoxy-derivatives give colorations when submitted to the brucine test, from which it appears that brucine contains two methoxy-groups in the *o*-position to each other.

J. S. H. DAVIES.

Acyl derivatives of hydrazine. F. J. WILSON, A. B. CRAWFORD, and E. C. PICKERING (J. Royal Tech. Coll., 1925, [2], 47—52).—See A., 1925, i, 318, 935.

Reactions of semicarbazides. I. V. HOPPER (J. Royal Tech. Coll., 1925, [2], 42—47).—See A., 1925, i, 895.

Mechanism of coupling. J. S. P. BLUMBERGER (Chem. Weekblad, 1926, **23**, 106—113).—A discussion of the various theories of the constitution of the diazo-compounds and hypothetical stages of the coupling reaction. Whilst the suggestion that the conjugated double linkings in the nucleus play the chief part meets most support from the experimental evidence, it seems clear that no one explanation can cover all cases.

S. I. LEVY.

Stereoisomeric *o*-methyl*cyclo*pentanols. M. GODCHOT and P. BEDOS (Compt. rend., 1926, **182**, 393—395; cf. A., 1925, i, 258, 537).—cis-*o*-*Methyl*cyclo*pentanol*, b. p. 148—149°, d_{16}^{16} 0·9389, n_D^{16} 1·4504 (*phenylurethane*, m. p. 94°, *allophanate*, m. p. 174°), is formed by the action of magnesium methyl iodide on *cyclo*pentene oxide. On oxidation with chromic acid in acetic acid solution *o*-methyl*cyclo*pentanone is produced. *cyclo*Pentene oxide is most readily prepared as follows: zinc adipate is heated in an iron retort, giving *cyclo*pentanone in 50% yield; the latter is reduced to *cyclo*pentanol by sodium in the presence of sodium hydrogen carbonate, the *cyclo*-

pentanol is dehydrated by heating with phthalic anhydride, and *cyclo*pentene oxide is obtained by the action of potassium hydroxide on the chlorohydrin which is readily obtained by the action of chlorocarbamide on *cyclo*pentene. Pure *trans-o*-methyl*cyclo*pentanol may be prepared by the action of sodium on *o*-methyl*cyclo*pentanone in the presence of sodium hydrogen carbonate; the following revised physical constants are given: b. p. 150—151°, d_{16}^{16} 0·9258, n_D^{16} 1·4499, phenylurethane, m. p. 89°, allophanate, m. p. 174°. L. F. HEWITT.

Geometric stereoisomerism in the *cyclo*hexane series. III. Chlorination of inactive *m*-methyl*cyclo*hexanone; constitution of some disubstituted derivatives of *cyclo*hexanol. M. GODCHOT and P. BEDOS (Bull. Soc. chim., 1926, [iv], **39**, 83—99).—To obtain confirmation of the structures previously attributed to 2-chloro-5-methyl*cyclo*hexanol and 2 : 5-dimethyl*cyclo*-hexanol and -hexanone (this vol., 280) the authors have repeated the work of Kötz and Steinhorst (A., 1911, i, 210), using inactive *m*-methyl*cyclo*hexanone in place of the active ketone. Chlorination of inactive *m*-methyl*cyclo*hexanone in cold aqueous solution in the presence of calcium carbonate yields a liquid and a solid monochloroketone. The latter, m. p. 55—56°, is identical with the ketone described by Favorski and Boshovski (A., 1915, i, 411), and with the main oxidation product (with chromic acid) of the methyl*cyclo*hexanols obtained from Δ^3-methyl*cyclo*hexene. It must accordingly be a 2-chloro-5-methyl*cyclo*hexanone, since this is the only structure compatible with both methods of formation. Magnesium methyl iodide converts this solid 2-chloro-5-methyl*cyclo*hexanone into the 2 : 5-dimethyl*cyclo*hexanone, the semicarbazide of which has m. p. 122°, and a little of the isomeride yielding a semicarbazide, m. p. 155°. These are identical with the 2 : 5-dimethyl*cyclo*hexanones obtained by oxidation of " 2 : 5 "-dimethyl*cyclo*hexanols previously described. Similarly, the liquid 2-chloro-5-methyl*cyclo*hexanone yields mainly the 2 : 5-dimethyl*cyclo*hexanone, semicarbazone, m. p. 155°, which is identical with the product obtained by Sabatier and Mailhe by catalytic reduction of 2 : 5-xylenol and subsequent oxidation. On distillation with quinoline, the mixture of 2-chloro-5-methyl*cyclo*hexanones yields inactive 5-*methyl*cyclo-Δ^2-*hexen*-1-*one*, b. p. 170°/760 mm., d^{20} 0·919, n_D^{20} 1·44635 (semicarbazone, m. p. 182°), which differs markedly from the 4-methyl*cyclo*-Δ^2-hexen-1-one described by Kötz and Steinhorst (*loc. cit.*). Earlier attempts by the authors to elucidate the constitution of these compounds by direct oxidation of 2 : 5-dimethyl*cyclo*hexanone, by hydrogenation of 2-chloro-5-methyl*cyclo*hexanols by Vavon or Nivière's methods, or by reduction of the dimethyl*cyclo*hexanols to the corresponding xylenols proved unsuccessful.

R. BRIGHTMAN.

Bromophenols. XVI. A new (3 : 4 : 5-)tribromophenol, and a new (4 : 5 : 6-)tribromo-*o*-cresol. M. KOHN and G. SOLTÉSZ (Monatsh., 1925, **46**, 245—251).—Bromination of 3 : 5-dibromophenol in acetic acid with rather less than 1 mol. of bromine gives 3 : 4 : 5-*tribromophenol*, m. p. 129° (triclinic crystals, details by K. HLAWATSCH), which differs from 2 : 3 : 5-tribromophenol (Bamberger and Kraus, A., 1907, i, 161). The *methyl ether*, m. p. 91—94°, b. p. 300—310°, is converted by fuming nitric acid into 3 : 4 : 5-*tribromo*-2 : 6-*dinitroanisole*, m. p. 127°. Dibromo-*o*-cresol, b. p. 283—286°, brominated in acetic acid, yields 4 : 5 : 6-*tribromo*-*o*-*cresol*, m. p. 106° (*methyl ether*, m. p. 105°, b. p. 320°).

C. HOLLINS.

Preparation of phenols from magnesium organo-derivatives. D. IVANOV (Bull. Soc. chim., 1926, [iv], **39**, 47—55).—From experiments with magnesium phenyl bromide and with magnesium *o*-, *m*-, and *p*-tolyl bromides, it is shown that the best yields of phenols are obtained when the Grignard reagent is oxidised at −20° (cf. Porter and Steel, A., 1921, i, 140). The concentration and speed of oxidation are relatively unimportant, but replacement of ether by benzene as solvent increases the yield of phenol by about 5%. Oxidation in the presence of an equimolecular proportion of an aliphatic magnesium compound increases the yield of phenol by approximately 50%. A second molecular proportion of the aliphatic compound only slightly increases the yield, but the yield increases with the mol. wt. of the aliphatic derivative employed, the highest yields (47—53%) being obtained in the presence of magnesium benzyl chloride. Temperature has less influence on the yield in the presence of the aliphatic compound. Since the thermal value of the oxidation is greater with the aliphatic magnesium compounds than with the aromatic derivatives, indicating that the former have the greater affinity for oxygen, it is suggested that in the oxidation of a mixture the aliphatic derivative is oxidised first, *e.g.*, AlkMgBr → AlkO·OMgBr, and that the peroxide thus formed reacts with the aryl derivative, thus, AlkO·OMgBr+ArMgBr= AlkO·MgBr+ArO·MgBr, which on decomposition yield the alcohol and phenol, respectively. The smaller yields of phenols which result when the aliphatic derivatives having the greater thermal value on oxidation are used is attributed to the greater reducing powers of such derivatives, the reaction, AlkO·OMgBr+AlkMgBr=2AlkO·MgBr, diminishing the yield of phenol. It is possible, however, that the low yield is due to secondary reactions induced by the greater supply of energy available under more exothermic conditions. Confirmation of the above theory is adduced in the observation that the yield of phenol in the oxidation of magnesium phenyl bromide is not proportional to the volume of oxygen absorbed, being greater proportionally with small volumes of oxygen than with large. The concentration of the reducing agent (unchanged magnesium phenyl bromide) being relatively high in the initial stages; the decomposition of the peroxide at first proceeds according to the scheme Ph·O·O·MgBr+ PhMgBr → 2Ph·OMgBr, but afterwards, owing to the lower concentration of the unchanged Grignard reagent, secondary reactions preponderate. Attempts to increase the yield of phenol by the use of such reducing agents as manganous chloride and ferrous sulphate failed. R. BRIGHTMAN.

Influence of substitution in the components of binary solution equilibria. XLIX. Binary systems of cinnamaldehyde and salicylaldehyde with phenols. R. K. KREMANN and E. ZECHNER (Monatsh., 1925, **46**, 177—192; cf. Kremann and Pogantsch, A., 1924, i, 52; also this vol., 394).—Setting-point curves are given, which show the probable existence of molecular compounds between cinnamaldehyde and *p*-nitrophenol (1 mol. : 1 mol.), *m*-nitrophenol (2 : 1), pyrocatechol (1 : 1), and resorcinol (1 : 1 and 2 : 1). Salicylaldehyde, on the other hand, forms no compound with phenol, α- and β-naphthols, pyrogallol, quinol, *o*-nitrophenol, or 2 : 4-dinitrophenol; two compounds of salicylaldehyde with picric acid (1 : 1 and 2 : 1) are obtained. It seems probable that the formation of molecular compounds between aldehydes and phenols is due less to the residual valency of the carbonyl group than to that of an unsaturated side-chain. C. HOLLINS.

Phenolic derivatives of tetrahydronaphthalene. J. D. RIEDEL A.-G.—See B., 1926, 217.

***p*-Alkyloxybenzhydrylamines.** C. TORRÈS Y GONZALÈS (Bull. Soc. chim., 1925, [iv], **37**, 1591—1596).—A number of substituted benzhydrylamines have been prepared by the reduction of the corresponding ketoxime with sodium amalgam in alcoholic solution. *p*-Ethoxybenzophenone (b. p. 215—225°/15 mm., m. p. 47—48°) yields an *oxime*, m. p. 135—136°, reduced to p-*ethoxybenzhydrylamine*,

$$CHPh(NH_2)\cdot C_6H_4\cdot OEt,$$

an undistillable oil (*hydrochloride*, m. p. 229°), which is resolved into its optical antipodes by means of ammonium *d*-bromocamphorsulphonate, the salt of the lævo-base (m. p. 201—202°) being obtained pure by crystallisation from aqueous alcohol: d-*base*, $[\alpha]_D$ +3·37° (*hydrochloride*, m. p. 223—224°), l-*base*, $[\alpha]_D$ −3·99° (*hydrochloride*, m. p. 221—222°).

p-*Propoxybenzophenone*, m. p. 65—66°, prepared from phenyl propyl ether and benzoyl chloride in presence of aluminium chloride, forms an *oxime*, m. p. 104—105°, reduced to p-*propoxybenzhydrylamine*, an oil (*hydrochloride*, m. p. 220—221°). p-*Butoxybenzophenone*, b. p. 235—245°, m. p. 38—39°, forms an *oxime*, m. p. 94—95°, reduced to p-*butoxybenzhydrylamine*, an oil (*hydrochloride*, m. p. 213—214°). p-iso*Amyloxybenzophenone*, b. p. 225—240°, is converted into its *oxime*, m. p. 93—94°, which is reduced to p-iso*amyloxybenzhydrylamine*, an oil (*hydrochloride*, m. p. 224—225°). Reduction of p-*phenoxybenzophenoneoxime*, m. p. 124°, yields p-*phenoxybenzhydrylamine*, an oil (*hydrochloride*, m. p. 218—219°). *p*-Hydroxybenzophenone condenses with ethyl chloroacetate in presence of sodium ethoxide to give *ethyl* p-*benzoylphenoxyacetate*, $Bz\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Et$, m. p. 84—85° (hydrolysed to the *acid*, m. p. 154—155°), of which the *oxime*, m. p. 78—79°, is reduced to p-*carbethoxymethoxybenzhydrylamine*,

$$CHPh(NH_2)\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Et,$$

an oil (*hydrochloride*, m. p. 183—184°). Reduction of phenylbenzylketoxime furnishes α : β-*diphenylethylamine*, an oil (*hydrochloride*, m. p. 251—252°); of *p*-anisylbenzylketoxime, α-*anisyl*-β-*phenylethylamine*, an oil (*hydrochloride*, m. p. 234°). p-*Ethoxyphenyl benzyl ketone*, m. p. 105—106°, prepared by the Friedel–Crafts reaction using phenylacetyl chloride, furnishes an *oxime*, m. p. 89—90°, reduced to p-*ethoxyphenylbenzylmethylamine*, an oil (*hydrochloride*, m. p. 203—204°). G. M. BENNETT.

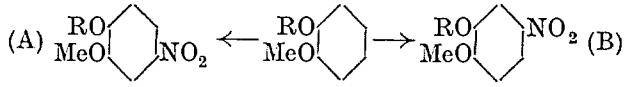
Mercuration of aromatic sulphides. G. SACHS and M. OTT (Ber., 1926, **59**, [*B*], 171—175).—Mercury *o*-methylthiolbenzoate is not decomposed in a uniform manner when heated at 170—230°. Diphenyl sulphide is incompletely mercurated by mercuric acetate at 100°, whereas at 200° insoluble products are formed; in addition to the latter p-*acetatomercuridiphenyl sulphide*, $Ph\cdot S\cdot C_6H_4\cdot Hg\cdot OAc$, m. p. 148°, is obtained at 150° (preferably in the presence of boiling amyl acetate). The *para*-position of the substituent in the molecule is established by transforming the latter by nitric acid into *p*-nitrodiphenylsulphone. The acetato-derivative is transformed by calcium chloride into p-*chloromercuridiphenyl sulphide*, m. p. 181°, which, with ammonia in alcoholic solution, affords the *compound*,

$$(Ph\cdot S\cdot C_6H_4Hg)_2NH_2Cl,$$

m. p. 164—170° (slight decomp.).

Phenyl thioacetate reacts with mercuric acetate in the same manner as the ethyl ester (Sachs, A., 1921, i, 762), affording, according to conditions, either phenylmercaptomercurichloride or mercury phenylmercaptide. H. WREN.

Relative directive powers of groups of the forms RO and RR'N in aromatic substitution. I. J. ALLAN and R. ROBINSON (J.C.S., 1926, 376—383).—A quantitative study of the products of nitration in cold glacial acetic acid of the ethyl, propyl, *iso*propyl, *n*-butyl, and benzyl ethers of guaiacol has been made. With the exception of veratrole, which yields only the 4-nitro-derivative, the ethers of guaiacol yield two mononitro-compounds, the 4- and 5-nitro-derivatives, the relative amounts being dependent on the ratio of the directive powers of the groups RO and MeO. Since the *meta*-directing influence of the alkoxy-group is zero, it is assumed that directive power of RO/directive power of MeO= % of (A) formed in the reaction/% of (B) formed in the reaction :



By the method of thermal analysis with the aid of f.-p. curves of mixtures of compounds of the above types, (A) and (B), prepared by alkylation with the appropriate halide and potassium hydroxide in alcoholic solution, and expressing the directive power of MeO in this series as 100, it is found that the directive powers of EtO, Pr$^{\alpha}$O, Pr$^{\beta}$O, *n*-BuO, and $CH_2Ph\cdot O$ are 135, 128, 150, 123, and 113, respectively. The preparation of the following nitroalkoxyanisoles is described : 4-nitro-2-ethoxy-, m. p. 102°, 5-nitroisomeride, m. p. 85°; 4-*nitro*-2-*propoxy*-, m. p. 106°, 5-*nitro*-isomeride, m. p. 72°; 4-*nitro*-2-iso*propoxy*-, m. p. 83°, 5-*nitro*-isomeride, m. p. 53°; 4-*nitro*-2-n-*butoxy*-, m. p. 74°, 5-*nitro*-isomeride, m. p. 56°; 4-*nitro*-2-*benzyloxyanisole* crystallises from alcohol in one of two forms, m. p. 93° and m. p. 98°, 5-*nitro*-

isomeride, m. p. 82°. 4 : 5-Dinitro-2-alkoxyanisoles were obtained by treatment of the mononitration products with nitric acid: *ethoxy-*, m. p. 150°, *propoxy-*, m. p. 143°, iso*propoxy-*, m. p. 129°, n-*butoxy-*, m. p. 97°. 4 : 5-Dinitro-2-ethoxyanisole, after reduction, combines with phenanthraquinone to form 3-*methoxy*-2-*ethoxyphenanthraphenazine*, m. p. 231°, and is converted by hydrogen sulphide in presence of aqueous alcoholic ammonia into 6'-*nitro*-3'(or 4')-*methoxy*-4'(or 3')-*ethoxyphenyl*-4 : 5-*thiotriazopyrocatechol methyl ethyl ether*, m. p. 175°.

J. S. H. DAVIES.

Relative directive powers of groups of the forms RO and RR'N in aromatic substitution. II. Nitration of some 2-benzyloxyanisoles substituted in the benzyl group. A. E. OXFORD and R. ROBINSON (J.C.S., 1926, 383—391).—The compounds studied were the *m*-nitrobenzyl, *p*-nitrobenzyl, and *m*-methoxybenzyl ethers of guaiacol. The procedure is similar to that indicated in the preceding abstract. The directive powers of the groups in the order named are 67, 67, and 92 (MeO= 100). The preparation of the following 2-benzyloxyanisoles is described: 2-m-*nitro-*, m. p. 47·5—48°, 4-nitro-derivative, m. p. 164—165°, 5-*nitro*-derivative, m. p. 140·5—141·5°; 2-*p*-nitro-, m. p. 63·5°, 4-*nitro*-derivative, m. p. 167—168°, 5-*nitro*-derivative, m. p. 163·5—164·5°; 2-m-*methoxy-*, m. p. 31·5°, 4-*nitro*-derivative, m. p. 116—117°, 5-*nitro*-derivative, m. p. 98·5—99·5°; 2-p-*methoxy-*, m. p. 94—96°, 4-*nitro*-derivative, m. p. 129—130°, 5-*nitro*-derivative, m. p. 109° with slight softening at 100°. It was not found possible to nitrate 2-*p*-methoxybenzyloxyanisole satisfactorily. J. S. H. DAVIES.

Relative directive powers of groups of the forms RO and RR'N in aromatic substitution. III. Nitration of some *p*-alkyloxyanisoles. R. ROBINSON and J. C. SMITH (J.C.S., 1926, 392—401).—The method of thermal analysis is utilised to determine the relative amounts of the mononitro-isomerides obtained by nitrating 4-ethoxy-, 4-propoxy-, and 4-*p*-nitrobenzyloxy-anisoles, for which, as well as for their 2- and 3-nitro-derivatives, 2- and 3-nitro-4-methoxyphenol, and quinol monomethyl ether, satisfactory methods of preparation are described. The directive powers of ethoxy-, *n*-propoxy-, and *p*-nitrobenzyloxy-groups in the order named are 163, 180, and 38 (MeO=100). The following nitro-4-alkyloxyanisoles were prepared: 3-*nitro*-4-*ethoxy-*, m. p. 39·5°, f. p. 39·0°; 2-*nitro*-isomeride, m. p. 37—39°, f. p. 38·4°; 3-*nitro*-4-*propoxy-*, m. p. 10·7° (attempts to prepare this compound from the silver salt of 2-nitro-4-methoxyphenol were unsuccessful); 2-*nitro*-isomeride, f. p. 32°; 4-p-*nitrobenzyloxy-*, m. p. 87·5°, 3-*nitro*-derivative, m. p. 153°, f. p. 152·8°, 2-*nitro*-derivative, m. p. 123·5°, f. p. 123·0°. *Ethyl* p-*methoxyphenyl carbonate*, m. p. 21°, formed by the interaction of ethyl chloroformate and quinol monomethyl ether in presence of sodium hydroxide, forms on nitration the 3-*nitro*-derivative, m. p. 66·5°, which on hydrolysis with an aqueous methyl-alcoholic solution of sodium hydrogen carbonate followed by acidification yields the dimorphous 3-nitro-4-methoxyphenol, m. p. 98—100°, the unstable modification of which appears to have m. p. 85°. Similarly, quinol monomethyl ether, m. p. 56°, when heated to about 200° and quickly cooled, has b. p. 243—244°, m. p. 53°, changing slowly to 55°. The crystals, m. p. 56°, also change on keeping and the m. p. becomes 55°. J. S. H. DAVIES.

Relative directive powers of groups of the forms RO and RR'N in aromatic substitution. IV. Discussion of the observations recorded in Parts I, II, and III. J. ALLAN, A. E. OXFORD, R. ROBINSON, and J. C. SMITH (J.C.S., 1926, 401—411; cf. preceding abstracts).—The results obtained are in harmony with a hypothesis of electronic displacements of two kinds. The general polar effect is partly propagated through the chain and partly distributed, the latter portion being sometimes in the same direction as the electronic displacements, and sometimes in the opposite direction. From this, the general rule follows that the disparities in the directive powers of particular groups in the pyrocatechol series are increased in the quinol series. A classification of conjugated systems is made, and the theory is applied to the general problem of orientation in aromatic substitution and to other examples of the interaction of general effects and conjugated systems.

J. S. H. DAVIES.

Relative directive powers of groups of the forms RO and RR'N in aromatic substitution. V. Nitration of *p*-methoxydiphenyl ether. T. R. LEA and R. ROBINSON (J.C.S., 1926, 411—413).—m-*Methoxydiphenyl ether*, b. p. 175°/20 mm., is obtained by heating a mixture of *m*-methoxyphenol, bromobenzene, potassium hydroxide, and copper-bronze. 4-*Methoxydiphenyl ether*, b. p. 186°/32 mm., solidifying at −10°, prepared similarly, when nitrated in glacial acetic acid, yields solely the 3-*nitro*-derivative, m. p. 73—74°, which, on hydrolysis with potassium hydroxide, yields 3-*nitro*-4-*hydroxydiphenyl ether*, m. p. 51—52°. *o*-Methoxydiphenyl ether yields a nitro-derivative, probably 3-*nitro*-6-*methoxydiphenyl ether*, m. p. 70—71°. These results show that the directive powers of phenoxy- and *p*-methoxyphenoxy-groups are very weak compared with that of methoxyl, a result which accords with the theoretical conceptions held. J. S. H. DAVIES.

Compounds of molybdic acid, tungstic acid, and quinquevalent molybdenum with polyhydric phenols and phenolic acids. R. WEINLAND, A. BABEL, K. GROSS, and H. MAI (Z. anorg. Chem., 1926, **150**, 177—209).—Molybdic acid forms complex anions containing 1 and 2 mols. of pyrogallol (cf. Fernandes, A., 1925, ii, 1061). Ammonium and pyridine *salts* of monopyrogallolmolybdic acid, $[O_2Mo(OH)\cdot O\cdot C_6H_3(OH)\cdot O\cdot]H$, and potassium, ammonium, pyridine, and piperidine *salts* of dipyrogallolmolybdic acid, $[O_2Mo\{\cdot O\cdot C_6H_3(OH)\cdot O\cdot\}_2]H_2$, were prepared. Most of these are stable in the air. Several *salts* of similar complex anions containing pyrocatechol were obtained. Complex anions in which the oxygen of the hydroxyl groups of the polyhydric phenol is replaced by the radicals Mo_2O_7 or Mo_3O_{10} are also formed, the *salts* obtained having the formulæ $[C_6H_3(Mo_2O_7)_3]H_3(NH_3)_4,6H_2O$ and $[C_6H_4(Mo_3O_{10})_2]H_2(NH_3)_4,10H_2O$.

Tungstic acid also forms anions containing 2 mols. of

pyrocatechol, and ammonium, piperidine, and aniline *salts* were prepared. Pyridine, quinoline, and *o*- and *p*-phenylenediamine *salts* were prepared which contained 3 mols. of pyrocatechol, but the third mol. is formulated as "pyrocatechol of crystallisation"; it may, however, be part of the anion. A piperidine *salt* of dipyrogalloltungstic acid was obtained. Tungstic acid forms a complex anion containing only 1 mol. of salicylic acid; potassium and sodium salts, $[O_2W(OH)\cdot O\cdot C_6H_4\cdot CO_2]K(Na)$, were prepared. Gallic acid forms a complex anion containing 2 mols. of the acid, and the pyridine *salt*,

$[O_2W\{\cdot O\cdot C_6H_2(OH)_2\cdot CO_2\}_2]H_2,(C_5H_5N)_2,3H_2O$,

was prepared. By the action of hydrochloric acid or barium chloride a monogallato-*acid* or its barium *salt*, $[O_2W<^{O}_{O}>C_6H_2(OH)CO_2]_2Ba$, is obtained. Molybdenum forms similar mono- and di-gallato-anions; pyridine and quinoline *salts* of the latter were obtained. An anion rich in molybdenum was also prepared as its pyridine *salt*,

$[(OH)_2Mo_2O_6{\cdot}C_6H_2(OH)\cdot CO_2]H,(C_5H_5N)_{1.5}$.

The emerald-green chloride, $MoOCl_3,2NH_4Cl$, of quinquevalent molybdenum forms compounds with gallic acid and ethylenediamine or guanidine; these contain 1 mol. of gallic acid to 1 atom of molybdenum.

A. GEAKE.

Pyrocatechol and pyrogallol compounds with stannic acid. R. WEINLAND and M. MAIER (Z. anorg. Chem., 1926, **150**, 217—230).—Complex compounds of stannic acid and pyrocatechol are prepared by adding pyrocatechol to a mixture of stannic chloride and water. Salts of the complex acid thus formed are obtained by the addition of an acetate or a base, and have the general formula $[Sn(C_6H_4O_2)_3]M_2$, the tin having the co-ordination number 6. Ammonium, potassium, silver, magnesium, calcium, barium, zinc, manganese, aluminium, pyridine, quinoline, piperidine, and ethylenediamine *salts* were prepared and contain varying amounts of water of crystallisation. Calcium and barium also form *salts* containing 6 mols. of pyrocatechol, but it is probable that the additional 3 mols. are bound by partial valencies to the basic metal, $[Sn(C_6H_4O_2)_3]Ba(....OH\cdot C_6H_4\cdot OH)_3$. Unlike the other salts, these give a strong green colour with ferric chloride. The complex anion is very stable, and those salts which are sufficiently soluble can be recrystallised from water or alcohol. Pyrogallol forms a similar complex anion, of which the ammonium and pyridine *salts* were prepared. A. GEAKE.

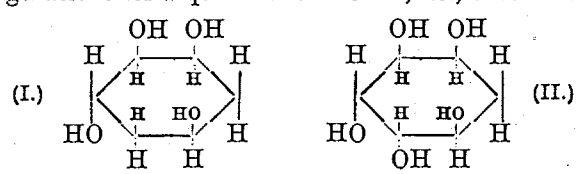
Dithiopyrocatechol. P. C. GUHA and M. N. CHAKLADAR (J. Indian Chem. Soc., 1925, **2**, 318—335).—When oxidised with iodine, dithiopyrocatechol (*dibenzoyl* derivative, m. p. 77°) yields a *disulphide*, $C_6H_4S_2$, yellow, m. p. 185—190°. The thiopyrocatechol is conveniently obtained by reduction of benzene-*o*-disulphonic chloride, m. p. 143°. Condensation of dithiopyrocatechol with *o*-nitrobenzaldehyde yields *o-nitrobenzylidenedithiopyrocatechol*, m. p. 106°, and with acenaphthenequinone it yields the *substance* $(C_{10}H_{16}CO)C{:}S_2{:}C_6H_4$, m. p. 190°.

4-*Bromodithiopyrocatechol*, m. p. 43—44° (*dibenzoyl* derivative, m. p. 85°, *diethyl ether*, m. p. 54°), is readily oxidised by iodine to the *disulphide*, $C_6H_3BrS_2$, m. p. 154°. The reactions of 4-bromodithiopyrocatechol with a variety of substances are recorded. When treated with an aqueous solution of potassium chloroacetate it yields *4-bromo-o-phenylenedithioglycollic acid*, m. p. 170°, whilst with free chloroacetic acid it yields a *substance*, $Br\cdot C_6H_3<^{S\cdot CH_2}_{S\cdot CO}$, m. p. 191°.

By the action of benzylidene chloride or benzaldehyde is formed *benzylidenebromodithiopyrocatechol*, m.p.170°. When the potassium salt of the thiopyrocatechol is heated in toluene solution with *s*-tetrabromoethane, it yields glyoxaldibromodithiopyrocatechol, which the authors consider may have the constitution $Br\cdot C_6H_3<^{S\cdot CH\cdot S}_{S\cdot CH\cdot S}>C_6H_3\cdot Br$, m. p. 236—238°. Thionyl chloride yields a *substance*, $C_6H_3Br{:}S_2{:}SO$, m. p. 220° (decomp.); oxalyl chloride yields *oxalylbromodithiopyrocatechol*, $Br\cdot C_6H_3<^{S\cdot CO}_{S\cdot CO}$, sublimes at 150°; thiocarbonyl chloride yields *bromodithiopyrocatechol thiocarbonate*, $BrC_6H_3<^{S}_{S}>CS$, m. p. 140°. When 4-bromodithiopyrocatechol is heated with a mixture of phthalic anhydride and zinc chloride a *substance*, possibly $C_6H_4<^{CO\cdot S}_{CO\cdot S}>C_6H_3Br$, is obtained which is readily hydrolysed to the original mercaptan. Condensation with phenanthraquinone proceeds in two stages, yielding, (1) $(C_{12}H_8CO)C<^{S}_{S}>C_6H_3Br$, m. p. 195°, and (2) $C_{12}H_8(C{:}S_2{:}C_6H_3Br)_2$, m. p. 115°.

R. W. WEST.

Configuration of *d*-quercitol. P. KARRER (Helv. Chim. Acta, 1926, **9**, 116—117; cf. Karrer, Widmer, and Riso, A., 1925, i, 673).—The oxidation of quercitol to mucic acid by means of nitric acid (Kiliani and Scheibler, A., 1889, 581) limits the possible configurations for *d*-quercitol to I or II, *i.e.*, those which



possess similar asymmetry to α-inositol. The difficulty in methylating quercitol, or in effecting condensations with acetone or benzaldehyde (cf. Herzig and Orting, A., 1920, i, 879), shows that the similar inactivity of *meso*-inositol affords no clue to the position of its hydroxyl groups.

J. W. BAKER.

Derivatives of campholcarbinol [1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl-1-carbinol]. H. RUPE and F. FEHLMANN (Helv. Chim. Acta, 1926, **9**, 80—97).—1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl-1-carbinol [*phthalate*, m. p. 80°; *phenylthiourethane*, m. p. 101°; *acetate*, b. p. 101°/9 mm.; *propionate*, b. p. 112°/10 mm.; *camphorcarboxylate*, m. p. 145°; *phenylacetate*, b. p. 191°/12 mm.; *hydrocinnamate*, b. p. 206°/12 mm.; *cinnamate*, b. p. 217°/11 mm., 148°/0·5 mm.; *p-nitrobenzoate*, m. p. 95°; *p-aminobenzoate*, m. p. 74°, b. p. 242—243°/13·5 mm., *hydrochloride*, m. p.

140—146° (decomp.)], is prepared by the action of sodium and alcohol on ethyl campholate (cf. A., 1920, i, 383). It is purified through the sodium salt of the acid phthalate, and converted by the action of hydrobromic acid in glacial acetic acid solution into 1 : 2 : 2 : 3-*tetramethylcyclopentylbromomethane*, b. p. 94—95°/9 mm., which is readily decomposed in air and light, and on distillation at atmospheric pressure or by treatment with silver acetate in acetic acid solution loses hydrogen bromide to give a *compound*, $C_{10}H_{18}$, b. p. 163—164°/760 mm., 46—50°/9 mm. The bromomethane in ether solution reacts with magnesium, giving a mixture of hydrocarbons $C_{10}H_{18}$, $C_{10}H_{20}$, and a bimolecular *hydrocarbon*, $(C_{10}H_{19})_2$, b. p. 177—178°/10 mm. With aniline at 150°, it yields 1 : 2 : 2 : 3-*tetramethylcyclopentylmethylaniline*, m. p. 59°, b. p. 173°/9 mm. [unstable *hydrochloride*, m. p. 156° (decomp.); *nitrosoamine*]. 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl methyl ketone (A., 1919, i, 539), prepared from 1 : 2 : 2 : 3-tetramethyl*cyclo*pentane-1-carboxyl chloride and magnesium methyl iodide or zinc methyl, is accompanied by a *compound*, $(C_{10}H_{17}O)_2$, m. p. 67°, giving with phosphorus pentachloride a *chloride*, $C_{20}H_{33}OCl$, m. p. 117°. The formula $(C_9H_{17}\cdot CO)_2$ is deduced. The methyl ketone, on bromination in acetic acid, yields 1 : 2 : 2 : 3-*tetramethylcyclopentyl bromomethyl ketone*, m. p. 35°, b. p. 138—142°/12 mm., unstable in light and air; it has an irritant action on the skin and is converted by treatment with potassium acetate in boiling acetic acid solution into 1 : 2 : 2 : 3-*tetramethylcyclopentyl acetoxymethyl ketone*, b. p. 146°/12 mm., hydrolysed to 1 : 2 : 2 : 3-*tetramethylcyclopentyl hydroxymethyl ketone*, b. p. 123—125°/12 mm. (*benzoate*, m. p. 82°; *double* compound with calcium chloride; *phenylacetate*, b. p. 224°/12 mm.), reduced by sodium or aluminium amalgam to 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone and a little 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl-1-glycol. Bromination of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone in carbon disulphide or chloroform gives 1 : 2 : 2 : 3-*tetramethylcyclopentyl dibromomethyl ketone*, m. p. 52°, b. p. 164°/12 mm., which with potassium methoxide yields 1 : 2 : 2 : 3-*tetramethylcyclopentyl dimethoxymethyl ketone*, b. p. 128—130°/12 mm. (*semicarbazone*, m. p. 181°). The monobromomethyl ketone reacts with potassium phthalimide, giving the *phthalimidomethyl ketone*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH_2\cdot CO\cdot C_9H_{17},$$

m. p. 98—99°, which with alcoholic potassium hydroxide yields the *acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot C_9H_{17},$$

m. p. 143° (decomp.). When hydrolysed, this gives 1 : 2 : 2 : 3-*tetramethylcyclopentyl aminomethyl ketone*, b. p. 128°/12·5 mm. [*phenylthiocarbamide*, m. p. 105° (decomp.)], isolated as *hydrochloride*, m. p. 229° (decomp.). 1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl bromomethyl ketone reacts with methylamine in alcohol solution, giving the *methylaminomethyl ketone*, b. p. 123°/11 mm. (*hydrochloride*, *hydrobromide*, *phenylthiocarbamide*, m. p. 147°), and the *compound* $(C_9H_{17}\cdot CO\cdot CH_2)_2NMe$ as *hydrochloride*, m. p. 199°. With aniline, it gives the *compound*

$$(C_9H_{17}\cdot CO\cdot CH_2)_2NPh,$$

m. p. 212°; with trimethylamine it gives the *quaternary bromide*, m. p. 230° (decomp.), and with pyridine a *pyridinium bromide*, m. p. 214°. In ether solution the bromomethyl ketone reacts with magnesium, giving the methyl ketone and a *compound*, $C_{23}H_{40}O_2$, m. p. 82°. The methyl ketone, on treatment with sodium ethoxide and amyl formate, gives a *hydroxymethylene* derivative, $C_9H_7\cdot CO\cdot CH{:}CH\cdot OH$, b. p. 122—123°/12·5 mm. (*copper* salt, *ferric* salt), yielding on reduction 1 : 2 : 2 : 3-*tetramethylcyclopentyl β-hydroxyethyl ketone*, b. p. 146—148°/13 mm.

M. CLARK.

Dehydration of benzyl alcohol by the xanthate method. S. NAMETKIN and D. KURSANOV (J. pr. Chem., 1926, [ii], **112**, 164—168).—When *methyl benzylxanthate*, m. p. 29° (*ethyl* ester, b. p. 170—171°/14 mm.; *amide*, m. p. 61·5—62°), is heated at 350° it decomposes mainly according to the scheme: $2C_7H_7\cdot O\cdot CS\cdot SMe = 2COS + 2MeSH + CHPh{:}CHPh$. In this way, 23 g. of methyl ester yield about 5 g. of stilbene and a *substance*, $C_{28}H_{26}S$, m. p. 184—185°.

R. W. WEST.

Semipinacoline transformation. Necessity for the presence of a phenyl group in molecular transpositions. II. (MLLE.) J. LÉVY (Bull. Soc. chim., 1926, [iv], **39**, 67—72; cf. A., 1924, i, 283).—The theory that a phenyl group attached directly to the secondary alcohol group is an essential condition of intramolecular change in glycol dehydration is supported by the behaviour of three new glycols. *Dibenzylmethyl glycol* (*α-phenyl-β-benzylbutane-βγ-diol*), b. p. 241—243°/34 mm., m. p. 34—35°, from ethyl lactate and magnesium benzyl chloride, on dehydration with sulphuric acid (50%), yields *α-phenyl-β-benzylbutan-γ-one*, b. p. 200—205°/20 mm. (*semicarbazone*, m. p. 154—155°). The ketone was also obtained by oxidising *α-phenyl-β-benzylbutan-γ-ol*, b. p. 215—220°/25 mm., from magnesium methyl iodide and dibenzylacetaldehyde. *αα-Diphenyl-γ-methylbutane-βγ-diol*, b. p. 235—236°/37 mm., similarly prepared from *ethyl diphenylmethylglycollate*, $CHPh_2\cdot CH(OH)\cdot CO_2Et$, m. p. 66°, on dehydration yields αα-diphenyl-γ-methylbutan-β-one. Similarly, *ααγγ-tetraphenylpropane-αβ-diol*, m. p. 110—111°, analogously prepared, yields *s*-tetraphenylpropanone.

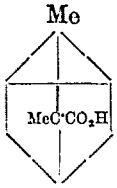
R. BRIGHTMAN.

Cholesterol. H. FISCHER and A. TREIBS (Annalen, 1926, **446**, 241—259).—When cholesterol is distilled under reduced pressure by a method involving the breaking down of the molecule by means of a hot platinum wire, a number of products can be isolated: (*a*) 10% of naphthalene; (*b*) small amounts of styrene; (*c*) a *hydrocarbon*, $C_{15}H_{12}$, m. p. 91—92° (*picrate*, m. p. 155°), volatile in steam; (*d*) a *hydrocarbon*, $C_{18}H_{14}$, m. p. 203° (*dibromide*, m. p. 217°); (*e*) a *hydrocarbon*, $C_{14}H_{10}$, m. p. 124° (*picrate*, m. p. 139°); (*f*) gaseous products containing hydrogen 5%, unsaturated hydrocarbons 30%, and saturated hydrocarbons 65%. The application of this degradation process to several cholesterol derivatives led only to indefinite results. Experiments in catalytic reduction showed that cholesteryl oleate cannot be reduced further than the stearate and that

cholesterol yields a mixture of three crystalline compounds: a *substance*, $C_{27}H_{46}O$, m. p. 134°, which seems to be an isomeride of cholesterol; a *substance*, m. p. 202°, and a *substance*, m. p. 218°, which are reduction products of cholesterol or its isomerides.

R. W. WEST.

Constitution of teresantalic acid. L. RUZICKA and F. LIEBE (Helv. Chim. Acta, 1926, **9**, 140—144).—The relationship of teresantalic acid to α-santalol (cf. Semmler and Zaar, A., 1910, i, 573) and santene, the constitution of which is certain (cf. Semmler and Bartelt, A., 1908, i, 195), only leaves the position of the carboxyl group uncertain. Teresantalol (cf. Semmler and Bartelt, A., 1907, i, 703), on oxidation with chromic acid, yields the corresponding aldehyde, m. p. 217°, the semicarbazone of which, on treatment with sodium ethoxide for 8 hrs. at 180°, yields tricyclene, which was converted by means of acetic and sulphuric acids into *iso*bornyl acetate and hence into camphor. Teresantalic acid (annexed formula) therefore possesses the camphor skeleton, the position of the carboxyl group being determined by the above reactions. Whether teresantalic acid possesses the camphor or camphene type of formula (cf. Semmler, A., 1910, i, 573) is immaterial, since these are merely different plane projections of the same space model (cf. Ruzicka and Stoll, A., 1923, i, 119).



J. W. BAKER.

Hydrogenation of aromatic acids and their salts under pressure. I. V. IPATIEV and G. RASUVAJEV (Ber., 1926, **59**, [*B*], 306—311; cf. Ipatiev and Philipov, A., 1908, i, 342).—Sodium, potassium, lithium, calcium, and barium benzoates are converted into the corresponding hexahydrobenzoates when mixed with nickel oxide and heated under high pressure in an atmosphere of hydrogen at 275—300°. Under similar conditions, zinc, nickel, and ferrous benzoates undergo profound change, yielding gaseous products containing much methane and carbon dioxide and an intensely red sublimate which has not been investigated fully. Sodium salicylate is very readily hydrogenated, with loss of the carboxyl group and formation mainly of *cyclo*hexanol; salicylic and *p*-hydroxybenzoic acids are much more slowly reduced, giving homogeneous *cyclo*hexanol unaccompanied by *cyclo*hexanone. Mandelic acid is not hydrogenated, owing to the ease with which it yields resinous compounds, whereas sodium mandelate loses its aliphatic hydroxyl group and becomes converted into phenylacetic acid, which suffers partial reduction to *cyclo*hexylacetic acid.

H. WREN.

Thermal decomposition of unsymmetrical diacyl peroxides. F. FICHTER and H. ERLENMEYER (Helv. Chim. Acta, 1926, **9**, 144—152).—The thermal decomposition of various unsymmetrical diacyl peroxides in a sealed bomb, at their explosion points, has been investigated to determine whether the formation of the resulting hydrocarbons occurs in accordance with the scheme (*a*) $(RCO_2^-)_2 \longrightarrow R{\cdot}R + 2CO_2$; or (*b*) $(R{\cdot}CO_2^-)_2 \longrightarrow 2R + 2CO_2$ and $R + R \longrightarrow R{\cdot}R$. The former is shown to be correct. Thermal decomposition of acetyl benzoyl peroxide yields, in addition to carbon dioxide, toluene, ethane, benzene, and some diphenyl, the last three products being obtained by the decomposition of the toluene, at the higher temperature produced by the explosion, in accordance with the schemes: $2Ph{\cdot}Me \longrightarrow C_6H_6 + CHPh{:}CH_2 + H_2$; $2Ph{\cdot}Me \longrightarrow Ph{\cdot}Ph + C_2H_6$ (cf. Furko, A., 1887, 572). An equimolecular mixture of diacetyl peroxide and dibenzoyl peroxide (which, on thermal decomposition, should yield the same products as acetyl benzoyl peroxide if the liberation of free radicals intervenes) gives mainly diphenyl and ethane, together with some benzene, which is a secondary decomposition product of the diphenyl, since the latter, on passage through a tube at 500—600°, is shown to decompose in accordance with the scheme: $2Ph{\cdot}Ph \longrightarrow C_6H_6 + C_6H_4Ph_2$; *pp'*-diphenylbenzene could also be isolated from the products of the thermal decomposition of dibenzoyl peroxide. When diacetyl peroxide is exploded in the presence of iodine, no methyl iodide is produced (cf. Kaufler and Herzog, A., 1909, i, 870). Hence free alkyl radicals are not liberated in the thermal decomposition of diacyl peroxides.

J. W. BAKER.

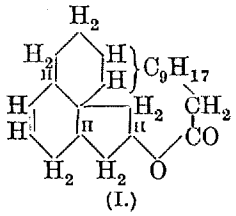
Isomeric transformation of *allo*-cinnamylideneacetic acid into the normal form with iodine as photo-catalyst. J. C. GHOSH and S. GUPTA (J. Indian Chem. Soc., 1925, **2**, 241—252).—The velocity of transformation in chloroform solution of *allo*-cinnamylideneacetic acid into the normal form is dependent on the intensity of light, but not on its state of polarisation. The amounts of the two forms of the acid in the reaction mixture are found by removal of the catalyst, evaporation of the solvent, and subsequent dissolution of the residue in benzene. The normal form of the acid is so slightly soluble in benzene that a solubility factor may be used and determination of the *allo*-form is possible. Within the range of experiments the velocity of reaction is independent of the iodine concentration, showing that the whole of the incident light is absorbed by the lowest concentration ($0{\cdot}4096 \times 10^{-2}$ g.-mol. per litre) of the catalyst.

R. W. WEST.

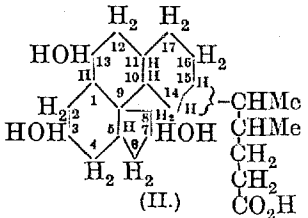
Preparation of β-naphthol-3-carboxylic anilide. CHEM. FABR. ROHNER A.-G. PRATTELN.—See B., 1926, 185.

Bile acids. XXIV. Separation of water with formation of neutral substances. H. WIELAND and O. SCHLICHTING [with V. WIEDERSHEIM] (Z. physiol. Chem., 1925, **150**, 267—275).—The lactone obtained by distillation of deoxycholic acid (A., 1917, i, 685; 1925, i, 1065) is further investigated. It contains a double linking. The corresponding saturated compound, 7-hydroxycholanolactone, melts at 236° (not 232°, as formerly given). Hydrolysis of the latter compound by alcoholic potassium hydroxide gives *isolithocholic acid* (*7-hydroxycholanic acid*), m. p. 90—95° (with slight decomp.), *methyl* ester, m. p. 119—120°, *ethyl* ester, m. p. 136°. By heating, the acid is reconverted to the lactone. The acid yields the known 7-ketocholanic acid when oxidised with chromic acid. This fact shows that the ring structure has not undergone change, and formula (I)

is suggested for the unsaturated lactone. On heating at 330°, 7-ketocholanic acid loses carbon dioxide and water to give the unsaturated *hydrocarbon*, $C_{23}H_{36}$, m. p. 117°. When deoxycholic acid is similarly treated, it gives a very small yield of the unsaturated compound, $C_{23}H_{34}O$, m. p. 103°. The formula (II) is suggested for cholic acid.



(I.)



(II.)

H. I. COOMBS.

Formation of deoxybilianic acid from bilianic acid and of deoxycholic (? deoxybilianic) and *iso*deoxybilianic acids from *iso*bilianic and deoxycholic acids. R. KARASAWA (J. Biochem. [Japan], 1925, **5**, 105—112).—Bromine is gradually added to a solution of *iso*bilianic acid in potassium hydroxide, and the acid liquid after concentration and suitable dilution is left over-night. The yellow substance which afterwards precipitates from the acidified filtrate is converted into the barium salt, and extracted with water after evaporation to dryness with sodium carbonate. Acidification then yields *iso*deoxybilianic acid, m. p. 247—248°. Bilianic acid similarly yields deoxybilianic acid, m. p. 294—295°. The barium salt obtained from deoxycholic acid consists of a fraction soluble in hot water, yielding deoxybilianic acid, and an insoluble fraction giving *iso*deoxybilianic acid. CHEMICAL ABSTRACTS.

***Gypsophila* sapogenin. II.** P. KARRER and H. LIER (Helv. Chim. Acta, 1926, **9**, 26—30; cf. A., 1924, i, 1091).—Loss of only 1 mol. of carbon monoxide on heating with 80% sulphuric acid at 100—120°, previously adduced as evidence that *Gypsophila* sapogenin (albsapogenin) is an α-keto-carboxylic acid, may imply alternatively an α-hydroxycarboxylic acid structure, since similar reaction occurs with albsapogenol, the oxime of albsapogenin, albsapogenic acid, and albsapin. Albsapogenic acid, which cannot have a hydroxycarboxylic acid structure, is formulated as $C_{25}H_{41}\cdot CO\cdot CO_2H$; and albsapogenin becomes alternatively $C_{25}H_{41}\cdot CH(OH)\cdot CO\cdot CO_2H$ or $C_{25}H_{41}\cdot CO\cdot CH(OH)\cdot CO_2H$. Further data, so far, fail to confirm these formulæ for albsapogenin.

Further oxidation of albsapogenin by a cold mixture of chromic and acetic acids gives, not degradation products of albsapogenic acid, but, owing to the ease with which the $C_{25}H_{41}$ residue takes up oxygen atoms, a series of crystalline but difficultly separable compounds of higher oxygen content. One such *compound*, $C_{26}H_{40}O_6$, m. p. 226°, a monobasic acid, yields a dioxime and, therefore, contains two ketonic oxygen atoms. It does not react with acetic anhydride. Titration gives a consistently high mol. wt. of 492, instead of 448. A second *compound*, m. p. 235°, gives a titration figure 587, but identical analytical results. Reduction of albsapogenic acid by boiling with amalgamated zinc in a mixture of hydrochloric and glacial acetic acids gives a *compound*, $C_{27}H_{42}O_2$ (or $C_{27}H_{44}O_2$), m. p. 314°. It is without acid reaction, is unchanged by boiling with sodium hydroxide, and is without action towards phenylhydrazine. After loss of carbon monoxide, on heating with 80% sulphuric acid, albsapogenic acid yields a *compound*, m. p. 306°, which is no longer acid. It fails to decolorise potassium permanganate in acetic acid solution and is soluble in sulphuric acid in the cold, without evolution of gas on warming. It has mol. wt. 433, C 78·7%, and H 9·9%. The same substance is obtained by boiling albsapogenic acid with a mixture of sulphuric and acetic acids.

M. CLARK.

Action of magnesium benzyl chloride on benzylidenephthalide. R. WEISS, K. GROBSTEIN, and R. SAUERMANN (Ber., 1926, **59**, [*B*], 301—306).—The action of magnesium benzyl chloride on benzylidenephthalide in ether or benzene and ether affords *dibenzylidenephthalan*, $C_6H_4<^{C(:CHPh)}_{C(:CHPh)}>O$, m. p. 159°, in small and varying yield and *dibenzylbenzylidenephthalan*, $C_6H_4<^{C(CH_2Ph)_2}_{C(:CHPh)}>O$, m. p. 139—149°, the structure of which is deduced from its conversion in boiling benzene into dibenzylphthalide, m. p. 207—209°; the main product of the reaction is a substance, $C_{22}H_{16}O$, m. p. 135°, which, from analogy with the compounds obtained by Weiss and Sauermann by the action of magnesium aryl bromides on benzylidenephthalide (this vol., 294), is regarded as 2-*phenyl*-3-*benzylindone*. The indone structure is also assigned to derivatives of this compound, although a phthalan structure is not regarded as excluded. 2-Phenyl-3-benzylindone is converted by hydrogen bromide and glacial acetic acid at 55° into 2-*phenyl*-3-*benzylidenehydrindone*, m. p. 164—165°. Either compound is converted by bromine in the presence of chloroform into 2-*phenyl*-3-α-*bromobenzylindone*, m. p. 143—145°, which is transformed by boiling glacial acetic acid and sodium acetate into 2-*phenyl*-3-α-*acetoxybenzylindone*, m. p. 164—168°. Prolonged treatment with boiling ethyl alcohol converts 2-phenyl-3-α-bromobenzylindone into 2(?3)-*ethoxy*-2-*phenyl*-3-α-*bromobenzylhydrindone*, m. p. 168—169°, whereas after a shorter period of reaction a *hydroxy*-2-*phenyl*-3-*benzylhydrindone*, m. p. 101—102°, is obtained. Oxidation of 2-phenyl-3-α-acetoxybenzylindone dissolved in acetone by potassium permanganate yields a *substance*, $C_{24}H_{18}O_5$, m. p. 143—145°, which is transformed by alcoholic potassium hydroxide into a *compound*, m. p. 256—257°. 2-Phenyl-3-benzylindone dissolved in cold acetone decolorises potassium permanganate with formation of a yellow *substance*, $C_{22}H_{16}O_3$, m. p. 138—140°, and a colourless *compound*, $C_{22}H_{16}O_3$, m. p. 112—114°. 2-Phenyl-3-benzylidenehydrindone is oxidised in warm acetone solution to a *compound*, $C_{44}H_{30}O_2$, m. p. 263—265°, and further to an *acid*, $C_{15}H_{10}O_2$, possibly tolane-*o*-carboxylic acid.

H. WREN.

Action of organic acids on beryllium carbonate. S. EINHORN (Bul. Soc. Chim. România, 1926, **7**, 100—101).—*Beryllium acetylsalicylate*,

$C_{18}H_{14}O_9Be_2$, is prepared by adding excess of beryllium carbonate to a hot aqueous solution of acetylsalicylic acid, followed by filtration and crystallisation. It forms anhydrous crystals, d^{15} 1·0978, soluble in water and alcohol. On heating, it decomposes without melting. It is insoluble in concentrated hydrochloric acid, but soluble in most other hot inorganic acids. The structural formula is probably

$$OAc\cdot C_6H_4\cdot C(O_2Be)\cdot O\cdot C(O_2Be)\cdot C_6H_4\cdot OAc.$$

Beryllium carbonate is soluble in aqueous thiosalicylic acid, but the resulting solution will not crystallise. Sebacic, mucic, and hippuric acids have no action on beryllium carbonate, whilst with thioacetic acid, hydrogen sulphide is evolved, and beryllium acetate, $Be_4O(OAc)_6$, is formed.

W. HUME-ROTHERY.

Decarboxylation of tyrosine and leucine. G. ZEMPLÉN (Helv. Chim. Acta, 1926, **9**, 115).—A reply to the criticism of Waser (this vol., 65) that the author's patented process for the preparation of tyramine from tyrosine (D.R.-P. 389881, 1924) is the same as the method of Graziani (A., 1916, i, 481). The author used diphenylamine as a solvent, and not diphenylmethane, as erroneously stated by his critic.

J. W. BAKER.

Acetylation of aromatic hydroxycarboxylic acids. R. LESSER and G. GAD (Ber., 1926, **59**, [*B*], 233—236).—Aromatic hydroxycarboxylic acids which do not contain the hydroxyl group in the *ortho*-position to the carboxy-radical are readily and frequently quantitatively acetylated by the addition of a slight excess of acetic anhydride to the acid dissolved in aqueous alkali. Salicylic, 1-hydroxy-2-naphthoic, and 2-hydroxy-3-naphthoic acids are not acetylated, whereas 2 : 4-dihydroxybenzoic acid affords exclusively *2-hydroxy-4-acetoxybenzoic acid*, m. p. 152—153°, and 2 : 5-dihydroxybenzoic acid gives *2-hydroxy-5-acetoxybenzoic acid*, m. p. 131—132°. Analogously, phloroglucinolcarboxylic acid yields 2 : 6-*dihydroxy-4-acetoxybenzoic acid*, m. p. 177—178° (decomp.), which very readily loses carbon dioxide, whereas *m*- and *p*-hydroxybenzoic acids are converted smoothly into the corresponding acetylated acids. Gallic and protocatechuic acids are readily transformed into the corresponding tri- or di-acetyl compounds. In partial acetylation the hydroxyl group in the *meta*-position to the carboxy-radical is first attacked; thus gallic acid affords 4-hydroxy-3 : 5-diacetoxybenzoic acid, m. p. 174—175°, and 4 : 5-dihydroxy-3-acetoxybenzoic acid, m. p. 225° (decomp.), and protocatechuic acid appears to yield 4-hydroxy-3-acetoxybenzoic acid, m. p. 202—203°, probably identical with the product described by Fischer, Bergmann, and Lipschitz (A., 1918, i, 172).

H. WREN.

Catalytic reduction of several acid chlorides. F. ZETZSCHE, C. FLÜTSCH, F. ENDERLIN, and A. LOOSLI (Helv. Chim. Acta, 1926, **9**, 182—185).—Catalytic reduction of phthaloyl chloride with a palladium–kieselguhr catalyst in tetralin solution at 150° with the addition of a large proportion of quinoline-*s*, gives only a 5% yield of phthalaldehyde, the main product being a semi-solid, oily mass. Benzyl-, methylbenzyl-, and diethyl-malonyl dichlorides yield no aldehydes on reduction, whilst the acid chlorides of lutidine- and collidine-dicarboxylic acids give very small yields. Lutidinedicarboxylic chloride forms a double *compound*, decomp. 200—230°, with phosphorus pentachloride, from which is prepared the *anilide*, decomp. 278—281°. The corresponding double *compound* of collidinedicarboxylic acid chloride has m. p. 125—132°, *anilide*, m. p. 288—290°. *2-Acetoxynaphthalene-1-carboxylic acid*, m. p. 130·5—131·5°, and its *chloride*, m. p. 140—141°, are described.

J. W. BAKER.

Reduction of phenylene-1-acetic-2-propionic acid and various aromatic amines by hydrogen in the presence of platinum oxide–platinum-black as catalyst. XII. G. S. HIERS and R. ADAMS (Ber., 1926, **59**, [*B*], 162—170).—Hydrogenation of phenylene-1-acetic-2-propionic acid has been effected by Helfer (A., 1923, i, 1229) in the presence of platinum-black, but not of colloidal platinum or platinum oxide–platinum-black. More recently, however, Skita (A., 1925, i, 140) has found colloidal platinum more effective than platinum-black in this reaction. Comparative experiments show that platinum oxide–platinum-black in the presence of 95% alcohol is the most efficient of all catalysts, but the hexahydro-product which is quantitatively formed appears less uniform in character than that obtained by Skita, and is probably composed of a mixture of isomerides.

Comparison of the reduction of aniline, methylaniline, dimethylaniline, and benzylamine in the presence of colloidal platinum and of the corresponding hydrochlorides dissolved in 75% alcohol in the presence of platinum oxide–platinum-black shows the latter to be a very powerful catalyst for these reactions, the amount requisite for the production of a given degree of hydrogenation being considerably less than that of colloidal platinum. Complete reduction of amine is effected by colloidal platinum only when highly concentrated, whereas increase of the concentration of platinum oxide–platinum-black beyond a certain point does not expedite the change. Skita has observed that secondary and tertiary amines are much more readily reduced than primary amines, whereas in the presence of Adams' catalyst reaction occurs with decreasing readiness in the sequence methylaniline, aniline, dimethylaniline. Identical products are obtained in the presence of either catalyst. It is incidentally recorded that *cyclo*hexylamine forms a mixture of constant b. p. with water (b. p. 94—95°/748 mm.). Phenyltrimethylammonium chloride is slowly converted in the presence of platinum oxide–platinum-black into trimethylamine hydrochloride and *cyclo*hexane.

Whereas addition of ferrous salts causes a great increase in the catalytic activity of platinum oxide–platinum-black towards aldehydes and the fatigued catalyst can be revived by oxygen, in the case of amines the ferrous salt behaves as a poison and oxygen does not re-activate the exhausted product.

H. WREN.

Parallel between diphenylfulgide and dibenzylidenethiodiglycollic anhydride. H. STOBBE, G. LJUNGREN, and J. FREYBERG (Ber., 1926, **59**, [*B*], 265—272).—Diphenylfulgenic (dibenzylidenesuccinic) acid is readily converted into diphenylfulgide by the action of cold acetyl chloride, whereas treatment during 6—8 hrs. with the boiling reagent is necessary for the conversion of dibenzylidenethiodiglycollic acid into the corresponding anhydride, $S<^{C(:CHPh)\cdot CO}_{C(:CHPh)\cdot CO}>O$. Conversely, dibenzylidenethiodiglycollic anhydride is much more readily hydrated than diphenylfulgide when dissolved in benzene or acetic acid. Differences in stability of the unsubstituted rings of succinic, glutaric, and thiodiglycollic anhydrides are not so obvious. The colour and absorption spectra of diphenylfulgide and dibenzylidenethiodiglycollic anhydride are closely similar. The colour of diphenylfulgide is attributed to the doubly *ortho*-quinonoid tetrahydrofuran nucleus and the phenyl groups attached at the two streptostatic double linkings; the same causes must also be operative in dibenzylidenethiodiglycollic anhydride, whence it follows that the sulphur atom is of little importance optically. It does not function as a chromophore, is highly saturated, and displays little residual affinity. This assumption is confirmed by the observation that halochromism is much less distinct with the thioanhydride than with the fulgide. The absence of considerable residual affinity in the case of the sulphur atom of unsubstituted thioxan has been established by Clarke (J.C.S., 1912, **101**, 1788) and Macbeth (*ibid.*, 1915, **107**, 1824). Diphenylthiodiglycollic anhydride may therefore be represented by the formula $S<^{C(:CHPh)\cdot CO}_{C(:CHPh)\cdot CO}>O$.

The proportions of diphenylfulgenic and γ-phenylitaconic acids produced by the condensation of benzaldehyde with ethyl succinate depend more on the nature of the solvent, temperature, and condensing agent than on the ratio of ester to aldehyde or the duration of the change. Diphenylfulgenic acid predominates at low temperatures in the presence of ether, whereas at 35° phenylitaconic acid is the main product. The latter acid is almost the sole product in alcoholic solution. Diphenylfulgenic acid is almost quantitatively formed by the action of alcoholic sodium ethoxide (2 mols.) on a mixture of ethyl phenylitaconate and benzaldehyde (1 mol.). Dibenzylidenethiodiglycollic acid is produced in good yield from benzaldehyde and ethyl thiodiglycollate and alcoholic sodium ethoxide solution or solid sodium ethoxide in the presence of ether. *Dibenzylidenethiodiglycollic anhydride* has m. p. 110°.

H. WREN.

Colour and chemical constitution. XX. J. MOIR (Trans. Roy. Soc. Sth. Africa, **13**, 131—138).—Commercial naphtholphthalein is a mixture of a brown substance, m. p. 234° (cf. Copisarow, J.C.S., 1915, **107**, 884), which is the 2 : 2′-derivative, with a white substance (λ 650 in alkali), which may be the 2 : 4′- or 4 : 4′-derivative, or a mixture of both. The former is converted by cold sulphuric acid into α-naphthafluoran (λλ 496 and 470 in sulphuric acid). The colours obtained by warming fluoran or α-naphthafluoran in alcoholic potassium hydroxide are probably due to oxonium salt formation, and not to formation of *o*-phthaleins. The *methyl ether* [λ (*a*), in alkali 470, (*b*), in sulphuric acid 572] and the *carboxymethyl ether* [λ (*a*) 485, (*b*) 592] of 4 : 4′-phenol-α-naphtholphthalein are obtained by treating *p*-hydroxybenzoylbenzoic acid with α-naphthyl methyl ether and α-naphthoxyacetic acid, respectively. Hydrolysis of the latter yields a little pure 4 : 4′-*phenol-α-naphtholphthalein* [λ (*a*) 601, (*b*) 587]. The unknown 2 : 4′-phenol-α-naphtholphthalein (cf. A., 1917, ii, 557) must have, approximately, λ (*a*) 610—615, (*b*) 550. Commercial α-naphtholphthalein gives with hydroxylamine a *naphthoylbenzoic acid* [λλ (*a*) 379, (*b*) 417 and 500], apparently identical with the product obtained by heating together α-naphthol, phthalic anhydride, and stannic chloride. Both products yield the white α-naphtholphthalein with α-naphthol. 4-Methoxynaphthoylbenzoic acid [λλ (*b*) 525 and 495] could not be demethylated. In the monocyclic series, the naphthalene/benzene colour factor is about 1·13, in the dicyclic series it is 1·08. 4-Hydroxy-1-naphthaldehyde gives, with β-naphthol, 2 : 4′-*dihydroxy*-1 : 1′-*dinaphthylcarbinol* [λ (*b*) 680, vague]; with α-naphthol, 4 : 4′-*dihydroxy*-1 : 1′-*dinaphthylcarbinol* [λ (*a*) 635, (*b*) 640], and 1 : 4′-*dihydroxy*-2 : 1′-*dinaphthylcarbinol* [λ (*a*) 648, (*b*) 640]; and with dimethylaniline, 4-*dimethylaminophenyl*-4′-*hydroxynaphthylcarbinol* [λλ 635 and 500]. 4-*Dimethylaminophenyl*-2′-*hydroxynaphthylcarbinol* has λλ 638 and 575. Examination of the data recorded above indicates that the white naphtholphthalein is probably the 4 : 4′-derivative. 2 : 4′-Phenolphthalein and its 5-amino-derivative have been re-examined [λλ (*a*) 552 and 570, respectively; cf. A., 1919, i, 78]. Absorption bands are recorded for some fifteen new mixed phthaleins, six benzhydrol derivatives, sixteen azo-dyes, three hydrazones, some thioquinhydrones and related substances, and a number of miscellaneous compounds.

H. E. F. NOTTON.

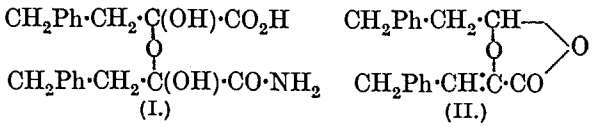
Effect of different substituents on the stability of carboxyl groups in substituted aromatic acids. Effect of a second carboxyl group and relative influence of chlorine and bromine. F. HEMMELMAYR and T. MEYER (Monatsh., 1925, **46**, 143—156; cf. A., 1913, **i**, 468).—The presence of a second carboxyl group in 2 : 3- and 2 : 5-dihydroxybenzoic acids reduces the tendency of the acids to lose carbon dioxide when boiled with water or aniline; the 2 : 5-dihydroxy-acids are more stable than the 2 : 3-isomerides. α- and β-Resodicarboxylic acids [2 : 4-dihydroxy*iso*phthalic and 3 : 5-dihydroxyphthalic (?) acids], on the other hand, are appreciably less stable than the resorcylic acids. 2 : 3-Dihydroxyterephthalic acid is not attacked by bromine; the 2 : 5-isomeride loses both carboxyl groups and gives tetrabromo-*p*-benzoquinone; α- and β-resodicarboxylic acids are brominated readily and the stability of the carboxyl groups is thereby enhanced. Attempts to nitrate dihydroxybenzenedicarboxylic acids without decarboxylation were unsuccessful. The intro-

duction of a single halogen atom into β-resorcylic acid stabilises the carboxyl group, chlorine being more effective than bromine. The same holds for α-resodicarboxylic acid. The dihalogenated β-resorcylic acids are, on the other hand, less stable, the dibromo-acid being more readily decomposed than the dichloro-acid.

5-Bromo-2 : 4-dihydroxyisophthalic acid (*bromo-α-resodicarboxylic acid*), m. p. 303° (*barium* and *silver* salts described), is formed, together with a small amount of *dibromo*-compound, from α-resodicarboxylic acid and rather more than 2 mols. of bromine in hot acetic acid. Bromination of the β-acid in ether or acetic acid gives *dibromo-β-resodicarboxylic acid* $[Br_2:(OH)_2:(CO_2H)_2$ probably 4 : 6 : 3 : 5 : 1 : 2], m. p. 245° (*barium* and *silver* salts described). By the action of chlorine (1 mol.) on β-resorcylic acid in hot glacial acetic acid solution there is obtained *5-chloro-2 : 4-dihydroxybenzoic acid*, m. p. 175°, different from Fabre's 3-chloro-derivative (A., 1922, i, 1147). The *dichloro*-acid (*barium* and *silver* salts described) melts at 229°. *5-Chloro-2 : 4-dihydroxyisophthalic acid* (*chloro-α-resodicarboxylic acid*; *barium* and *silver* salts described) has m. p. 297° (decomp.). α-Resodicarboxylic acid is converted by methyl sulphate and sodium hydroxide into *methyl* 2(or 4)-*hydroxy*-4(or 2)-*methoxyisophthalate*, m. p. 108°. β-Resodicarboxylic acid gives *methyl dimethoxyphthalate*, m. p. 122°. These ethers could not be nitrated without decarboxylation. Nitration of β-resodicarboxylic acid yields a small quantity of an impure *dinitro*-acid, m. p. 207°. C. Hollins.

4 : 5 : 6-Trimethoxybenzene-1 : 3-dicarboxylic acid. K. Feist and W. Awe (Ber., 1926, **59**, [*B*], 175—177).—4 : 5 : 6-Trihydroxybenzene-1 : 3-dicarboxylic acid is prepared by heating gallic or pyrogallolcarboxylic acid with glycerol and potassium hydrogen carbonate at 170—180° in an atmosphere of carbon dioxide. It is transformed by diazomethane into *methyl* 4 : 5 : 6-*trimethoxybenzene*-1 : 3-*dicarboxylate*, m. p. 35—36° (corr.), which is hydrolysed to 4 : 5 : 6-trimethoxybenzene-1 : 3-dicarboxylic acid, m. p. 189—190° (corr.). The m. p. of the acid is not greatly influenced by the solvent from which it is crystallised. H. Wren.

An hydrated ketone ether. J. Bougault (Compt. rend., 1926, **182**, 136—138; cf. A., 1925, i, 921, 1152; this vol., 167).—Hydrolysis of the acid amide (I) with hydrochloric acid in acetic acid solution yields a mixture of lactones, one (II) m. p. 120°, and the other m. p. 82°. The former (II) is soluble in



(I.) (II.)

dilute alkalis, insoluble in a slight excess, and when boiled in alkaline solution yields β-phenylpropionaldehyde and benzylpyruvic acid. L. F. Hewitt.

New degradation products of digitogenin. A. Windaus and S. V. Shah (Z. physiol. Chem., 1926, **151**, 86—97; cf. A., 1925, i, 1082).—Oxidation of digitoic acid with fuming nitric acid leads to loss of four carbon atoms and formation of a dibasic *acid*, $C_{22}H_{31}O_{10}N$, darkening at 230°, m. p. 242° (decomp.); *dimethyl* ester, m. p. 194—195° (decomp.). The latter eliminates nitrous acid on warming with potassium hydroxide; on oxidation with potassium permanganate, the acid yields a tribasic *acid*, $C_{22}H_{30}O_{10}$, m. p. 113°, and after re-solidification 172°. It is thought that the four carbon atoms lost from digitoic acid have been removed from the side-chain, the compound $C_{22}H_{31}O_{10}N$ being the nitric ester of a lactol; the tenth oxygen atom is accounted for by assuming the oxidation of a tertiary hydrogen atom to hydroxyl; the effect of subsequent permanganate oxidation is to oxidise the lactol to a lactone and simultaneously to oxidise the carbonyl group of one of the rings to carboxyl. Oxydigitogenic acid with nitric acid loses five carbon atoms, yielding a tribasic *acid*, $C_{21}H_{31}O_{11}N$, m. p. 218—220° (decomp.), which loses nitrous acid on heating with potassium hydroxide; it gives a *trimethyl* ester, m. p. 171°, which, on heating in a vacuum, loses nitrous acid to give $C_{24}H_{36}O_9$, m. p. 142°, which, in turn, on hydrolysis, gives a tribasic *acid*, $C_{21}H_{30}O_9$, m. p. 215—216°; this series of reactions is explained similarly to those described above, with the addition, in this case, of the oxidative degradation of the $\cdot CO\cdot CO_2H$ group of oxydigitogenic acid to $\cdot CO_2H$. The amorphous tribasic acid $C_{26}H_{36}O_9$, previously described (A., 1925, i, 1086) as an oxidation product of digitogenic acid, can be obtained from the latter by oxidation with cold chromic acid, and therefore probably retains the carbonyl-containing ring intact; from the trimethyl ester of this acid there was obtained, by fractional hydrolysis with acetic and sulphuric acids, a *dimethyl* ester, m. p. 125°, and a *monomethyl* ester, m. p. 201°; further, on heating the trimethyl ester with acetic and hydriodic acids, opening of the oxide ring and reduction took place, with formation of an *acid*, $C_{26}H_{37}O_8I$(?), m. p. 240—250° (decomp.), *trimethyl* ester, m. p. 122° and 105° (dimorphic); with zinc dust, the iodine-containing acid gave a tribasic *acid*, $C_{26}H_{38}O_8$, m. p. 273—274°, *trimethyl* ester, m. p. 125—126°. C. R. Harington.

New synthesis of *o*-acetoveratrole [2 : 3-dimethoxyacetophenone]. F. Mauthner (J. pr. Chem., 1926, [ii], **112**, 57—60).—2-Hydroxy-3-methoxybenzoic acid is converted by treatment with methyl sulphate and subsequent esterification into methyl 2 : 3-dimethoxybenzoate, which by the Claisen reaction with ethyl acetate yields *ethyl* 2 : 3-*dimethoxybenzoylacetate* (*pyrazolone* derivative, m. p. 125—126°). Dilute mineral acids bring about ketonic hydrolysis of the ester with formation of 2 : 3-dimethoxyacetophenone (*p-nitrophenylhydrazone*, m. p. 155—156°). R. W. West.

New syntheses of *o*-vanillin and *o*-veratraldehyde. F. Mauthner (J. pr. Chem., 1926, [ii], **112**, 60—64).—When 2-hydroxy-3-methoxybenzoic acid is treated with methyl chloroformate and dimethylaniline in benzene solution, it yields 2-*carboxy*-6-*methoxyphenyl methyl carbonate*,

$$MeO\cdot C_6H_3(CO_2H)O\cdot CO_2Me,$$

m. p. 145—146°, of which the *chloride*, m. p. 43—44°,

by catalytic reduction and subsequent hydrolysis, yields 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) (p-*nitrophenylhydrazone*, m. p. 217—218°). 2 : 3-Dimethoxybenzoic acid (*amide*, m. p. 93—94°) is converted by phosphorus pentachloride into 2 : 3-*dimethoxybenzoyl chloride*, m. p. 54—55°, which by catalytic reduction in xylene solution yields *o*-veratraldehyde (p-*nitrophenylhydrazone*, m. p. 205—206°).

R. W. WEST.

Purification of xylene for use as solvent for catalytic reduction. F. ZETZSCHE and O. ARND (Helv. Chim. Acta, 1926, **9**, 173—177; cf. A., 1925, i, 1415).—In the catalytic reduction of acid chlorides in toluene or xylene solution, the preliminary method of treatment of the solvent has a large effect on the yield of aldehyde obtained. By preliminary treatment of xylene with phosphoryl chloride or phosphorus pentachloride, under certain prescribed conditions, the yield of aldehyde (from benzoyl chloride) was considerably reduced, and in one case (boiling the xylene with phosphoryl chloride for 1·5 hrs., followed by distillation) almost to zero, with an accompanying increase in the yields of ester and non-volatile hydrocarbon products. The effects of other purifying reagents was investigated, and treatment with either aluminium chloride or concentrated sulphuric acid was found to produce a solvent in which very little or no formation of aldehyde occurred, the products being mainly hydrocarbons.

J. W. BAKER.

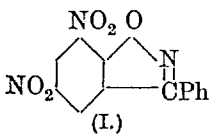
Utility of various solvents for the catalytic synthesis of aldehydes from acid chlorides. F. ZETZSCHE, F. ENDERLIN, C. FLÜTSCH, and E. MENZI (Helv. Chim. Acta, 1926, **9**, 177—181).—The utility of a large number of substances as solvents in the catalytic reduction of benzoyl chloride, first in the commercial state at their b. p., then after purification, and finally with the addition of a regulator (quinoline-*s*) has been investigated. Decalin and tetralin, which, having themselves been prepared by catalytic reduction, are free from catalyst poisons, give good yields of benzaldehyde in their crude state, and after purification and with the addition of a small quantity of a regulator give, respectively, 86% and 82% yields after 2 hrs. at 180°. The maximal yield obtained with anisole as a solvent is 84%, whilst with redistilled turpentine in the presence of a regulator, a 92% yield of benzaldehyde is obtained in 1·75 hrs. Solvents which are themselves reduced and can interact with the benzoyl chloride have also been investigated. Thus with amyl and "hexalin" acetates the corresponding benzoates are obtained; with phenetole, phenyl benzoate; and with acetic anhydride, benzoic anhydride, this reaction providing a ready method for the preparation of acid anhydrides from acid chlorides. In *s*-tetrachloroethane solution, the products are benzaldehyde (17%) and benzyl benzoate (70%), whilst with nitrobenzene as solvent are obtained the aldehyde and ester, benzanilide and benzoyldiphenylamine, the relative proportions varying with the proportions of benzoyl chloride and nitrobenzene in the original mixture.

J. W. BAKER.

Reduction of oximes by means of sodium and absolute alcohol. Resolution of the amines thus obtained into their optical antipodes by means of *d*-tartaric acid. P. BILLON (Compt. rend., 1926, **182**, 470—473).—The following oximes have been reduced to the corresponding amines in 85—100% yield by sodium and absolute ethyl alcohol: benzophenoneoxime to benzhydrylamine, phenyl-*p*-tolylketoxime to ω-aminophenyl-*p*-tolylmethane, m. p. 40°, phenyl-*p*-anisylketoxime to ω-aminophenyl-*p*-anisylmethane, acetophenoneoxime to α-amino-α-phenylethane, propiophenoneoxime to α-amino-α-phenylpropane, phenyl*iso*propylketoxime to α-amino-α-phenyl-β-methylpropane, and phenyl-*n*-propylketoxime to β-amino-α-phenylbutane. *dl*-α-Amino-α-phenylpropane has been resolved into its optical antipodes ($[\alpha]_D$ +9·5° and −10·5°, respectively) by crystallisation of the d-*tartrate* (m. p. 166°) from absolute alcohol.

L. F. HEWITT.

Beckmann transformation. VI. Configuration of oximes of benzophenone, acetophenone, and benzaldehyde. J. MEISENHEIMER, P. ZIMMERMANN, and M. VON KUMMER (Annalen, 1926, **446**, 205—228; cf. A., 1925, i, 1073).—Previous work on *o*-substituted benzophenoneoximes (A., 1924, i, 433) has been extended to include nitro-derivatives in which the *o*-substituent (Cl, Br, or ·OMe) is more reactive. When treated with hydroxylamine 2-*bromo*-3 : 5-*dinitrobenzophenone*, m. p. 153—154°, obtained by the Friedel–Crafts reaction from 2-*bromo*-3 : 5-*dinitrobenzoic acid*, m. p. 213°, yields 4 : 6-*dinitro*-2-*phenylbenz*iso*oxazole* (I), m. p. 242—243° (decomp.), which is converted by alcoholic potassium hydroxide into the *potassium* salt of 3 : 5-*dinitro*-2-*hydroxybenzophenoneoxime*. This salt is decomposed by water with regeneration of the *iso*oxazole, which is also formed by the action of hydroxylamine on 2-chloro-3 : 5-dinitrobenzophenone and 3 : 5-dinitro-2-methoxybenzophenone. The *o*-substituents are not so reactive in the mononitro-series and the oximes may be isolated. Thus, 2-*chloro*-5-*nitrobenzophenoneoxime*, m. p. 180°, is rapidly converted by the action of dilute alkali into 4-*nitro*-2-*phenylbenz*iso*oxazole*, m. p. 143°, and by the Beckmann change, using phosphorus pentachloride, it yields 2-*chloro*-5-*nitrobenzanilide*, m. p. 158°, and a *substance*, $C_{13}H_{10}O_6N_2ClP$, m. p. 136—138°. 2-*Bromo*-5-*nitrobenzophenone*, m. p. 121°, and 5-*nitro*-2-*methoxybenzophenone*, m. p. 129°, react in the same way as the chloro-compound and yield the following substances: 2-*bromo*-5-*nitrobenzophenoneoxime*, m. p. 195—196°; a *substance*, $C_{13}H_{10}O_6N_2BrP$, m. p. 135—139°; 5-*nitro*-2-*methoxybenzophenoneoxime*, m. p. 195°; 5-*nitro*-2-*methoxybenzanilide*, m. p. 195—196°. The ease with which the *iso*oxazole ring is formed suggests that these oximes have the configuration $NO_2 \cdot C_6H_3Br \cdot \underset{HO \cdot N}{\overset{\|}{C}} \cdot Ph$, and the formation of bromonitrobenzanilide is in accordance with the new conception of the Beckmann change.



(I.)

When treated with bromine, 2-*bromo*-5-*nitroacetophenone*, m. p. 88—89°, yields 2 : ω-*dibromo*-5-*nitro*-

acetophenone, m. p. 66—67°, which condenses with hydroxylamine (3 mols.) to give the *hydroxylamine-dioxime*, $[NO_2 \cdot C_6H_3Br \cdot C(:NOH) \cdot CH_2]_2N \cdot OH$, m. p. 195°. 2-Bromo-5-nitroacetophenone yields two oximes, α-*oxime*, m. p. 171°, and β-*oxime*, m. p. 132°. The β-oxime is rapidly converted by cold dilute alkali solution into 4-*nitro*-2-*methylbenzisooxazole*, m. p. 129°, but gives no Beckmann rearrangement. The α-oxime reacts only slowly with boiling alkali solution, but gives 2-bromo-5-nitroacetanilide by the Beckmann change. These facts support the new theory, and the α- and β-oximes must have respectively the *cis*-methyl and *trans*-methyl structures. The action of hydroxylamine on 2-*chloro*-5-*nitrobenzyl chloride*, m. p. 66°, yields N-*di*-(2-*chloro*-5-*nitrobenzyl*)-*hydroxylamine*, m. p. 225°.

The results obtained by Brady and Bishop (A., 1925, i, 930) are confirmed as regards the oximes of 2-chloro-5-nitrobenzaldehyde, but as 5-*nitro*-2-*hydroxybenzaldoxime*, m. p. 225°, is not converted into the *iso*oxazole by the action of acids or alkalis, it is contended that the conversion by alkali of the β-oxime into 5-nitrosalicylonitrile must pass through the intermediate stage of the *iso*oxazole ring.

It is shown that there is nothing anomalous in the formation of benzoic acid and benzonitrile by the alkaline hydrolysis of benzoyl-α-benzilmonoxime. By the action of cold sodium hydroxide solution, acetyl-α-benzilmonoxime is converted into a mixture of α-benzilmonoxime, benzonitrile, and benzoic acid. Under similar conditions *propionyl*-α-*benzilmonoxime*, m. p. 70°, is completely converted into benzonitrile and benzoic acid, and *cinnamoyl*-α-*benzilmonoxime*, m. p. 117°, is slowly converted into benzoic and cinnamic acids. R. W. WEST.

Optically active esters of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl hydroxymethyl ketone and 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl β-hydroxyethyl ketone. H. RUPE and J. PERRET (Helv. Chim. Acta, 1926, **9**, 97—115; cf. this vol., 398).—1 : 2 : 2 : 3-Tetramethyl*cyclo*pentyl bromomethyl ketone, d_4^{20} 0·9055, has, in 10% benzene solution, $[\alpha]_C^{20}$ +49·74°, $[\alpha]_D^{20}$ +63·77°, $[\alpha]_{E\ Hg}^{20}$ +76·36°, $[\alpha]_F^{20}$ +102·8°. The hydroxymethyl ketone has d_4^{20} 1·0002, $[\alpha]_C^{20}$ +68·98°, $[\alpha]_D^{20}$ +87·16°, $[\alpha]_{E\ Hg}^{20}$ +103·07°, $[\alpha]_F^{20}$ +134·33°; similar constants are given for the acetate, benzoate, *propionate*, b. p. 157°/11 mm., n-*butyrate*, b. p. 167·5°/11 mm., phenylacetate, *hydrocinnamate*, b. p. 136—138°/high vac. Reduction of the acetate in alcoholic solution with sodium amalgam gives 1 : 2 : 2 : 3-tetramethyl-*cyclo*pentyl methyl ketone and 1 : 2 : 2 : 3-*tetramethyl*-cyclo*pentyl*-1-*glycol*, m. p. 108° (*diacetate*, b. p. 205—207°/9 mm.; *monobenzoate*, b. p. 198—199°/12 mm., losing a little benzoic acid at 130—140°), d_4^{20} 0·8863, giving, in 10% benzene solution, $[\alpha]_C^{20}$ +38·91°, $[\alpha]_D^{20}$ +47·60°, $[\alpha]_{E\ Hg}^{20}$ +55·45°, $[\alpha]_F^{20}$ +70·45°, and oxidised by nitric acid to the hydroxymethyl ketone. Rotation constants are given for the following esters of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl-1-carbinol: acetate, propionate, n-*butyrate*, b. p. 128·5—129°/11 mm., phenylacetate, hydrocinnamate, and cinnamate. The hydroxymethylene derivative of 1 : 2 : 2 : 3-tetramethyl*cyclo*pentyl methyl ketone,

$$C_9H_{17} \cdot CO \cdot CH{:}CH \cdot OH,$$

d_4^{20} 0·9946, $[\alpha]_C^{20}$ +48·03°, $[\alpha]_D^{20}$ +59·85°, $[\alpha]_{E\ Hg}^{20}$ +69·72°, $[\alpha]_F^{20}$ +87·56° [*nickel* salt; *benzoate*, m. p. 65°, slowly decomposing into benzoic acid and $C_6H_3(CO \cdot C_9H_{17})_3$ (see later); *hydrocinnamate*, b. p. 216—218°/10 mm., slowly decomposed on keeping; *condensation product* with *p*-toluidine, $C_9H_{17} \cdot CO \cdot CH{:}CH \cdot NH \cdot C_6H_4Me$, m. p. 80°], is prepared in better yield by the action of sodium ethoxide and *iso*amyl formate (cf. this vol., 399) on the methyl ketone. A *compound*, m. p. 136°, regarded as tricamphoylbenzene, $C_6H_3(CO \cdot C_9H_{17})_3$, occurs in about 10% yield in the synthesis of the hydroxymethylene derivative. It is obtained in 40% yield by heating the latter in ether solution with dry potassium acetate. 1 : 2 : 2 : 3-*Tetramethyl*cyclo*pentyl* β-*hydroxyethyl ketone*, b. p. 143°/12 mm., d_4^{20} 0·9974, $[\alpha]_C^{20}$ +42·76°, $[\alpha]_D^{20}$ +52·94°, $[\alpha]_{E\ Hg}^{20}$ +61·29°, $[\alpha]_F^{20}$ +76·03° (*phenylthiourethane*, m. p. 154°, p-*nitrobenzoate*, m. p. 51°), is obtained by catalytic reduction of the hydroxymethylene compound with nickel and purified through the calcium chloride double *compound*. Rotation constants are given for the following esters of the hydroxyethyl ketone: *acetate*, b. p. 159°/12 mm.; *propionate*, b. p. 93—94° in a high vacuum, decomp. by distillation at higher pressures; n-*butyrate*, b. p. 104—106° in a high vacuum, unstable; *benzoate*, unstable on distillation even in a high vacuum. Hydrolysis of the esters is accompanied by formation of a *polymeric methylene* compound,

$$(C_9H_{17} \cdot CO \cdot CH{:}CH_2)(CH{:}CH_2)_x,$$

m. p. above 250°. 1 : 2 : 2 : 3-*Tetramethyl*cyclo-*pentyl* β-*bromoethyl ketone*, b. p. 130—131°/9 mm., d_4^{20} 1·2042, $[\alpha]_C^{20}$ +39·87°, $[\alpha]_D^{20}$ +49·77°, $[\alpha]_{E\ Hg}^{20}$ +57·98°, $[\alpha]_F^{20}$ +72·86°, is obtained by the action of hydrobromic acid in acetic acid solution on the hydroxyethyl ketone. Attempts to obtain the compound $C_9H_{17} \cdot CO \cdot CH{:}CH_2$ from either the bromoethyl or hydroxyethyl ketone or from the esters of the latter gave in every case the polymeric methylene compound obtained by hydrolysis of the esters. Mol. wt. determinations gave values for x ranging from 4 to 7. The bromoethyl ketone is moderately stable towards alcoholic potassium hydroxide, but gives the polymeric compound on boiling with aniline.

Rotation–dispersion constants are given for the whole series of compounds. The original paper must be consulted for these and for the rotations of the esters. M. CLARK.

***o*-Alkyl derivatives of benzoylacetone and the *iso*oxazoles derived therefrom.** L. CLAISEN (Ber., 1926, **59**, [*B*], 144—153).—According to Weygand (A., 1925, i, 1288), the product of the action of ethyl orthoformate on benzoylacetone is converted by hydroxylamine into a phenylmethyl*iso*oxazole, m. p. 68°, instead of into an isomeric phenylmethyl*iso*-oxazole, m. p. 42°, described by Claisen (A., 1907, i, 940); it must therefore have the constitution CPh(OEt):CHAc (instead of CHBz:CMe·OEt assigned by Claisen) and be identical with the product described by Ruhemann and Watson (J.C.S., 1904, **85**, 464, 1180). In spite of close physical similarity, the two ethers are not identical and differ markedly in their behaviour towards reagents. With hydroxylamine in the presence of an excess of alkali, Claisen's ether affords 3-phenyl-5-methyl*iso*oxazole, m. p. 43°, in

80—90% yield, whereas Ruhemann's compound yields 5-phenyl-3-methyl*iso*oxazole, m. p. 68° (*benzoylacetonedioxime*, m. p. 98—99° after softening at 93°, is formed in small amount as by-product). Weygand's result is due to the use of hydroxylamine hydrochloride and consequent hydrolysis of the ethers to free benzoylacetone by liberated hydrogen chloride. In all known cases in which one of the keto-groups of benzoylacetone is replaced by another residue, the acetyl group is preponderatingly affected, whereas the benzoyl group suffers little change. The action of ammonia or aniline on Claisen's ether gives products identical with those obtained from benzoylacetone, the alkoxy-group being exchanged for the respective residue, whereas the isomeric ether, CPh(OEt):CHAc, is converted by ammonia into the isomeric *amide*, CPh(NH_2):CHAc, m. p. 86—87°, and by aniline and other primary and secondary bases into compounds which do not crystallise readily. Detailed description is given of the conditions under which the ethers are transformed into the phenylmethyl*iso*oxazoles, and the separation of the latter substances from their mixtures by means of cadmium chloride or mercuric chloride is discussed in detail. 5-Phenyl-3-methyl*iso*oxazole is transformed by magnesium phenyl bromide into diphenyl and the amide, CHBz:CMe·NH_2, whereas an analogous reaction could not be effected with the isomeric *iso*oxazole. Examination of the product of the action of diazomethane on benzoylacetone when treated with ammonia or hydroxylamine shows it to be a mixture of the isomeric methyl ethers instead of the individual CPh(OMe):CHAc assumed by Weygand (*loc. cit.*). H. WREN.

4- and 4'-Methoxybenzoylbenzoins. H. GREENE (J.C.S., 1926, 328—336).—It has been shown previously (Greene and Robinson, *ibid.*, 1922, **121**, 2182) that the benzoin condensation of benzoylated cyanohydrins with aldehydes in the presence of sodium ethoxide involves the migration of the benzoyl group. Similar results have now been obtained in the following condensations, and the optimum conditions for the preparation of the various isomerides have been studied. The normal condensation products of benzoyl-*p*-methoxymandelonitrile with benzaldehyde, and of benzoylmandelonitrile with anisaldehyde, are 4-methoxybenzoylbenzoin, m. p. 119·5—120·5° (previously described by Greene and Robinson as the 4'-methoxy-isomeride), and 4'-methoxybenzoylbenzoin, m. p. 127—128°, respectively. The former condensation, however, gives rise abnormally to benzoylbenzoin, and the latter to 4-methoxybenzoylbenzoin, probably on account of a double decomposition of the reactants, a fact which is supported by the condensations of benzoylmandelonitrile and furfuraldehyde, on the one hand, and of benzoylfurfuraldehydecyanohydrin and benzaldehyde, on the other, when mixtures of benzoylbenzoin, m. p. 125°, benzoylfuroin, m. p. 92—93° (also obtained by the interaction of benzoylfurfuraldehydecyanohydrin and furfuraldehyde), and benzfuroin, m. p. 141·5—143·5°, are obtained. *Piperonoyl-α-furylcarbinyl benzoate*, CH_2O_2:C_6H_3·CO·CH(OBz)·C_4H_3O, m. p. 132·5—133·5°, is obtained from benzoyl-3 : 4-methylenedioxymandelonitrile and furfuraldehyde, whilst *α-furoylpiperonylcarbinyl benzoate*,

C_4H_3O·CO·CH(OBz)·C_6H_3:O_2CH_2,

m. p. 140—141°, is obtained from piperonal and benzoylfurfuraldehydecyanohydrin. Better methods are described for the preparation of 3 : 4- and 3' : 4'-methylenedioxybenzoylbenzoins. It was not found possible to benzoylate benzfuroin, whilst attempts to synthesise the isomeric benzoyl derivatives also failed. J. S. H. DAVIES.

Colouring matters of fungi. V. Constitution of polyporic acid. F. KÖGL (Annalen, 1926, **447**, 78—85; cf. A., 1925, i, 1440).—Stahlschmidt's "polyporic acid" (cf. A., 1877, ii, 620; 1879, 382) has been identified as 3 : 6-dihydroxy-2 : 5-diphenylbenzoquinone (cf. Fichter, A., 1908, i, 658). It is present in *Polyporus nidulans*, Fr. to the extent of 18% of the weight of the fungus. The diacetate has m. p. 209°, the dimethyl ether m. p. 192°. When distilled with zinc dust, polyporic acid yields *pp'*-diphenylbenzene, whilst benzoic acid is formed when the acid is oxidised with chromic acid in glacial acetic acid. Polyporic acid forms glistening, brownish-violet, dichroic, rhombic plates, plane angle 94°, with diagonal extinction. F. G. WILLSON.

β-Methylanthraquinone derivatives. VII. Nitro-derivatives of 1-hydroxy-3-methylanthraquinone and related products. R. EDER and O. MANOUKIAN (Helv. Chim. Acta, 1926, **9**, 51—59; cf. A., 1924, i, 528).—1-Hydroxy-3-methylanthraquinone is obtained in 60—70% yield by dissolving 2'-hydroxy-4'-methyl-*o*-benzoylbenzoic acid (1 part) and boric acid (1 part) in sulphuric acid monohydrate (2 parts) and warming on the water-bath for 4 hrs. after addition of 20% "oleum" (10 parts). The method of Bentley, Gardner, and Weizmann (J.C.S., 1907, **91**, 1626) gives only 20—25% of the theoretical yield. Nitration with potassium nitrate and concentrated sulphuric acid gives 2 : 4-*dinitro*-1-*hydroxy*-3-*methylanthraquinone*, m. p. 275—276° (decomp.) (*sodium* salt, flesh-coloured needles), accompanied by smaller amounts of 2-*nitro*-1-*hydroxy*-3-*methylanthraquinone*, m. p. 272—273° (decomp.), and 4-*nitro*-1-*hydroxy*-3-*methylanthraquinone*, m. p. 241—242°. Acetylation of the hydroxy-group before nitration and subsequent hydrolysis again gives the dinitro-compound as the main product. The three substances are separated by fractional crystallisation from glacial acetic acid and acetone. The constitution of the dinitro-compound is shown by its oxidation with alkaline permanganate to phthalic acid and by reaction with sodium methoxide followed by treatment with concentrated hydrochloric acid under pressure at 190°, when 1 : 2 : 4-trihydroxy-3-methylanthraquinone is obtained. Reduction gives 2 : 4-*diamino*-1-*hydroxy*-3-*methylanthraquinone*, m. p. 259—260°. Reduction of the 4-nitro-compound gives 4-amino-1-hydroxy-3-methylanthraquinone (A., 1920, i, 54). This compound is also obtained by the action of sulphuric and boric acids (D.R.-P. 203083) on the bromination product of 1-amino-2-methylanthraquinone (A., 1903, i, 498). The bromination product is thus 1-bromo-4-amino-3-methylanthraquinone. The remaining mononitro-derivative, converted by further nitration

into the 2 : 4-dinitro-compound, gives an amine of lower m. p. than the 4-amino-derivative. It is, therefore, the 2-nitro-derivative, yielding on reduction *2-amino-1-hydroxy-3-methylanthraquinone*, m. p. 238°. M. CLARK.

Anthraquinone series. I. Anthraquinonylamides of substituted anthraquinonecarboxylic acids. A. ROLLETT [with O. HAIDER and A. MERKA] (Monatsh., 1925, **46**, 131—136; cf. Seer and Weitzenböck, A., 1910, i, 570).—*1-Chloroanthraquinone-2-carboxyl chloride*, m. p. 210°, prepared from the acid and thionyl chloride, condenses with 2-aminoanthraquinone in boiling benzene to give *1-chloroanthraquinone-2-carboxyl-2'-anthraquinonylamide*, m. p. 317°, which is converted by 10% aqueous ammonia in sealed tubes at 200—210° into *1-aminoanthraquinone-2-carboxyl-2'-anthraquinonylamide*, m. p. 365°, dyeing cotton a fast bluish-pink from the vat. *1-Chloroanthraquinone-2-carboxyl-1'-chloro-2'-anthraquinonylamide*, m. p. 363°, yields with ammonia a *substance*, m. p. 368°, giving also a bluish-pink on cotton from the vat. *1-Chloroanthraquinone-2-carboxyl-1'-anthraquinonylamide*, m. p. 241°, dyes cotton a weak greenish-yellow from the vat, and by the action of ammonia is converted into *1-aminoanthraquinone-2-carboxyl-1'-anthraquinonylamide*, m. p. 331°, which dyes cotton pure red from the vat, together with a black *substance*, m. p. 293°, which cannot be vatted. *1-Chloroanthraquinone-2-carboxyl-5'-nitro-1'-anthraquinonylamide* dyes cotton a weak brownish-red from the vat. C. HOLLINS.

Vat dyes from benzanthrone. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 148.

Condensation products [vat dyes] of the anthraquinone series. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 148.

Vat dyes [from dibenzanthrone derivatives]. KALLE UND CO.—See B., 1926, 149.

Anthraquinone derivatives containing nitrogen [*iso*oxazolones]. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 149.

Manufacture of 2-aminoanthraquinone. O. D. CUNNINGHAM.—See B., 1926, 185.

Molecular configurations of polynuclear aromatic compounds. V. Identity of the nitration products derived from 2:7- and 4:5-dinitrophenanthraquinones. G. H. CHRISTIE and J. KENNER (J.C.S., 1926, 470—476).—Both 2 : 7- and 4 : 5-dinitrophenanthraquinone (Schmidt and Kämpf, A., 1904, i, 71) nitrate further to form the same trinitrophenanthraquinone, probably the 2 : 4 : 7-trinitro-compound (*quinoxaline* derivative, m. p. 307°) because the derived 4 : 6 : 4'-trinitrodiphenic acid appears to be reduced by tin and hydrochloric acid to a *diaminophenanthridonecarboxylic acid*. The identity of the trinitro-compounds thus obtained from two different dinitrophenanthraquinones, coupled with the fact that a tetranitrophenanthraquinone could not be obtained by further vigorous nitration, renders it possible that the trinitro-compound is derived from the initially formed tetranitrophenanthraquinone by elimination of a nitro-group under the experimental conditions. 4 : 6 : 4' : 6'-Tetranitrodiphenic acid, when reduced with stannous chloride, furnishes the corresponding *diaminophenanthridone*, of which both the neutral and basic *sulphates* were isolated. 3 : 5 : 3' : 5'-*Tetranitrobenzil*, m. p. 168° (*quinoxaline* derivative, m. p. 274°), together with 3 : 5-dinitrobenzoic acid, is readily obtained by the further nitration of 3 : 3'-dinitrobenzil. The prefixes, *d* and *l*, used previously (J.C.S., 1923, **123**, 779) for the optically active forms of 4 : 6 : 4'-trinitrodiphenic acid, m. p. 292°, require to be interchanged. The following constants are now given: *d*-4 : 6 : 4'-trinitrodiphenic acid, m. p. 281—282° (decomp.), $[\alpha]_D$ +23·47°, sodium salt, $[\alpha]_D$ −151·1°; *l*-4 : 6 : 4'-trinitrodiphenic acid, m. p. 280—282°, $[\alpha]_D$ −15·14°, sodium salt, $[\alpha]_D$ +136·6°; *quinine d*-4 : 6 : 4'-*trinitrodiphenate*, m. p. 222·5° (decomp.), $[\alpha]_D^{19}$ −156·1°; *quinine l*-salt, m. p. 176° (decomp.), $[\alpha]_D^{19}$ −77·5°; *quinidine d*-salt, m. p. 178°, $[\alpha]_D$ +109·9°; *quinidine l*-salt, m. p. 228°, $[\alpha]_D$ −189·2°. J. S. H. DAVIES.

Existence of *iso*pulegone in nature. Isolation of α(*iso*)- and β(ordinary)-pulegone and their enolic isomerides. V. GRIGNARD and J. SAVARD (Compt. rend., 1926, **182**, 422—425; cf. this vol., 72).—Pulegone obtained from various peppermint oils is separable, by treatment with sodium hydrogen sulphite, into β(ordinary)-pulegone, b. p. 88—89°/6 mm., d_4^{13} 0·9346, n_D^{13} 1·4894, $[\alpha]_D$ +21°, which forms a crystalline hydrogen sulphite compound, and α-(*iso*)pulegone, b. p. 78°/5 mm., d_4^{14} 0·9097, n_D^{14} 1·4633, $[\alpha]_D$ +34°, semicarbazone, m. p. 172°, hydrobromide, m. p. 40—41°, identical with the synthetic product save in rotatory power. α-Pulegone does not react with sodium hydrogen sulphite. The enolic forms of the pulegones possess the following properties: *enol* of *α-pulegone*, b. p. 80—81°/6 mm., d_4^{14} 0·8965, n_D^{14} 1·4673, $[\alpha]_D$ −4·3° (5% solution in toluene); *enol* of *β-pulegone*, b. p. 88°/6 mm., d_4^{13} 0·9160, n_D^{13} 1·4831, $[\alpha]_D$ +24·6°. The exaltation in molecular refractivity of the enolic forms indicates conjugation of unsaturated linkings. L. F. HEWITT.

Preparation of solid camphene free from chlorine, from pinene hydrochloride. E. MEYER and W. CLAASEN.—See B., 1926, 216.

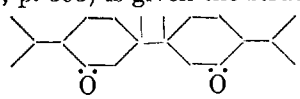
Constitution of Manasse's hydroxycamphor. M. O. FORSTER and P. P. SHUKLA (J. Indian Inst. Sci., 1925, **8A**, 267—273).—See A., 1925, i, 1161.

Terpene and sesquiterpene of Mitsuba-zeri. N. HIRANO (J. Soc. Chem. Ind. Japan, 1926, **29**, 48—52).—By steam distillation of Mitsuba-zeri [*Cryptotaenia Japonica*, Hassk. (*Umbelliferæ*)], a terpene, $C_{10}H_{16}$, and a sesquiterpene, $C_{15}H_{24}$, have been isolated and named *cryptotaenene* and *mitsubaene*, respectively. Cryptotaenene has b. p. 67—68°/15 mm., $[\alpha]_D^{19·8}$ +2·66°, d_4^{25} 0·8128, n_D^{25} 1·47476. It forms a *triozonide*, but only a *tetrabromide*, which shows the presence of a conjugated double linking. Decomposition of the triozonide yielded carbon dioxide, formic acid, acetone, acetone peroxide,

succinic acid, and a carbonyl compound. The formula of cryptotaenene is, therefore, either $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH{:}CH_2$ or $CMe_2{:}CH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$. Mitsubaene has b. p. 142—143°/15 mm., $[\alpha]_D^{21\cdot9}$ +8·31°, d_4^{25} 0·9175, n_D^{25} 1·50381. It forms a *tetrabromide*. On heating mitsubaene with sulphur and treating the product with picric acid, a *picrate*, m. p. 90°, is obtained, the m. p. being identical with that of eudaline picrate. Mitsubaene is therefore a sesquiterpene of the eudesmol type. Carbon dioxide and formic acid were isolated from the ozonide by decomposition.

K. KASHIMA.

Derivatives of 1 : 1′-bismenthone. P. G. CARTER and J. READ (J.S.C.I., 1925, **45**, 44—46T).—The ketone obtained by reducing piperitone in aqueous alcoholic solution by sodium amalgam (Baker and Smith, "A Research on the Eucalypts," 2nd ed., Sydney, 1920, p. 393) is given the structure



and is named 1 : 1′-bis(menthen-3-one), or 1 : 1′-bismenthone, Wallach's α-dicarvelone (A., 1899, i, 530) being called on the same system 6 : 6′-bis-($\Delta^{8(9)}$-menthen-2-one). Of the six possible inactive forms of 1 : 1′-bismenthone, two should be internally compensated. The following new derivatives have been prepared: 1 : 1′-*Bismenthol*, m. p. 179—182°; *phenylurethane*, softens at 150—152°, m. p. 198—200°; *diacetate*, m. p. 111—112°. 1 : 1′-*Bismenthylamine hydrochloride*, m. p. above 250°; *chloroplatinate*; *dibenzoyl* derivative, darkening at 210° and beginning to decompose at 245°; *dibenzylidene* derivative, m. p. above 270°; *disalicylidene* derivative, m. p. above 270°.

Tannin occurring in the kino of *Eucalyptus calophylla*. A. MCGOOKIN and I. M. HEILBRON (J. Pharm. Exp. Ther., 1926, **26**, 421—446).—The main constituent of the kino of *Eucalyptus calophylla* is a tannin obtained as a dark reddish-brown, brittle solid yielding a dark bluish-green coloration with ferric chloride and a precipitate with all tannin reagents. A small quantity of aromadendrin is also present. The tannin yields a buff-coloured *trimethyl* derivative, $C_{15}H_{11}O_4(OMe)_3$, and an almost colourless *triacetyl* derivative, $C_{15}H_{11}O_4(OAc)_3$. Vacuum distillation of kino tannin yielded a small quantity of guaiacol and pyrocatechol. A rather larger quantity of guaiacol along with other undetermined products is obtained by the vacuum distillation of methylated kino tannin. The vacuum distillation of kino-red, obtained by the action of acid on the original tannin, yields products similar to those from kino tannin itself. Methylated kino tannin when oxidised by potassium permanganate yields veratric acid. By the action of potassium hydroxide on kino tannin, protocatechuic acid and pyrocatechol are formed.

W. O. KERMACK.

Purification of digitonin. Accompanying saponins. A. WINDAUS (Z. physiol. Chem., 1925, **150**, 205—210).—Crude digitonin may be purified by precipitation, twice or thrice repeated, of its aqueous solution by ether. The accompanying saponins remain in solution. Commercial digitonin contains 70—80% of digitonin, 10—20% of gitonin, and 5—15% of other saponins. A crystalline *diketone*, $C_{26}H_{38}O_4$, m. p. 227—228°, has been isolated from the products of the oxidation of crude digitonin with cold chromic acid. A related *monoketone*, $C_{26}H_{40}O_3$, m. p. 204—205°, has also been found in very small quantities in the product of this reaction.

H. D. KAY.

Tetrahydro-1 : 4-pyrones. IV. W. BORSCHE and R. FRANK (Ber., 1926, **59**, [*B*], 237—242; cf. Borsche and Mehner, A., 1915, i, 574; Borsche and Thiele, A., 1923, i, 1110, 1220).—2 : 6-Dimethyltetrahydropyran-4-ol may be prepared directly from 2 : 6-dimethyl-1 : 4-pyrone by catalytic hydrogenation at the atmospheric pressure in presence of water and platinum-black; the p-*nitrobenzoate*, m. p. 96°, and p-*toluenesulphonate*, m. p. 88—89°, are described. The alcohol is converted by phosphorus trichloride at a low temperature into a mixture of 4-*chloro*-2 : 6-*dimethyltetrahydropyran*, b. p. 65°/20 mm., 58°/12 mm., and *di*-2 : 6-*dimethyltetrahydropyran*-4-*yl phosphite*, b. p. 197°/20 mm.; the chloro-compound is preferably prepared from the alcohol and phosphorus pentachloride in the presence of light petroleum. Thionyl chloride in the presence of pyridine transforms 2 : 6-dimethyltetrahydropyran-4-ol into the corresponding *normal sulphite*, $C_{14}H_{16}O_5S$, m. p. 76—77°. The action of fuming hydrochloric acid on the alcohol at 110° gives a *compound*, $C_{12}H_{24}OCl_2$, b. p. 74°/20 mm., which has not been investigated completely. Phosphorus pentabromide and 2 : 6-dimethyltetrahydropyran-4-ol in the presence of light petroleum give a mixture of 4-*bromo*-2 : 6-*dimethyltetrahydropyran*, b. p. 70—80°/13 mm., the *substance*, $C_{12}H_{24}OBr_2$, b. p. 66—70°/13 mm. (compare the chloro-compound described above), and more highly brominated products, including probably a *tribromodimethylpyran*, $C_7H_7OBr_3$, b. p. 110°/14 mm. 2 : 6-Dimethyltetrahydropyran-4-ol and hydrobromic acid at 100° afford the compound $C_{12}H_{24}OBr_2$, b. p. 94—99°/35 mm. 4-Chloro-2 : 6-dimethyltetrahydropyran reacts sluggishly with magnesium in the presence of dry ether, and the product is converted by carbon dioxide into a mixture of 2 : 6-*dimethyltetrahydropyran*-4-*carboxylic acid*, m. p. 120° (*amide*, m. p. 197°; *anilide*, m. p. 177°), and *di*-2 : 6-*dimethyltetrahydro*-4 : 4′-*dipyryl*,

$$O\begin{<}{CHMe\cdot CH_2}{CHMe\cdot CH_2}\end{>}CH\cdot CH\begin{<}{CH_2\cdot CHMe}{CH_2\cdot CHMe}\end{>}O,$$

m. p. 104°.

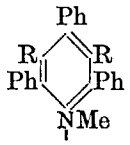
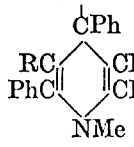
1 : 4-Pyrone is slowly hydrogenated in the presence of water and platinum-black to *tetrahydropyran*-4-*ol*, b. p. 84°/12 mm. (p-*nitrobenzoate*, m. p. 69—70°), which is converted by phosphorus pentachloride in the presence of chloroform into 4-*chlorotetrahydropyran*, b. p. 46°/12 mm. The action of phosphorus pentabromide on tetrahydropyran-4-ol proceeds with little uniformity.

H. WREN.

Reduction of thionaphthen. R. FRICKE and G. SPILKER (Ber., 1926, **59**, [*B*], 349).—The following additional data are recorded (cf. A., 1925, i, 1311): *o*-Ethylthiolphenol, d_4^{20} 1·0349, n_D^{20} 1·56995, *o*-ethyl-

phenyl methyl sulphide, d_4^{20} 1·0253, n_D^{20} 1·57083; 2 : 3-dihydrothionaphthen, d_4^{37} 1·1036, n_D^{37} 1·60330; thionaphthen, d_4^{37} 1·4250, n_D^{37} 1·63740. H. WREN.

Tervalent carbon. IV. Polyaryl-1-methyldihydropyridyls. K. ZIEGLER and F. A. FRIES (Ber., 1926, **59**, [*B*], 242—248).—Polyphenyl-1-methylpyridinium salts have been investigated with the expectation that they would be readily transformable into pyridinium radicals (cf. I) which would

(I.)  (II.) 

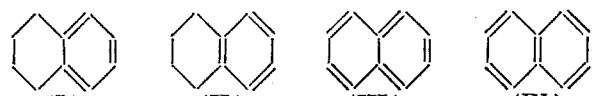
pass by re-arrangement of valencies into stable dihydropyridyls (cf. II) with a tervalent carbon atom. 2 : 4 : 6-Triphenyl-1-methylpyridinium chloride dissolved in water forms a blue layer over metallic zinc or magnesium, which inhibits further action; if, however, an organic liquid non-miscible with water (particularly ethyl acetate) is present it becomes intensely reddish-violet, but is decolorised on contact with air. With light petroleum, a solid compound separates. Similar solutions are formed by the action of magnesium phenyl bromide on 2 : 4 : 6-triphenyl-1-methylpyridinium chloride, and similar amorphous material is precipitated during the electrolysis of its aqueous solution. It therefore appears probable that 2 : 4 : 6-triphenyl-1-methyldihydropyridyl (II, R=H) exists possibly as a unimolecular radical with very little tendency towards association. Similar observations are made with pentaphenyl-1-methylpyridinium salts, which, however, are not very suitable materials for the investigation on account of their sparing solubility. 2 : 3 : 5 : 6-Tetraphenyl-1-methylpyridinium salts do not exhibit analogous behaviour. The possibility that the new radical contains quadrivalent nitrogen appears to be excluded by the observation that an amalgam is not formed when 2 : 4 : 6-triphenyl-1-methylpyridinium salts are electrolysed at a mercury cathode, whilst also it is stable at temperatures which generally cause the conversion of quadrivalent nitrogen into the tervalent state.

The following salts are incidentally described: 2 : 4 : 6-*triphenyl*-1-*methylpyridinium methosulphate*, readily formed from triphenylpyridine and methyl sulphate at 100°, m. p. (+H_2O) 101°, anhydrous, 174° (decomp.); 2 : 4 : 6-*triphenyl*-1-*methylpyridinium chloride* (+2·5H_2O), and the corresponding *hydrochloride*, $C_{24}H_{20}NCl,HCl,2H_2O$, m. p. 118—120°, decomp. 122° when rapidly heated, decomp. 143° after softening at 104°, and re-solidifying at 123° when slowly heated. The corresponding *bromide*, *iodide*, *perchlorate*, *nitrate*, *sulphate*, *permanganate*, and the double *compounds* with zinc chloride and mercuric chloride have been prepared. H. WREN.

Course of the 2-methylquinoline synthesis with aminotetrahydronaphthalenes. 2-Methyl-7 : 8 : 9 : 10-tetrahydro-α-naphthaquinoline. J. LINDNER and A. SIEGEL (Monatsh., 1925, **46**, 225—229; cf. Lindner, Djulgerowa, and Mayr, A., 1924, i, 1102).—α- and β-Nitrotetralins (*ar*-nitrotetrahydronaphthalenes; Schroeter, A., 1922, i, 123), separated by fractional distillation in a vacuum, are best reduced with reduced iron and alcohol in the presence of calcium chloride (Knueppel, A., 1900, i, 187). *Benzoyl*-ar-α-*tetrahydronaphthylamine* has m. p. 154°. *ar*-α-Tetrahydronaphthylamine, by the method used for the β-compound (*loc. cit.*), gives a 27% yield of 2-*methyl*-7 : 8 : 9 : 10-*tetrahydro*-α-*naphthaquinoline*, m. p. 55° (*hydrochloride*, m. p. 236°; *hydrobromide*, m. p. 309—310°; *hydriodide*, decomp. 190°; *picrate*, m. p. 199°). C. HOLLINS.

Course of the 2-methylquinoline synthesis with *ar*-tetrahydro-β-naphthylamine. II. J. LINDNER and M. STAUFER (Monatsh., 1925, **46**, 231—240; cf. A., 1924, i, 1102, and preceding abstract).—A nearly quantitative separation of the *ang.* and *lin.* isomerides obtained from *ar*-tetrahydro-β-naphthylamine by the 2-methylquinoline synthesis is effected by means of the hydriodides, that of the *ang.* base being precipitated almost pure on addition of aqueous potassium iodide to a dilute hydrochloric acid solution of the mixed bases liberated by ammonia from the mixed picrates. The total yield is 35% of the theoretical, of which 65% is the *ang.* base (3-methyl-7 : 8 : 9 : 10-tetrahydro-β-naphthaquinoline) and 35% is the *lin.* base (2-methyl-6 : 7 : 8 : 9-tetrahydro-α-anthrapyridine). Dehydrogenation of the latter by distillation in a current of carbon dioxide over heated lead oxide yields 2-*methyl*-α-*anthrapyridine*, m. p. 129° (*hydrochloride*, m. p. 200°; *picrate*, m. p. 216°), which by oxidation with chromic-acetic acid is converted into anthrapyridinequinone (von Braun and Gruber, A., 1922, i, 762), probably by way of the quinonecarboxylic acid.

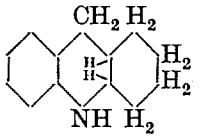
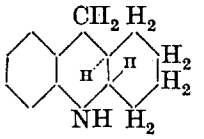
It is concluded that the tetramethylene group in tetrahydronaphthalene derivatives exerts no appreciable directive power in the fusion of a third ring. The theoretical interpretation of this is discussed. A consideration of thermal data shows that the structure (II) contains less energy than structure (I), and (III) considerably less than (IV); (I) and (III) would yield linear tricyclic compounds, (II) and (IV)


(I.) (II.) (III.) (IV.)

angular. The energy difference between (III) and (IV) is so marked that angular tricyclic compounds are formed exclusively from β-naphthylamine. The difference is smaller between (I) and (II), and hence, although angular tricyclic compounds preponderate, a proportion of linear isomerides is obtained from *ar*-tetrahydro-β-naphthylamine. C. HOLLINS.

Tetrahydroacridine, octahydroacridine, and their derivatives. II. Resolution of the octahydroacridines (*A*) and (*B*). W. H. PERKIN, jun., and W. G. SEDGWICK (J.C.S., 1926, 438—445; cf. A., 1925, i, 63).—In the conversion of tetrahydroacridine into the two octahydroacridines by treatment with tin and hydrochloric acid, no intermediate reduction product can be detected. By resolution of both the octahydroacridines into active constituents by means of the *d*- and *l*-camphorsulphon-

ates, it is proved that they are represented by the configurations (I) and (II). *dl*-Octahydroacridine

(I.)  (II.) 

(*A*) m. p. 82°, gives l-*octahydroacridine* (*A*) d-*camphorsulphonate*, m. p. 183°, and d-*octahydroacridine* (*A*) l-*camphorsulphonate*, m. p. 182°, from which sodium hydroxide liberates, respectively, l-*octahydroacridine* (*A*), m. p. 85°, $[\alpha]_D$ in alcohol −32°, and d-*octahydroacridine* (*A*), m. p. 84·5°, $[\alpha]_D$ in alcohol +34° [d-*octahydroacridine* (*A*) d-*camphorsulphonate*, m. p. 180°, is also described]. Similarly, *dl*-octahydroacridine (*B*), m. p. 72°, gives l-*octahydroacridine* (*B*) d-*camphorsulphonate*, m. p. 172°, and d-*octahydroacridine* (*B*) l-*camphorsulphonate*, m. p. 172°, which yield, respectively, l-*octahydroacridine* (*B*), m. p. 73°, $[\alpha]_D$ −24°, and d-*octahydroacridine* (*B*), m. p. 73°, $[\alpha]_D$ +22°. On heating, the *d*- and *l*-modifications gradually change into the inactive form; by acetic anhydride *l*-octahydroacridine (*A*) is converted into the acetyl derivative of *dl*-octahydroacridine (*A*). The camphorsulphonates of octahydroacridine (*B*) are more soluble than those of (*A*). Since reduction of tetrahydroacridone with sodium amalgam gives solely modification (*A*), this probably has the configuration (I). The octahydroacridinecarboxylic acids (*A*) and (*B*) (cf. A., 1925, i, 63) are regarded as *dl*-modifications corresponding with (I) and (II).

On heating 1-methyl*cyclo*hexan-3-one at 100—130° with *o*-aminobenzaldehyde, the product is 6(or 8)-*methyltetrahydroacridine*, m. p. 70—71° (III) [*picrate*, m. p. 182° (darkening)], whilst by heating 1-methyl*cyclo*hexan-3-one with isatin, in presence of alcohol and potassium hydroxide, the product is 6(or 8)-*methyltetrahydroacridinecarboxylic acid*, m. p. 296° (decomp.), which on heating gives (III). Reduction of (III) with tin and hydrochloric acid yields a mixture of 6(or 8)-*methyloctahydroacridine* (*A*), m. p. 92°, with 6(or 8)-*methyloctahydroacridine* (*B*), m. p. 80° (*sulphate* described), but only modification (*A*) is produced by reduction of 6(or 8)-methyltetrahydroacridone with sodium amalgam. (*A*) has been resolved by means of the *d*- and *l*-camphorsulphonates and the d- and l-6(or 8)-*methyloctahydroacridines* (*A*) show $[\alpha]_D$ +20° and −28°, respectively.

F. M. Hamer.

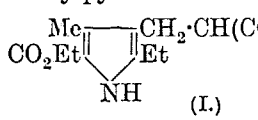
Action of pyridine and cyanogen bromide on certain pyrroles. H. Fischer and P. Ernst (Ber., 1926, **59**, [*B*], 138—144).—The action of pyridine and cyanogen bromide on 3-acetyl-2 : 4-dimethylpyrrole under the conditions described previously (Fischer and Zimmermann, A., 1914, i, 319) is now shown to afford a colourless *compound*, $C_{27}H_{30}O_2N_6$, m. p. 218° (decomp.). It is hydrolysed by concentrated hydrochloric acid to 3-acetyl-2 : 4-dimethylpyrrole (2 mols.) and is converted by bromine into 5-bromo-3-acetyl-2 : 4-dimethylpyrrole. It contains two active hydrogen atoms corresponding with the presence of two pyrrole nuclei. Two mols. of pyridine are present and two atoms of nitrogen, which are evolved as ammonia during hydrolysis of the compound. The direct action of pyridine and cyanogen bromide on 3-acetyl-2 : 4-dimethylpyrrole in the presence of halogen acid yields a blue, crystalline *dye* which has not been investigated further. Attempts to obtain further insight into the reaction by the use of other tri- or tetra-substituted pyrroles were unsuccessful. Ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate and ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate fail to react. Ethyl 2 : 4-dimethylpyrrole-3-carboxylate yields a *compound*, $C_{20}H_{24}O_3N_4$, m. p. 151°, which, however, contains only one pyrrole nucleus. It is hydrolysed by concentrated hydrochloric acid to ethyl 2 : 4-dimethylpyrrole-3-carboxylate. The action of concentrated hydrochloric acid on the substance dissolved in alcohol affords a blue dye, isolated as the *dihydrochloride*, $C_{23}H_{30}O_4N_2Cl_2$, decomp. 190—194°, which, when dried in a vacuum at 100°, gives the compound $C_{20}H_{31}O_4N_2Cl$, decomp. 190—194°. Concentrated hydrobromic acid in the presence of alcohol transforms the compound $C_{20}H_{24}O_3N_4$ into cyanogen bromide and the *hydrobromide*, $C_{21}H_{27}O_4N_2Br$, decomp. 220—225° after softening at 215° (obtained also by addition of concentrated hydrobromic acid to a mixture of ethyl 2 : 4-dimethylpyrrole-3-carboxylate, pyridine, and cyanogen bromide in alcohol and ether). The corresponding free base has little ability to crystallise (cf. König, Z. angew. Chem., 1925, **38**, 743, 868); the *perchlorate*, $C_{32}H_{44}O_{14}N_3Cl$, decomposes explosively above 300°. H. Wren.

Synthesis of 2 : 4-dimethyl-5-ethylpyrrole-3-propionic acid. H. Fischer and B. Walach (Annalen, 1926, **447**, 38—48).—2 : 4-Dimethylpyrrole is conveniently prepared by treating the corresponding 3 : 5-dicarbethoxy-derivative with sulphuric acid (*d* 1·4) at 100° until evolution of carbon dioxide ceases, neutralising the reaction mixture at 25° or below with aqueous 40% sodium hydroxide, and steam-distilling. Conversion of the product into the 5-ethyl derivative is best effected by heating with only a slight excess of alcoholic sodium ethoxide under pressure at 215—220° for 6 hrs. 2 : 4-*Dimethyl-5-ethylpyrrole-3-aldehyde*, m. p. 128°, is obtained from the above dimethylethylpyrrole by treatment with anhydrous hydrocyanic acid, followed by hydrolysis with cold, concentrated hydrochloric acid. The following derivatives are described: *oxime*, m. p. 118·5°; *nitrile*, $C_9H_{12}N_2$, m. p. 112° (from the oxime); *aldazine*, $C_{18}H_{26}N_4$, m. p. 207° with darkening; *semicarbazone*, m. p. 203°; *azlactone*, $C_{18}H_{18}O_2N_2$, orange-red, m. p. 193°, and from this the *benzamidoacrylic acid*, m. p. 183°. The attempted conversion of ethyl 2 : 4-dimethylpyrrole-3-carboxylate into the corresponding methene afforded always the methene of ethyl 2 : 4-dimethylpyrrole-3-carboxylate, m. p. 212°. When heated with hydrazine hydrate and alcoholic sodium ethoxide for 6 hrs. at 150° the above aldehyde derivative yields 2 : 3 : 4-*trimethyl-5-ethylpyrrole*, m. p. 38—39°, b. p. 114—115°/27 mm. (*picrate*, m. p. 102—103°), whilst treatment with malonic acid and piperidine in boiling alcoholic solution affords 2 : 4-*dimethyl-5-ethyl-3-acrylic acid*, m. p. 205°. Reduction of the latter

in aqueous alkaline solution with sodium amalgam affords 2 : 4-*dimethyl*-5-*ethylpyrrole*-3-*propionic acid*, m. p. 43—44°, b. p. 200°/1 mm., turning brown when kept in air.

When heated with phthalic anhydride for 6 hrs. at 190°, with subsequent alkaline hydrolysis of the resulting phthalide, and reduction with hydriodic acid in acetic acid, 2 : 4-dimethyl-3 : 5-diethylpyrrole yields 2 : 4-dimethyl-3-ethylpyrrole (cf. Fischer and Krollpfeiffer, A., 1913, i, 93). Treatment of 2 : 3 : 4-trimethylpyrrole with alcoholic sodium ethoxide at 230° (cf. Fischer, *ibid.*, 643) affords 2 : 3 : 4-trimethyl-5-ethylpyrrole. Treatment of 2 : 4-dimethyl-5-carbethoxypyrrole-3-aldehyde with hydrazine hydrate and alcoholic sodium ethoxide for 12 hrs. at 140—160° affords 2 : 3 : 4-trimethylpyrrole in 71% yield [*picrate*, m. p. 147°; *α-aldehyde*, m. p. 147° (semicarbazone, m. p. 230°); *dipyrrylmethene*, m. p. 187—188° (*hydrochloride*, m. p. 287—288°; *picrate*, decomp. 230—231°; *mercuric chloride* additive compound, m. p. 234°)]. F. G. Willson.

Synthesis of tetra-(4-methyl-2-ethyl-3-propionylpyrryl)ethylene and of xanthopyrrolecarboxylic acid, and transformations of some pyrroles. H. Fischer and J. Klarer (Annalen, 1926, **447**, 48—63; cf. A., 1925, i, 577).—Ethyl 4-methyl-2-ethyl-3-propionylpyrrole-5-carboxylate is obtained by adding saturated sodium nitrite solution to a solution of ethyl acetoacetate in acetic acid below 0°, and then adding, at the ordinary temperature, a suspension of copper dipropionylmethane in acetic acid, followed by zinc dust, the temperature being kept below 70°. When all the copper salt is dissolved, the mixture is heated for 3 hrs. at 100°, and then poured into water, when the pyrrole separates. Hydrolysis with concentrated alcoholic potassium hydroxide and subsequent acidification in the cold affords 4-*methyl*-2-*ethyl*-3-*propionylpyrrole*-5-*carboxylic acid*, m. p. 180°, with evolution of carbon dioxide and formation of 4-*methyl*-2-*ethyl*-3-*propionylpyrrole*, m. p. 90°, b. p. 283°. Treatment of the latter with formaldehyde in alcohol in presence of concentrated hydrochloric acid affords *bis*-(4-*methyl*-2-*ethyl*-3-*propionylpyrryl*)*methane*, which, when boiled with aqueous ferric chloride, yields the corresponding *methene hydrochloride*, m. p. 183°, from which the free *methene*, yellow, m. p. 167°, is obtained by the action of alcoholic ammonia. The following salts of this methene are described: *copper*, m. p. 220°; *cobalt*, m. p. 247°; *zinc* and *cadmium*. Treatment of 4-methyl-2-ethyl-3-propionylpyrrole in ether with aqueous diazobenzenesulphonic acid affords 4-*methyl*-2-*ethyl*-3-*propionylpyrroleazobenzenesulphonic acid*, decomp. when heated. Phthalic anhydride at 180°, in acetic acid, converts the above pyrrole into the corresponding *phthalide*, yellow, m. p. 105°, whilst treatment with anhydrous hydrocyanic acid in absolute ether, followed by cold hydrolysis with hydrochloric acid, affords 4-*methyl*-2-*ethyl*-3-*propionylpyrrole*-5-*aldehyde*, m p 140° (*oxime*, m. p. 212°). When boiled with glyoxal in alcohol in presence of a trace of hydrochloric or nitric acid, the pyrrole is converted into *tetra*-(4-*methyl*-2-*ethyl*-3-*propionylpyrryl*)*ethane*, m. p. 249°, similar condensation in acetic acid affording an intensely red solution. Oxidation of the above ethane with dilute aqueous ferric chloride at 40° affords the corresponding *tetra*-(4-*methyl*-2-*ethyl*-3-*propionylpyrryl*)*ethylene*, yellow, m. p. 209°, whilst concentrated ferric chloride solution converts the ethane into the methene, m. p. 167°, described above. Reduction of the above ethylene with sodium amalgam and alcohol yields the ethane, whilst hydriodic acid in boiling acetic acid affords 4-methyl-2-ethylpyrrole, the same product being also obtained similarly from the above tetrapyrrylethane. Treatment of ethyl 4-methyl-2-ethyl-3-propionylpyrrole-5-carboxylate with hydrazine hydrate and alcoholic sodium ethoxide at 145°, affords 4-*methyl*-2-*ethyl*-3-*propylpyrrole*, b. p. 82°/12 mm., unstable in air (*picrate*, m. p. 168°). When heated with aqueous 70% sulphuric acid, the above 5-carbethoxy-derivative affords 4-*methyl*-2-*ethylpyrrole*, b. p. 93°/40 mm., resinifying in air (*picrate*, m. p. 86°). 4-*Methyl*-2-*ethylpyrroleazobenzenesulphonic acid* undergoes fission with alkali, with production of the pyrrole. When 4-methyl-2-ethylpyrrole is boiled with alcoholic formic acid and perchloric acid, the *perchlorate*, decomp. 240°, of the corresponding *methene* is obtained (*copper* salt; *cobalt* salt; *iron* salt, m. p. 190°). When boiled with alcoholic ethyl methoxymethylmalonate and hydrochloric acid, ethyl 4-methyl-2-ethylpyrrole-5-carboxylate affords *ethyl* 5-*carbethoxy*-4-*methyl*-2-*ethylpyrrole*-3-β-*methylmalonate* (I), m. p. 78°, which, on hydrolysis with dilute aqueous-alcoholic sodium hydroxide, yields the corresponding β-*methylmalonic acid*, m. p. 162°, with evolution of carbon dioxide and formation of 5-carbethoxy-4-methyl-2-ethylpyrrole-3-propionic acid. The latter, when heated with concentrated aqueous sodium hydroxide, affords the corresponding *carboxypyrrole*-3-*propionic acid*, which loses carbon dioxide when crystallised from water, with formation of xanthopyrrolecarboxylic acid (4-methyl-2-ethylpyrrole-3-propionic acid), m. p. 126° (picrate, m. p. 143°). Whilst the m. p. of xanthopyrrolecarboxylic acid previously given (A., 1925, i, 578) agrees with that of Piloty's acid obtained from blood (cf. A., 1915, i, 451), the higher m. p. now reported throws doubt on the identity of Piloty's acid, although the picrates of the two acids have the same m. p. Condensation of xanthopyrrolecarboxylic acid with phthalic anhydride at 180° affords the *phthalide*, m. p. 133°. Reduction of 5-carbethoxy-4-methyl-2-ethylpyrrole-3-acrylic acid in ether with aluminium amalgam and water affords the above corresponding pyrrole-3-propionic acid, m. p. 138°.



(I.)

F. G. Willson.

Preparation of ketones of the pyridine series. Chem. Fabr. auf Actien (vorm. E. Schering).—See B., 1926, 216.

Benzene-4-hydrazo- and -azo-pyridine derivatives. E. Koenigs, W. Freigang, G. Lobmayer, and A. Zscharn (Ber., 1926, **59**, [*B*], 321—333).—*Benzene*-4-*hydrazopyridine hydrochloride*, m. p. 255° (corr. decomp.), is obtained by the action of phenyl-

hydrazine on 4-chloropyridine in alcoholic solution at 170—180°. The free *base*, $C_5H_4N{\cdot}NH{\cdot}NHPh$, m. p. 171—172°, oxidises readily when exposed to air; it has no tendency towards benzidine or semidine transformation. It is oxidised by mercuric oxide, potassium ferricyanide, nitric acid, or, preferably, nitrous acid to *benzene-4-azopyridine*, m. p. 98—99° (corr.), b. p. above 300°, which behaves as a dye towards wool or cotton mordanted with tannin, thus establishing the ability of the pyridine residue to function as an auxochrome. It dissolves in cold, concentrated hydrochloric acid to a dark violet solution which soon becomes brown, particularly when warmed, owing to the production of p-*chlorobenzene-4-hydrazopyridine hydrochloride*, m. p. 243° (corr.) after darkening. The corresponding *base* has m. p. 106—107°; the position of the chlorine atom is established by its reduction to *p*-chloroaniline. p-*Chlorobenzene-4-azopyridine*, smoothly prepared from the hydrazo-compound by oxidation in boiling alkaline solution with air, has m. p. 99—100° (corr.). Boiling, concentrated hydrochloric acid transforms it with moderate rapidity into op-*dichlorobenzene-4-hydrazopyridine hydrochloride*, m. p. 241—242° (corr.) after darkening. The corresponding *base*, m. p. 135° (corr. decomp.) after softening at 120°, is reduced by stannous chloride and hydrochloric acid to 2 : 4-dichloroaniline and oxidised by air to op-*dichlorobenzene-4-azopyridine*, m. p. 110—111° (corr.); if, however, the oxidation is effected in boiling, 50% sodium hydroxide solution, *chlorohydroxybenzene-4-azopyridine*, m. p. 114° (corr.), is produced. *op*-Dichlorobenzene-4-azopyridine is unaffected by methyl-alcoholic hydrogen chloride, but is reduced by warm, concentrated aqueous hydrochloric acid to *op*-dichlorobenzene-4-hydrazopyridine hydrochloride mixed with a colourless crystalline compound which could not be isolated; the fate of the liberated chlorine atoms has not been elucidated. The action of hydrochloric acid on benzene 4-azopyridine probably follows the course $NPh{:}N{\cdot}C_5H_4N \longrightarrow NPh(Cl){\cdot}NH{\cdot}C_5H_4N \longrightarrow NPhCl{\cdot}NH{\cdot}C_5H_4N \longrightarrow C_6H_4Cl{\cdot}NH{\cdot}NH{\cdot}C_5H_4N$. Benzene-4-azopyridine is transformed by a concentrated solution of hydrogen bromide in glacial acetic acid at the atmospheric temperature into p-*bromobenzene-4-hydrazopyridine hydrobromide*, m. p. 227° (corr.) after softening and darkening at 220°. p-*Bromobenzene-4-hydrazopyridine*, m. p. 87—89° (corr.), is oxidised in boiling 50% sodium hydroxide solution to p-*bromobenzene-4-azopyridine*, m. p. 140—141° (corr.). op-*Dibromobenzene-4-hydrazopyridine hydrobromide*, m. p. 239° (corr.), op-*dibromobenzene-4-hydrazopyridine*, m. p. 104—105° (corr.), and op-*dibromobenzene-4-azopyridine*, m. p. 138—139° (corr.), are described. In an analogous manner, benzene-4-azo-2 : 6-dimethylpyridine (cf. Marckwald and Rudzik, A., 1903, i, 514) is transformed into p-*chlorobenzene-4-hydrazo-2 : 6-dimethylpyridine hydrochloride*, m. p. 276° (corr.), which affords p-*chlorobenzene-4-hydrazo-2 : 6-dimethylpyridine*, m. p. 82° (decomp.), and p-*chlorobenzene-4-azo-2 : 6-dimethylpyridine*, m. p. 99—100° (corr.). The latter compound is converted by methyl-alcoholic hydrogen chloride into op-*dichlorobenzene-4-hydrazo-2 : 6-dimethylpyridine hydrochloride*, m. p. 246° (corr.). Benzene-4-hydrazo-2 : 6-dimethylpyridine-3-carboxylic acid (cf. Michaelis and von Arend, A., 1903, i, 292) is converted by cautious oxidation with 2*N*-nitric acid into *benzene-4-azo-2 : 6-dimethylpyridine-3-carboxylic acid nitrate*, m. p. 98—99°, whereas more drastic treatment affords *nitrobenzene-4-azo-2 : 6-dimethylpyridine-3-carboxylic acid*, m. p. above 300°. The nitrate is transformed by cautious treatment with methyl-alcoholic hydrogen chloride into p-*chlorobenzene-4-hydrazo-2 : 6-dimethylpyridine-3-carboxylic acid hydrochloride*, m. p. 293° (decomp.).

H. WREN.

Condensation of 3-bromo- and 3-nitro-4-dimethylaminobenzaldehyde with ethyl acetoacetate and ammonia. L. E. HINKEL and W. R. MADEL (J.C.S., 1926, 161—163).—A bromine atom or nitro-group *ortho* to the dimethylamino-group in *p*-dimethylaminobenzaldehyde renders the aldehydo-group stable towards nitrous acid. In Hantzsch's pyridine condensation, the effect is to increase the yield of dihydrodimethylpyridine derivative, which no longer yields a methiodide (cf. Hinkel and Cremer, *ibid.*, 1920, **117**, 137), and to cause it to react normally with nitrous acid. *Ethyl* 4-(m-*bromo*-p-*dimethylaminophenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*, prepared in 82% yield from 3-bromo-4-dimethylaminobenzaldehyde, has m. p. 133°, and is oxidised by nitrous fumes to *ethyl* 4-(m-*bromo*-p-*dimethylaminophenyl*)-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 91°. 3-Nitro-4-dimethylaminobenzaldehyde and ethyl β-aminocrotonate give a 70% yield of *ethyl* 4-(m-*nitro*-p-*dimethylaminophenyl*)-2 : 6-*dimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*, m. p. 127°, oxidised to *ethyl* 4-(m-*nitro*-p-*dimethylaminophenyl*)-2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*, m. p. 109°.

H. E. F. NOTTON.

4-Pyridylhydrazine. E. KOENIGS, W. WEISS, and A. ZSCHARN (Ber., 1926, **59**, [*B*], 316—321).—4-Chloropyridine-2 : 6-dicarboxylic acid is converted by hydrazine hydrate in alcoholic solution at 130—135° into 4-*hydrazinopyridine*-2 : 6-*dicarboxylic acid*, decomp. above 295° [the *hydrochloride*, m. p. 212°, *barium* salt (+$2H_2O$), and *benzylidene* derivative, m. p. 278—280° (corr. decomp.), are described]; decarboxylation of the acid could not be effected. 4-Chloropyridine and hydrazine hydrate in alcoholic solution at 100° afford 4-*pyridylhydrazine hydrochloride*, m. p. 238° (decomp.). The free base, b. p. 185—187°/18 mm., which is very sensitive to atmospheric oxidation, is isolated by treating the hydrochloride with the requisite quantity of sodium ethoxide in absolute-alcoholic solution, filtering off the sodium chloride, and distilling the filtrate; the *dihydrochloride*, m. p. 252° (corr.), is described. With benzaldehyde and acetone, 4-pyridylhydrazine gives the corresponding *benzylidene* and iso*propylidene* derivatives, m. p. 195° (corr.) and 170—171° (corr.), respectively, whilst with pyruvic acid it affords *pyruvic acid* 4-*pyridylhydrazone*, m. p. 239—240° (corr., decomp.). 4-Pyridylhydrazine and ethyl acetoacetate yield 1-γ-*pyridyl*-3-*methylpyrazolone*, $\begin{matrix}CMe{=}N\\ CH_2{\cdot}CO\end{matrix}\!>\!N{\cdot}C_5H_4N$, m. p. 198° (corr.), or, if

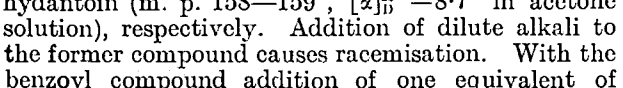
excess of the ester is used, a *compound*, $C_{15}H_{17}O_3N_3$, m. p. 165° (corr. decomp.). The *compound* $C_5H_4N{\cdot}NH{\cdot}NH{\cdot}CS{\cdot}SH,NH_2{\cdot}NH{\cdot}C_5H_4N$, m. p. 175° (corr.), is obtained from carbon disulphide and the hydrazine. H. WREN.

Condensations involving reactive methyl groups in heterocyclic bases. J. E. HUMPHRIES (J.C.S., 1926, 374—376).—2-Methylquinoline and Michler's hydrol condense in presence of acetic acid or zinc chloride, giving a pale yellow *compound*, $C_9H_6N{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NMe_2)_2$, m. p. 131°, which is oxidised by lead peroxide and acetic acid to a red *dye* (*oxalate* described). The similar condensation *product* of Michler's hydrol with 2 : 6-dimethylquinoline has m. p. 152°, and that with α-picoline has m. p. 187°. The methiodides of the heterocyclic bases react more readily than the bases themselves; in acetic acid or boiling alcoholic solution 2 : 6-dimethylquinoline methiodide and Michler's hydrol give the *compound* $C_{29}H_{34}N_3I$, m. p. 160° (decomp.). The quaternary salts do not react with benzenediazonium sulphate, but, unlike the corresponding bases, condense with *p*-nitrophenylnitrosoamine in cold, alcoholic solution: 2 : 6-dimethylquinoline methiodide yields the p-*nitrophenylhydrazone* of 6-methylquinoline-2-aldehyde methiodide, m. p. 244° [which is also prepared by addition of *p*-nitrophenylhydrazine to the product of hydrolysis of the *p*-dimethylaminoanil of quinoline-2-aldehyde methiodide (cf. Kaufmann and Vallette, A., 1912, i, 665)]; the similar products from 2-methylquinoline methiodide and ethiodide, and α-picoline methiodide, have m. p. 250°, 262°, and 260°, respectively. F. M. HAMER.

Dibromobarbituric acid. PARKE, DAVIS, AND CO.—See B., 1926, 173.

***CC*-Disubstituted barbituric acids and 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.** P. PFEIFFER.—See B., 1926, 172.

Enol-keto desmotropism in 2-thio-5-methylhydantoins. B. SJOLLEMA and L. SEEKLES (Rec. trav. chim., 1926, **45**, 232—235; cf. A., 1925, i, 1175).—Johnson's method for the preparation of thiohydantoins (A., 1912, i, 390; 1913, i, 203, 399, 1105) has been applied to *l*-alanine and *l*-benzoylalanine, to obtain *l*-2-thio-5-hydantoin (m. p. 161°, $[\alpha]_D^{20}$ −3·4° in aqueous solution) and *l*-1-benzoyl-2-thio-5-methylhydantoin (m. p. 158—159°, $[\alpha]_D^{20}$ −8·7° in acetone solution), respectively. Addition of dilute alkali to the former compound causes racemisation. With the benzoyl compound addition of one equivalent of alkali does not cause racemisation. A further equivalent of alkali decolorises the yellow solution and renders it optically inactive. This is due to the formation of a salt, on addition of the first equivalent of alkali, without disturbing the asymmetric centre. A second equivalent of alkali produces enolisation, as a result of which the asymmetric centre disappears:



J. S. CARTER.

Hydroxonic acid, 5-aminohydantoin, and the attempted preparation of 8-alkylallantoins. H. BILTZ and H. HANISCH (J. pr. Chem., 1926, [ii], **112**, 138—163).—Whilst the known facts are in agreement with the formula for allantoin proposed by Grimaux (A., 1877, ii, 741), yet the number of known isomeric alkyl derivatives suggests rather the hydroxyacetylenediureine formula, which by reason of its greater symmetry allows fewer isomerides. Attempts to prepare the possible 6- or 8-alkylallantoins by (*a*) condensing alloxanic acid with methyl- or ethylcarbamide and (*b*) preparing the methylamide of hydroxonic acid (*methylammonium* and *dipotassium* salts described) were unsuccessful. By prolonged boiling with water, diacetamidohydantoin yields 5-*acetamidohydantoin*, m. p. 218—219° (*sodium* and *silver* salts described), which by the action of diazomethane yields 5-*acetamido*-3-*methylhydantoin*, m. p. 210°. This last compound is converted by acetic anhydride into 5-*acetamido*-1-*acetyl*-3-*methylhydantoin*, m. p. 221—222°, which is also obtained by methylation of 5-acetamido-1-acetylhydantoin and by acetylation of 3-methylhydroxonic acid. A convenient method is described for the preparation of 5-aminohydantoin hydrochloride.

Methyl 3-*methyloxonate*, m. p. 214° (decomp.), readily loses carbon dioxide with formation of dimethylallantoxaidin, m. p. 164°, so that the positions of the methyl groups in the latter compound are now fixed as being 3 : 6 (cf. Biltz and Robl, A., 1921, i, 893). When boiled with 5% aqueous hydrochloric acid, 3-methylallantoxaidin yields ω-methylbiuret (cf. Biltz and Robl, *loc. cit.*). When 3-methyloxonic acid is reduced with sodium amalgam, it yields 3-*methylhydroxonic acid*, m. p. 246—247° (*ethyl* ester, m. p. 172—173°; *methyl* ester, m. p. 210—211°; *ammonium*, *potassium*, *silver*, *barium*, and *lead* salts are described). This acid cannot be obtained by direct methylation of hydroxonic acid.

When hydrolysed with a methyl-alcoholic solution of hydrogen chloride, 5-acetamido-1-acetyl-3-methylhydantoin yields 5-*amino*-3-*methylhydantoin hydrochloride*, m. p. 239—242°, which is converted into 3-methylallantoin by the action of potassium cyanate. When treated with magnesium oxide, the hydrochloride yields 5-*amino*-3-*methylhydantoin* as a light brown oil [*perchlorate*, m. p. 222°; *thiocyanate*, m. p. 188—189° (decomp.)]. This aminohydantoin does not react with alkylcarbimides to yield the alkylallantoins, probably owing to the insolubility of the base in the reagent. Prolonged boiling with phenylcarbimide brings about decomposition with formation of mono- and di-phenylcarbamides. R. W. WEST.

Preparation of 1-phenyl-2 : 3-dimethyl-4-dimethylamino-5-pyrazolone. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 218.

Pyrazolone dyes. G. L. HUGEL.—See B., 1926, 149.

Acylindazoles. J. MEISENHEIMER and O. SENN (Ber., 1926, **59**, [*B*], 199—202).—If the conception that the compound described previously as 1-acetylindazole is to be regarded as "4 : 5-benzo-7-methyl-

hept-1 : 2 : 6-oxdiazine," $C_6H_4<^{C(OH):N}_{N=CMe}>O$, be accepted (cf. Meisenheimer and Diedrich, A., 1924, i, 1348), it follows that the ready oxidisability of 1-acetyl-3-methylindazole (4 : 5-benzo-3 : 7-dimethylhept-1 : 2 : 6-oxdiazine) along similar lines is not to be expected. Actually, the substance is very stable towards perbenzoic acid, slowly yielding (?)methylanthranil and small amounts of *o*-aminoacetophenone; with potassium permanganate, it readily yields *o*-acetamidoacetophenone. The course of the oxidation is scarcely explicable if the indazole structure of the original material is accepted.

Unsuccessful attempts are described to convert *o-chlorobenzaldehydebenzoylhydrazone*, m. p. 192°, into 1-benzoylindazole; with concentrated sulphuric acid, it yields *oo'*-dichlorobenzaldazine, m. p. 142°. The halogen atom of *2-chloro-5-nitrobenzaldehydebenzoylhydrazone*, m. p. 135—138°, is, however, more mobile, since the compound is transformed by potassium carbonate, copper powder, and potassium iodide in boiling cumene into 4-nitro-1-benzoylindazole, m. p. 192—193°. In general, the position of the acyl group cannot be directly deduced from this mode of synthesis on account of the high temperature involved and the consequent liability of the acyl group to wander. The absence of migration in the present instance is shown by the identity of the product with that obtained by von Auwers and Schwegler (A., 1920, i, 640) under much less drastic conditions.

H. WREN.

Synthesis of substitution derivatives of indigotin. I. *o*-Nitrobenzoylacetic acid and related compounds. C. J. OVERMYER (J. Amer. Chem. Soc., 1926, **48**, 454—460).—The sodium salt of ethyl *o*-nitrobenzoylacetoacetate does not dissolve in aqueous ammoniacal ammonium chloride at the ordinary temperature (cf. Needham and Perkin, J.C.S., 1904, **85**, 151). At 35—40° it dissolves, with formation of a red oil, which, when treated with phenylhydrazine, affords ethyl 1-phenyl-3-*o*-nitrophenyl-5-methylpyrazole-4-carboxylate, of which the corresponding acid has m. p. 225° (cf. Knorr and Jödicke, A., 1885, 1247), indicating that hydrolysis of the acetyl group has not taken place. Production of the *o*-nitrobenzoylacetic acid is effected by hydrolysing the above ester with cold, concentrated sulphuric acid. It yields indigotin on reduction with dextrose, or with zinc dust and alkali. Reduction of ethyl *o*-nitrobenzoylacetoacetate with hot, alkaline ferrous sulphate affords ethyl 4-hydroxy-2-methylquinoline-3-carboxylate oxide (cf. McCluskey, A., 1922, i, 864), the corresponding acid having m. p. 214°. Reduction of the latter with zinc dust and hydrochloric acid affords 4-hydroxy-2-methylquinoline-3-carboxylic acid, m. p. 245° (cf. Conrad and Limpach, A., 1888, 1109), a reaction supporting the amine-oxide structure for this derivative, whilst the dibenzoyl derivative (McCluskey, *loc. cit.*) requires a tautomeric enol form. *4-Methoxy-2-methylquinoline-3-carboxylic acid oxide*, m. p. 190°, is described.

F. G. WILLSON.

Preparation of *O* : *O*-diacetyldiphenolisatin. F. HOFFMANN-LA ROCHE & Co.—See B., 1926, 186.

Interaction of *p*-toluenesulphonazide with malonic and substituted malonic esters. T. CURTIUS and W. KLAVEHN (J. pr. Chem., 1926, [ii], **112**, 65—87; cf. A., 1924, i, 998).—When a mixture of *p*-toluenesulphonazide and methyl malonate is digested for 6 hrs. at 100°/20 mm. and the product rendered alkaline, freed from unchanged material, and then acidified, the first product is *methyl 5-hydroxy-1-p-toluenesulphonyl-1 : 2 : 3-triazole-4-carboxylate*, a yellow oil which slowly ketonises to the corresponding *triazolone* derivative, m. p. 83°. The *sodium*, *barium*, *ammonium*, and *piperidine* salts of the enolic form are described as well-defined crystalline compounds.

If the condensation is carried out with ethyl sodiomalonate in alcoholic solution, a viscous oil is obtained (enol form) which in a short time isomerises to the solid *ethyl* ester, m. p. 85° (*sodium*, *lead*, *ammonium*, and *piperidine* salts of the enol form are described). Methyl sulphate, benzoyl chloride, and similar reagents are without action on the ethyl ester, and in general both esters react as though they have the constitution of diazo-esters, *i.e.*,

$$C_7H_7\cdot SO_2\cdot NH\cdot CO\cdot C(:N_2)\cdot CO_2R.$$

On hydrolysis with sodium hydroxide solution, the ethyl ester yields the enolic form of the acid as an oil, which rapidly solidifies to give *diazomalon-p-toluenesulphonylamic acid*,

$$C_7H_7\cdot SO_2\cdot NH\cdot CO\cdot C(:N_2)\cdot CO_2H,$$

m. p. 144°. When heated with water, the acid behaves as a normal diazo-acid, yielding nitrogen, carbon dioxide, and *glycol-p-toluenesulphonylamide*, m. p. 153°. By the prolonged action of aqueous ammonia on the ethyl ester, a product is obtained which on acidification yields *5-hydroxy-1-p-toluenesulphonyl-1 : 2 : 3-triazole-4-carboxylamide* as an oil, which on boiling with alcohol passes into *5-hydroxy-1 : 2 : 3-triazole-4-p-toluenesulphonylcarboxylamide*, m. p. 140° (decomp.). When the ester is treated with hydrazine hydrate, nitrogen and ammonia are evolved with formation of the *hydrazine* salt of *1-amino-5-hydroxy-1 : 2 : 3-triazole-4-p-toluenesulphonylcarboxylamide*, m. p. 212·5°, which on acidification yields the free *hydroxy-amide*, m. p. 164° (decomp.). This hydroxyamide condenses with aldehydes to give compounds of the type, $C_7H_7\cdot SO_2\cdot NH\cdot CO\cdot C<^{N=N}_{C(OH)}>N\cdot N:CHR$.

The condensation *products* with benzaldehyde, m. p. 212° (decomp.), *m*-nitrobenzaldehyde, m. p. 210° (decomp.), and salicylaldehyde, m. p. 190° (decomp.), are described.

p-Toluenesulphonazide does not react with either ethyl methylmalonate or ethyl ethylmalonate.

R. W. WEST.

Interaction of benzylsulphonazide with ethyl malonate. T. CURTIUS and B. JEREMIAS (J. pr. Chem., 1926, [ii], **112**, 88—116; cf. preceding abstract).—When a mixture of benzylsulphonazide and ethyl malonate is shaken with cold sodium hydroxide solution, the *sodium* salt of *ethyl 5-hydroxy-1-benzylsulphonyl-1 : 2 : 3-triazole-4-carboxylate* is deposited as a yellow oil which rapidly solidifies. Dilute acids liberate the free triazole, which rapidly isomerises into *ethyl diazomalonbenzylsulphonylamate*,

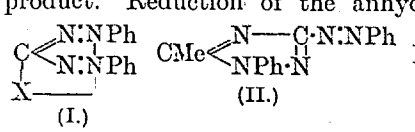
$C_7H_7\cdot SO_2\cdot NH\cdot CO\cdot C(:N_2)\cdot CO_2Et$, m. p. 123°. If warm sodium hydroxide solution is used in the first reaction, the main product after acidification consists of *ethyl benzylsulphonylmalonate*, m. p. 83° (*sodio*-derivative, m. p. 193°). By substituting ethyl sodiomalonate for the free ester, the reaction being carried out in alcoholic solution, a mixture of diazo-ester and benzylsulphonylmalonic ester is obtained. The diazo-ester is readily converted by the action of sodium ethoxide into the isomeric triazole [*sodium* salt, m. p. 184° (decomp.); *ammonium* salt, m. p. 140° (decomp.)]. By hydrolysis of the diazo-ester with sodium hydroxide and subsequent acidification, *diazomalonbenzylsulphonylamic acid* is obtained. This acid is an unstable substance which on warming with water yields nitrogen, carbon dioxide, and *glycol-benzylsulphonylamide*, m. p. 120°. By the prolonged action of concentrated aqueous ammonia on the diazo-ester a product is obtained which on acidification yields *5-hydroxy-1-benzylsulphonyl-1 : 2 : 3-triazole-4-carboxylamide* [*ammonium* salt, m. p. 155° (decomp.)] as an oil which on boiling with alcohol isomerises to *5-hydroxy-1 : 2 : 3-triazole-4-benzylsulphonylcarboxylamide*, m. p. 148° (decomp.). When the diazo-ester is treated with hydrazine hydrate and the product acidified, it yields *1-amino-5-hydroxy-1 : 2 : 3-triazole-4-benzylsulphonylcarboxylamide*, m. p. 155° (decomp.) [*hydrazine* salt, m. p. 179° (decomp.)]. The following condensation *products* of this compound with aldehydes and ketones are described (cf. preceding abstract): with benzaldehyde, m. p. 190° (decomp.); with acetone, m. p. 178° (decomp.); with salicylaldehyde, m. p. 187° (decomp.).

When ethyl benzylsulphonylmalonate is treated with hydrazine hydrate it yields a mixture of *benzylsulphonylacethydrazide*, m. p. 148° (*benzylidene* derivative, m. p. 179°), and *benzylsulphonylmalonhydrazide*, m. p. 253° (decomp.) [*hydrazine* salt, m. p. 232° (decomp.)]. When treated with nitrous acid, benzylsulphonylacethydrazide yields *benzylsulphonylacetazide*, m. p. 81° (decomp.), which when treated in ethereal solution with aniline or *p*-toluidine yields benzylsulphonylacetanilide or *benzylsulphonylacet-p-toluidide*, m. p. 151°. R. W. WEST.

Nitro- and amino-formazyl. E. BAMBERGER, R. PADOVA, and E. ORMEROD (Annalen, 1926, **446**, 260—307).—When nitroformazyl,

$$NPh{:}N\cdot C(NO_2){:}N\cdot NHPh,$$

is treated with amyl nitrite and acetic acid in acetone solution, the anhydride of 4-hydroxydiphenyltetrazolium hydroxide (I; X=O) is formed [*perchlorate*, explodes at 194°; *hydrochloride*, m. p. 193°; *picrate*, m. p. 169°; *chloroplatinate*, m. p. 196° (decomp.); *mercuric chloride* compound, $2C_{13}H_{10}ON_4,HgCl_2,2HCl$, m. p. 209·5° (decomp.)]. This compound is identical with diphenylcarbodiazide (Cazeneuve, A., 1901, i, 297). *Nitroindazole*, m. p. 85—85·5°, is formed as a by-product. Reduction of the anhydride (I; X=O)



(I.) (II.) (III.)

in alcoholic ammonia with hydrogen sulphide yields diphenylcarbazide, which forms a *dinitrosoamine*, $CO(NH\cdot NPh\cdot NO)_2$, m. p. 95° (decomp.), and gives *dibenzoyldiphenylcarbazone*, $NPh{:}N\cdot CO\cdot NBz\cdot NBz\cdot Ph$, m. p. 265·5—266·5° (decomp.), on benzoylation.

When reduced with hydrogen sulphide in alcoholic ammonia, nitroformazyl is converted into dihydroformazylmercaptan, $NHPh\cdot NH\cdot C(SH){:}N\cdot NHPh$, which is identical with diphenylthiocarbazide (Fischer, A., 1878, 302). The dihydromercaptan is rapidly oxidised in the air to formazylmercaptan, which is identical with diphenylthiocarbazone (Fischer and Besthorn, A., 1882, 1091). The following compounds of formazylmercaptan are described: *cupric* salt, m. p. 191·5—192°; *lead* salt, m. p. 230°; *mercuric* salt, m. p. 153—154°; *di-iodide*, m. p. 135°. Further oxidation yields a thiobetaine (I; X=S), which is identical with diphenylthiocarbodiazide (Fischer and Besthorn, *loc. cit.*). The mother-liquor from the reduction of nitroformazyl yields a *substance*, $C_8H_8O_2N_4$ (dihydro-3-nitro-1-phenyltriazole?), m. p. 201° (decomp.).

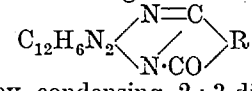
When nitroformazyl is reduced with sodium sulphide, *aminoformazyl*, m. p. 135—136° (*hydrochloride*, m. p. 141—142°), is obtained. This substance is converted by acetic anhydride into *3-benzeneazo-1-phenyl-5-methyl-1 : 2 : 4-triazole* (II), m. p. 178—178·5°, and by hydrochloric acid into *amino-α-hydrazochloroformazyl*,

$$NHPh\cdot N{:}C(NH_2)\cdot NH\cdot NH\cdot C_6H_4Cl$$

[*hydrochloride*, m. p. 175—176° (decomp.)]. The chloro-compound is readily oxidised to *amino-α-chloroformazyl*, $NHPh\cdot N{:}C(NH_2)\cdot N{:}N\cdot C_6H_4Cl$, m. p. 146° (decomp.). With hydrogen bromide, aminoformazyl yields *amino-α-bromoformazyl*, m. p. 114—115·5°. Oxidation of aminoformazyl using amyl nitrite and hydrochloric acid yields *aminodiphenyltetrazolium chloride* (III), m. p. 269° (decomp.) [*dichromate*, $C_{26}H_{24}O_7N_{10}Cr_2$, explodes at 189°; *dichromate-hydrochloride*, $C_{26}H_{24}O_7N_{10}Cr_2,2HCl$, m. p. 175° (decomp.); *chloroplatinate*, m. p. 249° (decomp.); *permanganate*, very explosive]. Ammonium sulphide reduces the chloride (III) to aminoformazyl, whilst nitrous acid converts it into *nitrosoiminodiphenyltetrazoliumbetaine* [I; X=·N(NO)], m. p. 177° [*hydrochloride*, m. p. 168°; *silver nitrate* compound, $C_{26}H_{20}O_5N_{13}Ag$, m. p. 157—161° (decomp.); *chloroaurate*, m. p. 119—122°], which regenerates the chloride on heating with dilute hydrochloric acid. When boiled with alcohol, the above nitroso-compound passes into iso-C-*nitrosoiminodiphenyltetrazoliumbetaine* (I; X=·N:N·O·), m. p. 154—155°. On benzoylation the chloride (III) yields *benzoyl-C-iminodiphenyltetrazoliumbetaine* (I; X=NBz·), decomp. at 232° [*hydrochloride*, m. p. 280·5°; *chloroplatinate*, m. p. 198° (decomp.); *dichromate*, m. p. 170·5°; *permanganate*, very explosive], which on reduction yields a *substance*, $C_{20}H_{17}N_5$, m. p. 222—223°.

R. W. WEST.

Heterocyclic compounds. I. A. C. SIRCAR and P. K. DE (J. Indian Chem. Soc., 1925, **2**, 312—318).—Compounds of the general formula



are obtained by condensing 2 : 3-diaminophenazine

with phthalic, camphoric, 1 : 8-naphthalic, and diphenic anhydrides: o-*camphorylene*-2 : 3-*phenazinoiminazole*, m. p. 215—219°; o-*benzoylene*-2 : 3-*phenazinoiminazole*; o-*naphthalylene*-2 : 3-*phenazinoiminazole*; o-*diphenylene*-2 : 3-*phenazinoiminazole* (cf. Rupe and Thiess, A., 1910, i, 71). Similar iminazoles of the form $C_{12}H_6N_2<^{NH}_{N}>CR$ are obtained by condensing 2 : 3-diaminophenazine with aldehydes: 4 : 5-*phenazino*-2-*phenyliminazole* from benzaldehyde; 4′-*methoxy*-4 : 5-*phenazino*-2-*phenyliminazole* from anisaldehyde; 3′-*nitro*-4 : 5-*phenazino*-2-*phenyliminazole* from *m*-nitrobenzaldehyde; 4′-*dimethylamino*-4 : 5-*phenazino*-2-*phenyliminazole* from *p*-dimethylaminobenzaldehyde. *Dihydroxyphenazinoquinoxoline* is formed by the action of oxalyl chloride on the diaminophenazine. When diazotised, 2 : 3-diaminophenazine yields 2 : 3-*phenazinoazoimide*, m. p. 280°, and when treated with *o*-tolylthiocarbimide it yields the 2-o-*tolylureide* of 3-*aminophenazine*, $C_{20}H_{17}N_5S$. The compounds described are coloured substances of high m. p. (undetermined). R. W. WEST.

Hetero-ring formations with thiocarbohydrazide. II. Condensations with diketones and aldehydes. P. C. GUHA and S. C. DEY (J. Indian Chem. Soc., 1925, 2, 225—239; cf. A., 1924, i, 948).—Certain 1 : 2-diketones react with thiocarbohydrazide, yielding closed-ring thiocarbohydrazones of the type $^{\cdot C:N\cdot NH}_{\cdot C:N\cdot NH}>CS$. In order to explain the insolubility of these compounds in alkali hydroxides, it is suggested that tautomerisation takes place to give the grouping $^{\cdot CH:N:N}_{\cdot CH:N:N}>CS$. From benzil, acenaphthenequinone, camphorquinone, and alloxan are obtained the compounds: 3-*thion*-6 : 7-*diphenyl*-1 : 2 : 4 : 5-*heptatetrazine*, m. p. 118—120°; 3-*thion*-*acenaphthene*-1 : 2 : 4 : 5-*heptatetrazine*, m. p. 253°; 3-*thioncamphor*-1 : 2 : 4 : 5-*heptatetrazine*; 3-*thion*-*alloxan*-1 : 2 : 4 : 5-*heptatetrazine*. It is suggested that *diphenanthraquinonethiocarbohydrazone*, m. p. 242°, *di*-β-*naphthaquinonethiocarbohydrazone*, and *diisatinthiocarbohydrazone*, m. p. 262° (decomp.), which would normally have the structure $\left(^{\cdot CO}_{\cdot C:N\cdot NH}\right)_2CS$, actually exist in the form $\left(^{\cdot C-O}_{\cdot C\cdot NH}>N\cdot\right)_2CS$.

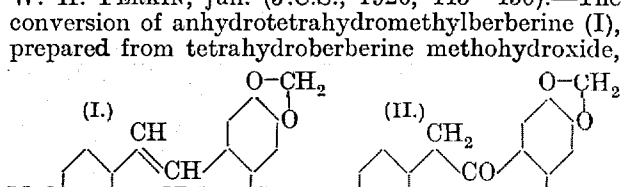
When *diacetylmonoximethiocarbohydrazone*, m. p. 285° (decomp.), is heated with hydrochloric acid it loses the elements of water and yields *thionbisdimethyl*-1 : 2 : 5-*triazole*, $\left(^{CMe:N}_{CMe:N}>N\right)_2CS$. In a similar manner, phenanthraquinonemonoxime yields *thionbisphenanthra*-1 : 2 : 5-*triazole*, m. p. 230°, whilst the monoxime of isatin yields *isatinmonoximethiocarbohydrazone*, m. p. 228° (decomp.), and thionbisisatin-1 : 2 : 5-triazole. With thiocarbohydrazide ketones and aldehydes form normal condensation products of the formula $CS(NH\cdot N:CRR')_2$. The following *thiocarbohydrazones* are described: of benzaldehyde, m. p. 194°; of *m*-nitrobenzaldehyde, m. p. 227°; of cinnamaldehyde, m. p. 235° (decomp.); of salicylaldehyde, m. p. 190° (decomp.); of anisaldehyde, m. p. 158°; of furfuraldehyde, m. p. 250° (decomp.); of piperonal, m. p. 195° (decomp.); of acetone, m. p. 195° (decomp.); of acetophenone, m. p. 185°; of benzophenone, m. p. 230° (decomp.); of methyl ethyl ketone, m. p. 220° (decomp.). R. W. WEST.

***iso*Oxazolones.** BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 149.

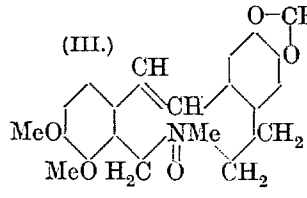
1-Methoxymethyl-3 : 7-dimethylxanthine. FARBENFABR. VORM. F. BAYER UND CO.—See B., 1926, 216.

Einhorn's so-called ecgonidine dibromide. H. LINDEMANN and H. HEINEMANN (Annalen, 1926, **447**, 85—96).—Whilst ecgonidine hydrobromide yields a *perbromide*, m. p. 154° (decomp.), when treated with bromine in acetic acid, this cannot be converted, by continued action of bromine in boiling glacial acetic acid, into Einhorn's ecgonidine dibromide hydrobromide (cf. A., 1891, 65). The perbromide decomposes when dried on porous earthenware or over potassium hydroxide, and is converted into ecgonidine hydrobromide when boiled with water or treated with acetone. Ecgonidine hydrochloride yields similarly a *perbromide*, yellowish-red, m. p. about 122°, which affords ecgonidine hydrochloride and hydrobromide when treated with acetone, and the hydrochloride when treated with an aqueous suspension of silver powder; the perbromide is converted, on warming to 90° in glacial acetic acid, into 4-*chloro*-3-*bromotropan*-2-*carboxylic acid hydrobromide*, m. p. 194°, identical with Einhorn's so-called ecgonidine dibromide hydrobromide (*loc. cit.*). When treated with silver carbonate (0·5 mol.) in aqueous solution, the latter yields 4-*chloro*-3-*bromotropan*-2-*carboxylic acid*, m. p. 168° [*hydrochloride*, m. p. 214°; *chloroplatinate*, m. p. 250° (decomp.); *chloroaurate*, m. p. 214°], and this, on reduction with stannous chloride and hydrochloric acid, affords a mixture of the hydrochloride and hydrobromide of ecgonidine. Ecgonidine chloroaurate has m. p. 194° (cf. Merck, A., 1887, 284). F. G. WILLSON.

Conversion of berberine into β-homochelidonine (α-*allo*cryptopine). R. D. HAWORTH and W. H. PERKIN, jun. (J.C.S., 1926, 445—450).—The conversion of anhydrotetrahydromethylberberine (I), prepared from tetrahydroberberine methohydroxide,



into β-homochelidonine (II) is difficult, since (I) shows a tendency to revert to tetrahydroberberine methohydroxide. When (I) reacts with perbenzoic acid in chloroform–ether solution below 5°, it is oxidised to *anhydrotetrahydromethylberberine oxide* (III), m. p. 135° (decomp.); *hydrochloride*, m. p. 203° (decomp.). In presence of acetic



acid and hydrochloric acid, (III) isomerises to β-homochelidonine. F. M. HAMER.

Preparation of alkyl ethers of the morphine series. E. MERCK.—See B., 1926, 216.

Strychnos alkaloids. XLVI. Degradation of derivatives of brucinonic acid. H. LEUCHS and W. SCHMIEDER (Ber., 1926, **59**, [*B*], 276—283).—Brucinonic acid is readily converted into the corresponding *phenylhydrazone*, $C_{29}H_{30}O_7N_4$, m. p. 225—228° after softening at 215°, which yields successively the *ethyl* ester, $C_{31}H_{34}O_7N_4$, m. p. 186—188° after softening at 180°, and the *hydrazide*, $C_{29}H_{32}O_6N_6$, m. p. 195—204°. The azide is amorphous and is hydrolysed mainly to an amorphous product of the approximate composition $C_{27}H_{30}O_6N_4$. The semicarbazone of brucinonic acid is transformed successively into the *ethyl* ester, $C_{26}H_{31}O_8N_5$ (also *trihydrate*), m. p. 192—196° (decomp.) after softening at 185°, $[\alpha]_D^{20}$ +231° in glacial acetic acid, the *hydrazide*, $C_{24}H_{29}O_7N_7$, m. p. 250—260° after softening at 235°, $[\alpha]_D^{20}$ +339° in glacial acetic acid, and the *azide*, m. p. 220—225° (decomp.) after softening at 205°, which is converted by boiling water into formaldehyde and a *substance*, $C_{22}H_{25}O_6N_5$, decomp. 235° after softening at 210°, $[\alpha]_D^{20}$ +322·7° in glacial acetic acid; the latter compound is identified as the semicarbazone of the ketone hydrate, $C_{21}H_{22}O_6N_2$, obtained from the hydrazone I of brucinonhydrazide. The conversion of the homogeneous brucinonic acid hydrazone into two isomeric ethyl esters I, m. p. about 182°, $[\alpha]_D^{13}$ +295·8°, II, m. p. 250°, $[\alpha]_D^{25}$ −171°, has been reported previously (Leuchs and Kanao, A., 1925, i, 61). Ester I gives a hydrazide, m. p. 188—210°, $[\alpha]_D$ +380°, whereas ester II affords a *hydrazide* II, $C_{23}H_{28}O_6N_6$, m. p. 220—230°, $[\alpha]_D^{20}$ −84·1° in water, so that isomerism persists in the hydrazides. The hydrazide II is converted by nitrous acid into a crystalline azide which is transformed by boiling water into the hydrate of the ketone, $C_{21}H_{20}O_5N_2$, which is also derived from hydrazide I. Isomerism therefore disappears when the group ·C:N·NH$_2$ is transformed into ·CO, and hence an instance of stereoisomerism is present instead of structural isomerism as assumed previously (*loc. cit.*). The hydrazone II of ethyl brucinonate is hydrolysed to *brucinonic acid hydrazone* II, m. p. 236° (decomp.) after softening at 230°, $[\alpha]_D^{20}$ −121° in glacial acetic acid. H. WREN.

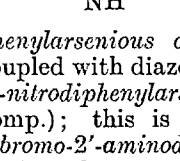
Application of the method of thermal analysis to determine quinquevalence in aromatic arsenicals. S. PEAT (Proc. Univ. Durham Phil. Soc., 1924—1925, **7**, 72—78).—The f.-p. curve for mixtures of tri-*p*-tolylarsine and *p*-iodotoluene shows that no compound is formed. A. DAVIDSON.

Organic compounds of arsenic. II. Mercurated arylarsinic acids. E. MASCHMANN (Ber., 1926, **59**, [*B*], 213—218; cf. A., 1924, i, 1357).—*3-Acetamido-4-hydroxy-5-hydroxymercuriphenylarsinic acid*, which remains unchanged below 300°, is prepared by adding mercuric acetate dissolved in dilute acetic acid to a solution of 3-acetamido-4-hydroxyphenylarsinic acid in 2*N*-sodium hydroxide and preservation of the mixture in the dark at the atmospheric temperature during 6—7 days. More slowly, but under similar conditions and with subsequent addition of hydrochloric acid, 3 : 5-diacetamido-4-hydroxyphenylarsinic acid is transformed into *3 : 5-diacetamido-4-hydroxy-2-chloromercuriphenylarsinic acid*. The acetyl groups could not be removed from these compounds without involving profound decomposition. The position of the new substituents is established by the conversion of the compounds into the known 5-iodo-3-acetamido-4-hydroxyphenylarsinic acid and 2-iodo-3 : 5-diacetamido-4-hydroxyphenylarsinic acid, respectively.

The behaviour of the compounds described by Raiziss, Kolmer, and Gavron (A., 1920, i, 196) shows that they do not contain mercury attached to the benzene nucleus; the mode of preparation is not conducive to the production of nucleus-mercurated compounds, and, further, almost all of them give an immediate precipitate of mercuric sulphide with cold ammonium sulphide. 3-Amino- and 3 : 5-diamino-4-hydroxyphenylarsinic acid cannot be directly mercurated on account of the reducing action of the hydroxyamino- and hydroxy-diamino-groups. Introduction of mercury into the nucleus of 4- or 3-carboxyphenylarsinic acid or 3 : 5-dinitro-4-hydroxyphenylarsinic acid could not be effected. H. WREN.

Manufacture of neoarsphenamine [neosalvarsan] etc. P. A. KOBER.—See B., 1926, 217.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. I. Synthesis, preparation, and properties of 10-chloro-5 : 10-dihydrophenarsazine. H. BURTON and C. S. GIBSON (J.C.S., 1926, 450—464).—The constitution ascribed to 10-chloro-5 : 10-dihydrophenarsazine (I) has been proved correct by the following synthesis. *o*-Bromophenylarsinic acid, m. p. 201° (decomp.) (prepared from *o*-aminophenylarsinic acid), is reduced to *o-bromophenylarsenious oxide*, m. p. 234—238°, which is coupled with diazotised *o*-nitroaniline to give *2-bromo-2′-nitrodiphenylarsinic acid*, m. p. 254—255° (decomp.); this is reduced by ferrous hydroxide to *2-bromo-2′-aminodiphenylarsinic acid*, m. p. 213—214° (decomp.) [*2-bromo-2′-methylaminodiphenylarsinic acid*, m. p. 193—194° (decomp.), *2-bromo-2′-dimethylaminodiphenylarsinic acid*, m. p. 220—221° (decomp.)], which on heating with amyl alcohol, potassium carbonate, and copper is converted into phenarsazinic acid; reduction of its alcoholic hydrochloric acid solution with sulphur dioxide, in presence of a trace of iodine, yields 10-chloro-5 : 10-dihydrophenarsazine, identical with the substance which is prepared by the action of arsenious chloride on diphenylamine (cf. Wieland and Rheinheimer, A., 1921, i, 371), and may be obtained in almost theoretical yield by heating these reagents in *o*-dichlorobenzene solution. At the ordinary temperature, diphenylamine and arsenious chloride form an additive compound, HCl,NHPh$_2$,AsCl$_3$, but formation of (I) only proceeds to a limited extent. The preparation of *N*-acyl derivatives of (I) (Burton and Gibson, A., 1925, i, 84) confirms the presence of the imino-group. It is suggested that on heating aniline with arsenious

(I.) 

chloride, trianilinoarsine hydrochloride is formed intermediately and reacts with aniline to give diphenylamine, whence is obtained (I), which is the final product (cf. Schmidt, A., 1922, i, 285). When arsenious chloride and β-naphthylamine are heated in *o*-dichlorobenzene solution, 14-chloro-7 : 14-dihydrodibenzophenarsazine is produced, identical with that obtained from di-β-naphthylamine and arsenious chloride.

In an attempt to prepare diphenylamine-*p*-arsenious chloride, *N*-acetyl-*p*-aminodiphenylamine has been converted into N-*acetyldiphenylamine*-p-*arsinic acid*, m. p. 126° (decomp.) (from water, $+H_2O$), which is hydrolysed to *diphenylamine*-p-*arsinic acid*, m. p. 265° (decomp.); but this on reduction suffers elimination of arsenic, although reduction of *N*-acetyldiphenylamine-*p*-arsinic acid yields *N*-acetyldiphenylamine-*p*-arsenious chloride, m. p. 141°. The ease of the *oo'*-substitution in diphenylamine is illustrated by the preparation of 10 : 10'-oxy-5 : 10-dihydrophenarsazine by heating diphenylamine and arsenious oxide in presence of phosphoric oxide at 160—170°; although this compound is converted by acetyl chloride into 10-chloro-5-acetyl-5 : 10-dihydrophenarsazine, with benzoyl chloride it yields (I), together with benzoic anhydride.

Molecular compounds of (I) with acetic acid, *s*-tetrachloroethane, chlorobenzene, *o*-dichlorobenzene, acetone, carbon tetrachloride, and arsenious chloride are described. 10-Bromo-5 : 10-dihydrophenarsazine, m. p. 217—218°, is obtained by heating diphenylamine with arsenious bromide in *o*-dichlorobenzene, but both it and 10-iodo-5 : 10-dihydrophenarsazine, m. p. 217—221° (decomp.), are best prepared by adding the corresponding halogen acid to the solution of 10-acetyl-(10 : 10'-oxy ?)-5 : 10-dihydrophenarsazine in acetic acid. 10-n-*Butoxy*-5 : 10-*dihydrophenarsazine*, m. p. 158—160°, and 10-*benzyloxy*-5 : 10-*dihydrophenarsazine*, m. p. 173—175°, have been prepared.

Condensation of arsenious chloride with *N*-methyldiphenylamine gives (I) and not 10-chloro-5-methyl-5 : 10-dihydrophenarsazine (cf. Wieland and Rheinheimer, *loc. cit.*), nor is this obtained by methylation of (I), or by reduction of the product prepared by heating 2-bromo-2'-methylaminodiphenylarsinic acid with amyl alcohol, potassium carbonate, and copper.

F. M. Hamer.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. II. Action of primary chloroarsines on diphenylamine and its homologues. H. Burton and C. S. Gibson (J.C.S., 1926, 464—470).—No compound of the type $XAs<^{R}_{R_1}>NH$, where X is a univalent hydrocarbon or substituted hydrocarbon radical, has been isolated. When phenyldichloroarsine (prepared by reducing phenylarsinic acid) is heated with diphenylamine and *o*-dichlorobenzene, an almost theoretical yield of 10-chloro-5 : 10-dihydrophenarsazine is obtained, instead of the 10-phenyl derivative; in the absence of solvent, benzene is a by-product. Similarly, phenyl-*p*-tolylamine and phenyldichloroarsine yield 10-*chloro*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 199—200° (decomp.), which is also obtained from phenyl-*p*-tolylamine and arsenious chloride, and from which have been prepared 10-*chloro*-5-*acetyl*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 154—155°, and 2-*methylphenarsazinic acid*, decomp. above 300° [*sodium* salt and *hydrochloride*, m. p. 209—211° (decomp.), described]; phenyldichloroarsine and *pp'*-ditolylamine give 10-*chloro*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*, m. p. 261—262° (decomp.), which is also prepared from *pp'*-ditolylamine and arsenious chloride, and from which are obtained 10-*chloro*-5-*acetyl*-2 : 8-*dimethyl*-5 : 10-*dihydrophenarsazine*, m. p. 164—165°, and 2 : 8-*dimethylphenarsazinic acid* [*sodium* salt, *hydrochloride*, m. p. 216° (decomp.), and N-*acetyl*-2 : 8-*dimethylphenarsazinic acid*, m. p. 240° (decomp.), described]; phenyldichloroarsine and phenyl-α-naphthylamine give 7-chloro-7 : 12-dihydrobenzophenarsazine. Lewis and Stiegler's results on the condensation of β-chlorovinyldichloroarsine with diphenylamine and phenyl-α-naphthylamine (A., 1925, i, 1470) have not been confirmed, but the product in the first case is 10-chloro-5 : 10-dihydrophenarsazine and, in the second, 7-chloro-7 : 12-dihydrobenzophenarsazine, with formation, in both experiments, of vinyl chloride. F. M. Hamer.

Organic bismuth compounds. I. Preparation of tricarboxytriphenylbismuth dichlorides and certain nitrotriaryl bismuth compounds. J. V. Supniewski and R. Adams (J. Amer. Chem. Soc., 1926, **48**, 507—517).—Triarylbismuthines are conveniently prepared by the action of Grignard reagents on bismuth trichloride in ether (cf. Pfeiffer and Pietsch, A., 1905, i, 164; Challenger, Proc. Chem. Soc., 1913, **29**, 76), purification of the crude product being effected by extraction in a Soxhlet apparatus with chloroform or carbon tetrachloride. *Tri*-o-*anisylbismuthine*, m. p. 169—170°, is described. Treatment of the triarylbismuthines with chlorine in carbon tetrachloride affords triarylbismuthine dichlorides, generally in quantitative yields. The corresponding bromides are obtained analogously. *Tri*-m-*tolylbismuthine dichloride*, m. p. 132—133°, and *dibromide*, m. p. 52°, are described, the latter decomposing rapidly in air. When boiled with lead acetate in glacial acetic acid, the dihalides yield the corresponding diacetates, of which *triphenylbismuthine diacetate*, m. p. 152—153°, is described. Oxidation of tri-*o*-tolylbismuthine dichloride with chromic acid in glacial acetic acid at 68—70° affords *tri*-o-*carboxytriphenylbismuthine dichloride*, m. p. 157—159°. *Tri*-p-*carboxytriphenylbismuthine dichloride*, m. p. 130° (*trimethyl* ester, m. p. 103°), is obtained similarly, or by oxidation of the tri-*p*-tolylbismuthine dichloride with permanganate in acetone. Treatment of triphenylbismuthine dinitrate (cf. Challenger, *loc. cit.*) with fuming nitric acid at 0° affords *tri*-p-*nitrotriphenylbismuthine dinitrate*, pale yellow, exploding at 147°, and decomposing on recrystallisation from glacial acetic acid. When boiled in acetone solution with concentrated aqueous hydrochloric acid, the above dinitrate affords the corresponding *dichloride*, m. p. 132—134°. *Trinitrotri*-p-*tolylbismuthine dinitrate*, exploding at about 160°, and *dichloride*, m. p. 156°, are obtained similarly. *Trinitro*-o-*tolyl*-

bismuthine dichloride, m. p. 149—150°, decomposes on keeping. *Trinitrotri*-p-*carbomethoxytriphenylbismuthine dinitrate*, exploding at 150—160°, and *dichloride*, m. p. about 250—260° (decomp.), are described. Reduction of the triarylbismuthine dihalides to the corresponding triarylbismuthines is effected by treatment in acetone solution at 0° with concentrated aqueous sodium hyposulphite. *Trinitrotriphenylbismuthine*, m. p. 121°, decomposing when kept, and *trinitrotri*-p-*tolylbismuthine*, m. p. 126°, were prepared in this way. Treatment of tri-*o*-tolylbismuthine dichloride with 98% sulphuric acid affords *tri*-o-*tolylbismuthine hydroxychloride*, decomposing at 100° with formation of a *compound*, m. p. 154°, insoluble in cold alkali. Treatment of bismuth trichloride with benzene diazonium chloride in concentrated hydrochloric acid affords an *additive* compound, PhN_2Cl_4Bi, exploding at about 120°. Bromination of *o*-bromotoluene in the light from a mercury lamp, with treatment of the product with methyl alcohol and potassium hydroxide, affords *o-bromobenzyl methyl ether*, b. p. 225°/745 mm. *p-Bromobenzyl methyl ether*, b. p. 201°/750 mm., 127°/30 mm., is obtained similarly. Grignard reagents could not be prepared from either of these ethers.

F. G. WILLSON.

Preparation of mercury derivatives of organic compounds. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 218.

Quantitative study of the action of mercuric salts on dialkylbarbituric acids. II. Diallyl and *iso*propylallyl derivatives. P. FLEURY (Bull. Soc. chim., 1926, [iv], **39**, 99—108).—The behaviour of diallyl- and *iso*propylallyl-barbituric acids with mercuric sulphate and chloride is in agreement with the results obtained in previous studies (this vol., 305). The precipitates obtained with mercuric sulphate always contain more than one atom of mercury for a mol. of acid, are formed without elimination of water between the acid molecule and mercuric oxide, and for *iso*propylallyl- and diallylbarbituric acids have a composition lying between those required by the formulæ 3AH,5HgO and 3AH,6HgO (AH=disubstituted barbituric acid). With *iso*propylallylbarbituric acid the composition of the precipitate varies with the acidity of the mercuric sulphate solution and the concentration of the barbituric acid. With a neutral solution, precipitation is complete. With the diallyl derivative, the composition of the precipitate is independent of the acidity, but varies considerably with the concentration of the barbituric acid and is only approximately complete with a large excess of reagent. Diallyl- and *iso*propylallyl-barbituric acids differ from the dialkylbarbituric acids previously examined in yielding precipitates with mercuric chloride. The reaction appears to be specific for allylbarbituric acids. Precipitation is complete only in the case of diallylbarbituric acid, and then in the presence of a large excess of reagent (11—12 mols.); the reaction affords a means of determining this acid. The precipitates are soluble in hot, concentrated hydrochloric acid and in ammoniacal cyanide solution, but only a part of the mercury can be determined by titration of the cyanide solution. The precipitates are regarded as adsorption compounds; they contain variable proportions of mercuric chloride and of water. The latter, which is not lost in a vacuum at 100—110°, is regarded as "water of constitution."

R. BRIGHTMAN.

Leaf-cell cytoplasm. Soluble proteins. A. C. CHIBNALL and C. E. GROVER.—See this vol., 441.

Alcohol-soluble protein from polished rice. W. F. HOFFMAN.—See this vol., 441.

Determination of unsaturated in presence of saturated and tricyclic hydrocarbons. The direction of dehydration of alcohols. S. NAMETKIN and L. BRÜSSOFF (J. pr. Chem., 1926, [ii], **112**, 169—176).—In order readily to distinguish unsaturated hydrocarbons from possible cyclic hydrocarbons formed by the dehydration of alcohols, some method of determining the former is desirable. Experiments with pure and mixed hydrocarbons show that the unsaturated hydrocarbons can be determined in the presence of saturated and cyclic hydrocarbons by the action of perbenzoic acid in chloroform solution. Excess of the oxidising reagent is used and the excess determined iodometrically. By this method, accurate determination is possible with small amounts (0·1—0·3 g.) of hydrocarbon. The method simplifies the study of the dehydration of alcohols.

R. W. WEST.

Determination of nitro-compounds by reduction with titanous chloride at the ordinary temperature. I. M. KOLTHOFF and C. ROBINSON (Rev. trav. chim., 1926, **45**, 169—176).—Aromatic nitro-compounds may be determined by reduction with a slight excess of acid titanous chloride solution in the presence of sodium citrate. An atmosphere of carbon dioxide is used and the complete removal of oxygen ensured by adding sodium hydrogen carbonate to the citrate solution before the acid titanous solution is introduced. After 2 min., the unchanged titanous chloride is titrated electrometrically with iron alum solution, using the apparatus of Kolthoff and Tomiček (A., 1924, ii, 870). Ordinary titration may also be used with ammonium thiocyanate as indicator, the solution being strongly acidified with hydrochloric acid. A slight correction has to be made for the effect of the citrate, but otherwise the titanous solution may be standardised against any standard substance, preferably dichromate, and, in contrast to other methods, it is not necessary to standardise with a nitro-compound. Errors from chlorination of the nitro-compound do not occur.

W. HUME-ROTHERY.

Determination of dihydroxyacetone. W. R. CAMPBELL.—See this vol., 443.

Determination of lactic acid and lactates. K. HANSEN.—See this vol., 444.

Determination of quinine. L. DAVID.—See B., 1926, 172.

Biochemistry.

Lactic acid of blood under respiration. BINET and COLLAZO (Médecine, 1925, **6**, 924).—With chloralosed dogs, the blood of the right heart contains more lactic acid (3 to 11 mg. per 100 c.c.) than that of the left. The lactic acid content is increased by asphyxia and reduced by panting. CHEMICAL ABSTRACTS.

***In vivo* permeability of the red corpuscles of the rabbit.** J. T. IRVING and H. D. KAY (J. Physiol., 1926, **61**, 113—121).—Only a small proportion of the reducing substance of the blood of normal rabbits is in the corpuscles. This is increased by injection of insulin, inactive insulin, and peptone. Addition of anticoagulants to shed blood alters the permeability of the corpuscles to reducing substance.

R. K. CANNAN.

Permeability of blood-corpuscles. L. BLUM, M. DELAVILLE, and C. M. JONES (Compt. rend. Soc. Biol., 1925, **93**, 704—706; from Chem. Zentr., 1925, II, 2280).—On treating hirudinised plasma with carbon dioxide, there is a decrease in phosphate and uric acid and an increase in sodium and calcium in the plasma. G. W. ROBINSON.

Chemical composition of beef blood. I. Concentrations of certain constituents in normal beef plasma. II. Composition of blood of cows and calves after calving. C. S. ROBINSON and C. F. HUFFMAN (J. Biol. Chem., 1926, **67**, 245—255, 257—266).—I. As the average result of analyses of 100 samples of the blood of normal adult cattle, there were found the following concentrations (in mg. per 100 c.c.): inorganic phosphorus 3·0—8·99, chlorine 294—357, calcium 7·7—14·7, potassium 16·4—41·3, and magnesium 0·31—3·08; the carbon dioxide was 41·4—75·8 vol. %.

II. The inorganic phosphate and the calcium of cow's blood were lower at the time of calving than those of the calf's blood; after calving, the phosphate concentration in the blood of both and the calcium concentration in that of the cow rose, whilst the calcium content of the calf's blood fell. The chlorine content of cow's blood was high at calving and fell subsequently; that of the calf's blood was lower, except for a short rise after birth. The hydrogen carbonate content of the blood of both cow and calf was lower than normal at the time of birth.

C. R. HARINGTON.

New sulphur-containing compound (thiasine) in blood. S. R. BENEDICT, E. B. NEWTON, and J. A. BEHRE (J. Biol. Chem., 1926, **67**, 267—277).—Proteins were removed from blood by boiling with dilute acetic acid and subsequent treatment with colloidal iron; the concentrated protein-free filtrate was treated with silver lactate and sodium tungstate and the washed precipitate of silver salts decomposed by boiling with dilute hydrochloric acid; the filtrate from the silver chloride was then treated with mercuric acetate and the resulting precipitate filtered off and decomposed with hydrogen sulphide; the filtrate from the mercuric sulphide yielded, on concentration, a *hydrochloride*, from which, by treatment with pyridine, was obtained a *substance* ("*thiasine*"), $C_{12}H_{20}O_3N_4S$, m. p. 262—263°, $[\alpha]_D$ +116°. The yield of the hydrochloride was 0·3—0·4 g. from 5000 c.c. of blood. The new compound has no amino-nitrogen, is stable towards boiling 20% hydrochloric acid and strong ammonia, does not reduce alkaline copper solutions nor give a colour with alkaline picrate solutions or with sodium nitroprusside; Millon's reaction is negative; hydrochloric acid was not removed from the hydrochloride by addition of silver nitrate to its aqueous solution and therefore appears to be held in a non-ionisable form. Thiasine gives a colour with the reagents used for the colorimetric determination of uric acid, and its presence in blood must therefore interfere with the latter determination. Thiasine has been obtained from pig's blood and human blood; in both cases it is contained entirely in the corpuscles (cf. Hunter and Eagles, this vol., 85). C. R. HARINGTON.

Presence of cyanate in blood. E. GOTTLIEB (Biochem. J., 1926, **20**, 1—5).—There is no difference in the ammonia formation of blood, whether at acid or alkaline reaction. On the other hand, on addition of potassium cyanate to blood, 60—70% of it is converted into ammonia at acid reaction, whilst in plasma 90—95% of the added cyanate can be accounted for in this way. Cyanate given intravenously or *per os* to dogs and rabbits was found to be toxic. Cyanate cannot be a precursor of urea (A., 1925, i, 455), nor can it be present in blood in concentrations exceeding 0·1 mg. per 100 c.c. of plasma. S. S. ZILVA.

Nomenclature of serum proteins and expression of serum viscosity. E. A. HAFNER (Biochem. Z., 1925, **165**, 29—32).—Precipitation by salts depends on electric polarisability. The polarisability of globulin is less than that of albumin, hence salting out by ammonium sulphate effects separation into substances chemically different in constitution. Recommendations are made for the expression of serum viscosity. C. RIMINGTON.

Refraction of serum proteins and the individuality of albumin and globulin. O. ARND and E. A. HAFNER (Biochem. Z., 1926, **167**, 440—473).—A reinvestigation of the refractometric determination of serum proteins in view of the criticisms of Starlinger and Hartl (A., 1925, i, 716). It is found that sodium sulphate can replace ammonium sulphate for the salting out of globulin without interfering with refractometric determinations. For nitrogen analysis by Kjeldahl's method, serum is fractionated with sodium sulphate at 37°, whilst for refractometric measurements the use of ammonium sulphate is retained. The refraction of the residue after tungstic acid precipitation differs often from that of the ultrafiltrate, due to the Donnan equilibrium effect in the latter case. In a number of pathological cases, no relationship could be found between the residual refraction and the residual nitrogen, the latter being independent of the electrolyte content. The individual residual refraction should therefore be separately determined for each refractometric measurement. The specific refraction of the total proteins was inde-

pendent of the non-protein substances of the serum, and change of p_H did not appear to influence the total refraction. The refractometric method is quite satisfactory when no greater accuracy than 0·3—0·5% is required. The relative amounts of albumin and globulin vary considerably, the differences being manifest immediately after separation from the cell proteins. Experiments indicate that, *in vitro*, albumin cannot be converted into globulin, and the results of a number of chemical, physico-chemical, biochemical, and immunological experiments suggest that albumin is fundamentally different from globulin and cannot be replaced by it. When lecithin sol is treated with serum and examined refractometrically, the globulin value is decreased and globulin is protected by lecithin from salting out by ammonium sulphate. The protective action by lecithin of euglobulin against salting out is still detectable after 36 hrs. It is believed that a lecithin–serum–protein complex is formed. P. W. CLUTTERBUCK.

Ultra-violet absorption spectra of blood-serum and certain amino-acids. W. STENSTRÖM and M. REINHARD (J. Biol. Chem., 1925, **66**, 819—827).—The typical ultra-violet absorption spectrum of blood-serum was shown to be due to the proteins and in particular to tyrosine and tryptophan. The absorption spectrum of serum could be very closely imitated by that of a mixture of tyrosine, tryptophan, phenylalanine, cystine, leucine, glycine, and glutamic acid in the proportions in which these amino-acids occur in the serum proteins. The absorption curves of tryptophan and tyrosine were determined; the latter was shifted in the direction of longer wave-lengths with increasing alkalinity of the solution.

C. R. HARINGTON.

Condition of calcium in serum. A. NITSCHKE (Biochem. Z., 1925, **165**, 229—237).—Calcium is more largely ionised in serum than appears from Rona's expression (A., 1913, i, 544). At alkaline reactions part only is ionised, but the proportion increases with greater acidity. At p_H 7·4 about 16% of the total calcium is united to protein. C. RIMINGTON.

Determination of the actual reaction of the capillary blood by means of the quinhydrone electrode. R. SCHAEFER (Biochem. Z., 1926, **167**, 433—439).—A method is described which permits of the measurement of the actual reaction of capillary blood, its natural carbon dioxide content being preserved. With normal men, the results correspond satisfactorily with those obtained for arterial blood.

P. W. CLUTTERBUCK.

Relation of true p_H of blood-serum or plasma to that observed colorimetrically. J. H. AUSTIN, W. C. STADIE, and H. W. ROBINSON (J. Biol. Chem., 1925, **66**, 505—519).—A series of determinations of the true p_H of blood-serum or plasma made electrometrically or by equilibration of the fluid with an analysed gas mixture and subsequent calculation from the Henderson–Hasselbalch equation, accompanied by simultaneous colorimetric determinations by the method of Hastings and Sendroy (A., 1924, ii, 869) or of Cullen (A., 1922, ii, 672), indicate considerable variations in the difference between the two values obtained. These variations could not be correlated with any definite factor, so that the authors suggest that the necessary correction, to be applied to convert the p_H observed colorimetrically to the true value, should be determined for each serum by equilibrating a sample and determining the difference between the colorimetrically observed and the calculated p_H of this sample. C. R. HARINGTON.

Effect of temperature on acid–base–protein equilibrium and on carbon dioxide absorption curve of whole blood, true and separated serum. W. C. STADIE, J. H. AUSTIN, and H. W. ROBINSON (J. Biol. Chem., 1925, **66**, 901—920).—Since the total base of the blood is constant and that part combined with strongly dissociated acids is also constant in whole blood or in separated serum, and since the base bound as phosphate is negligibly small, the sum of the remaining base bound as hydrogen carbonate, $[BHCO_3]$, and that bound by protein, [BPr], must also be constant, ([b]); in true serum, the relations are complicated by the possibility of migration of anions between cells and serum; in this case, the relationships $d[BHCO_3]_{true\,serum}=d[BHCO_3]_{whole\,blood}=-d[BPr]_{whole\,blood}$ hold good. Further mathematical treatment leads to the equations $p_H=pI+\{[b]-[BHCO_3]\}/\beta[Pr]$, and $\beta[Pr]=\{[BHCO_3]'-[BHCO_3]\}/(p_H-p_{H'})$, where pI is a constant close to the p_H of the isoelectric point of the protein and β is the buffer constant of the blood. These equations express the relationship between the carbon dioxide absorption curve and the base combined with protein at varying p_H. Experimental determinations of the change in the carbon dioxide absorption curve between 20° and 38° indicate that the term $\beta[Pr]$ does not vary with the temperature; assuming the constancy of $\beta[Pr]$, the change of pI with temperature (dpI/dt) is calculated as −0·017 to −0·023; this latter relationship makes possible the transposition of a carbon dioxide absorption curve determined at one temperature to its correct position for another temperature. The slope of the curve for true serum is about 1·1 times as great as that for whole blood at both temperatures. The change in p_H of whole blood or separated serum with change of temperature varies with the initial p_H, the initial tension of carbon dioxide, and initial value of $\beta[Pr]$; over physiological ranges, the variation may amount to 0·09 p_H, and is therefore a factor in the variability of the C correction of Cullen (cf. preceding abstract).

C. R. HARINGTON.

Total acid–base equilibrium of blood-plasma. I. Concentration of acids and bases in normal plasma. J. P. PETERS, H. A. BULGER, A. J. EISENMANN, and C. LEE. **II. Effect of tension of carbon dioxide on concentration of acids in oxygenated blood.** A. J. EISENMANN, H. A. BULGER, and J. P. PETERS. **III. Differences between arterial and venous blood.** J. P. PETERS, H. A. BULGER, and A. J. EISENMANN. **IV. Effects of stasis, exercise, hyperpnœa, and anoxæmia; and the causes of tetany. V. Miscellaneous pathological conditions.** J. P. PETERS, H. A. BULGER, A. J. EISENMANN, and C. LEE (J. Biol. Chem., 1926, **67**, 141—158, 159—164, 165—173, 175—218, 219—235).—I. The total base

of the blood-plasma of normal individuals and of patients with minor pathological conditions was 145—167 milliequivalents per 100 c.c., of which 135—155 milliequivalents were combined as hydrogen carbonate, chloride, phosphate, and proteinate; the residual base, apart from negligible amounts of sulphate, must have been in the form of salts of organic acids; this fraction never exceeded 20 milliequivalents. Considerably greater variations were observed in the concentrations of individual salts, but these variations balanced one another in such a way as to keep the total base within the above-mentioned limits.

II. Increase of the tension of carbon dioxide from 30 mm. Hg to 60 mm. Hg at 38° causes an increase of hydrogen carbonate of about 5 millimols. per 100 c.c., a decrease of chlorides of about 2 millimols., a diminution of the plasma volume of 0·6%, and a decrease of about 0·8 millimols. in the base-binding power of the plasma proteins, the net result being an increase in the total base-binding capacity of 2 millimols. per 100 c.c., which increase in acidity is balanced by the concentration of base due to diminution in plasma volume.

III. Differences, which were not consistent, but were outside the limits of error, were observed in the water and chloride content and the carbon dioxide absorption curve of arterial and venous blood.

IV. Venous stasis causes a concentration of the blood; since carbon dioxide cannot escape, the hydrogen carbonate increases and there is a resultant decrease in the chlorides. Brief and vigorous exercise causes a withdrawal of base from the tissues, which, for the most part, neutralises the lactic acid which is formed. Voluntary hyperpnœa, in a normal subject, carried so far as to induce symptoms of tetany, causes an increase of organic (chiefly lactic) acids, which is balanced by a decrease of chlorides, so that the total base remains unchanged. Anoxæmia, if accompanied by mild hyperpnœa, causes a fall in hydrogen carbonate which is balanced chiefly by withdrawal of hydrochloric acid from the tissues; extreme anoxæmia results in increase of organic acid which is neutralised by base from the tissues.

V. Vomiting has little effect on the electrolytes of the blood unless of a severe nature (*e.g.*, in eclampsia), in which case the chlorides are reduced in amount; the occurrence of a similar low concentration of chlorides, in a case in which actual vomiting was precluded by œsophageal obstruction, indicates that loss of hydrochloric acid from the stomach is not the sole cause of the change in the blood. Infections accompanied by high temperature result in reduction of the hydrogen carbonate of the blood except in the case of lobar pneumonia, in which the hydrogen carbonate remains normal, whilst the chloride is reduced. C. R. HARINGTON.

Methæmoglobin is richer in oxygen than hæmoglobin. V. BALTHAZARD and M. PHILIPPO (Compt. rend. Soc. Biol., 1925, **93**, 398—400; from Chem. Zentr., 1925, II, 1877).—In contradiction to Nicloux and Roche (A., 1925, i, 993), the authors consider that methæmoglobin is a peroxide.

G. W. ROBINSON.

Oxygen content of methæmoglobin. M. NICLOUX and J. ROCHE (Bull. Soc. Chim. biol., 1926, **8**, 71—97).—See A., 1925, i, 993.

Methæmoglobin formation. D. D. VAN SLYKE and E. VOLLMUND (J. Biol. Chem., 1925, **66**, 415—424).—The action of aniline on blood *in vitro* causes formation of methæmoglobin, but only after a more or less prolonged latent period; for complete conversion of the hæmoglobin into methæmoglobin, the aniline must be in large excess. No formation of methæmoglobin by nitrobenzene could be observed. The effect of poisoning rabbits with these two substances, by painting them on the abdomen, is to produce anæmia but no formation of methæmoglobin. The addition of excess of potassium ferricyanide to laked blood causes rapid and complete conversion of the hæmoglobin into methæmoglobin, but ferricyanide is without action on the intact red corpuscles; sodium nitrite, on the other hand, is able to penetrate the red corpuscles and thus to bring about an equally rapid formation of methæmoglobin in whole blood.

C. R. HARINGTON.

Tartarylhæmin of S. Hajdu. H. GOLDMAN (Biochem. Z., 1926, **168**, 456).—Further analytical data are given for the sample of tartarylhæmin prepared by Hajdu (this vol., 191). H. I. COOMBS.

Blood-sugar. I. Reduction and rotation of the blood-sugar after administration of dextrose *per os* and intravenously. H. K. BARRENSCHEEN, H. KAHLER, and H. HECHL (Biochem. Z., 1926, **167**, 77—91).—In the fasting normal subject, the amount of blood-sugar calculated from the rotation was less than that calculated from the reduction, and the specific rotation of the blood-sugar, calculated from the concentration as determined by reduction, lay in four cases between 25·7° and 38·5°. After administration of dextrose *per os*, the specific rotation corresponded with that of αβ-glucose. In the fasting diabetic, the specific rotation was equal to, or higher than, that of αβ-glucose, except in one case resistant to insulin. Administration of dextrose to normal subjects intravenously, or to diabetics *per os*, caused a rise in the specific rotation of the blood-sugar to a value considerably above that of αβ-glucose.

E. C. SMITH.

Abderhalden's blood reaction. H. SELLHEIM (Leopoldina, 1926, **1**, 43—48).—See this vol., 86.

Inactivation of serum. E. FREUND and B. LUSTIG (Biochem. Z., 1926, **167**, 374—379).—Absorption of water occurs at the inactivation temperature with normal and, to a greater extent, with immune sera. Refractometric methods did not distinguish between active and inactive sera.

P. W. CLUTTERBUCK.

Surface tension of serum. Physico-chemical changes following immunisation. P. L. DU NOÜY (Biochem. Z., 1925, **165**, 134—144).—Following antigen injection, the serum surface tension falls to a minimum on the thirteenth day, then returns to normal. Simultaneously, sodium chloride crystallising from concentrated sera develops a characteristic appearance. These changes do not occur *in vitro*;

neither are they due to alterations in the proportion of serum-albumin to globulin. C. RIMINGTON.

I. Changes in total iron in animals during rest. II. Changes in the iron reserve in newborn animals. III. Minimum daily excretion of iron by fully-grown young dogs. IV. Content of non-hæmoglobin iron in serum and its decrease during experimental anæmia. G. FONTÈS and L. THIVOLLE (Compt. rend. Soc. Biol., 1925, **93**, 681—689; from Chem. Zentr., 1925, II, 2214—2215).—In cats and rabbits, the iron content of the blood remains constant during rest, whilst in the case of dogs there is a marked increase. The content of iron in the blood is constant for each species at birth. Dogs have practically no iron reserves (total iron minus blood iron); cats and rabbits have, on the other hand, relatively large reserves and there are correspondingly large variations in total iron. In dogs, the excretion of iron in the fæces amounts to only a few mg. (? per diem). Horse-serum contains about 2 mg. of iron per litre. The ratio of "circulating" iron to hæmoglobin iron is 1 : 250. G. W. ROBINSON.

Isolation of an extremely active phosphorus-free anti-coagulant from organs by prolonged autolysis and acid alcohol. DOYON and I. VIAL (Compt. rend., 1926, **182**, 412—413).—The intestine of the horse is heated in an incubator for 3—4 months in a dilute saline solution containing chloroform. The liquid is treated with alcohol, the precipitate extracted with boiling water, and the extract precipitated by addition of acidified alcohol. The substance obtained possesses acidic properties, contains nitrogen but no phosphorus, and 1 g. prevents the coagulation of 3000 c.c. of blood. L. F. HEWITT.

Corpus luteum. IV. Acetone-soluble fat. G. F. CARTLAND and M. C. HART. **V. Lipins of the acetone extract.** M. C. HART and F. W. HEYL (J. Biol. Chem., 1925, **66**, 619—637, 639—651).—IV. By extraction of 5·5 kg. of dried corpus luteum with acetone, there were obtained, after removal of lecithins by means of cadmium chloride, 700 g. of fat which yielded 524 g. of fatty acids, and 105 g. of unsaponifiable matter of which 58 g. were cholesterol. In the fatty acid fraction were found palmitic acid 25%, stearic acid 11·2%, oleic acid 32·8%, linoleic acid 16·6%, arachidonic acid 8%, and an acid, $C_{20}H_{34}O_2$, 4·8%; the last-named acid was isolated as the hexabromide.

V. In addition to the fat above described, the acetone extract of corpus luteum contained small amounts of leucine, *iso*leucine, and valine, cholesterol, cholesteryl palmitate, and potassium stearate. By precipitation with cadmium chloride, there was further obtained a lecithin which was prepared free from kephalin and fat and having a nitrogen : phosphorus ratio of 1 : 1. C. R. HARINGTON.

Distribution of protein nitrogen in muscle. G. E. VLADIMIROV (Biochem. Z., 1926, **167**, 156—170).—The globulin of muscle plasma (myosin) can be separated from the nucleoprotein of the stroma (myostromin) by extraction with dilute acetic acid, which is preferable to the ammonium chloride solution previously used. The myostromin is extracted from the residue by treatment with 0·25% potassium hydroxide. Human heart-muscle, diaphragm, and ilio-psoas muscle contain decreasing amounts of myostromin. E. C. SMITH.

Pigments of butterflies' wing. I. *Melanargia galatea*. D. L. THOMSON (Biochem. J., 1926, **20**, 73—75).—The wings of *Melanargia galatea* yielded a yellow, crystalline pigment, m. p. 253° (corr.), having the properties of a flavone or flavonol. S. S. ZILVA.

Influence of cerebrospinal fluid on the precipitation by electrolytes of positively and negatively charged sols at a definite p_H. Differentiation of fluids rich in albumin and globulin. H. ROSENFELD (Biochem. Z., 1926, **167**, 343—354).—Mastic is precipitated ten times more readily by calcium chloride than by sodium sulphate, the action of the electrolytes being uninfluenced by the presence of normal cerebrospinal fluid. Mastic is, however, sensitised to fluid containing increased amounts of protein. Meningitic fluid sensitises mastic more strongly to sodium sulphate, and paretic and luetic fluids more strongly to calcium chloride. Night-blue is precipitated by sodium sulphate more readily than by calcium chloride, the action of the latter being somewhat irregular. Normal fluid, and still more so paretic fluid, protects night-blue against the action of sodium sulphate. At p_H 5, meningitic fluid sensitises night-blue to sodium sulphate, but in the absence of buffer there is no difference between normal, paretic, and meningitic fluids. The precipitation of night-blue may therefore be used for differentiation of fluids rich in albumin (meningitic) from those rich in globulin (paretic). P. W. CLUTTERBUCK.

Excretion of sugar in normal urine. N. R. BLATHERWICK, M. BELL, E. HILL, and M. L. LONG (J. Biol. Chem., 1925, **66**, 801—810).—Increased ingestion of dextrose, particularly of commercial glucose, caused an increase only in the fraction fermentable by yeast of the reducing substance found in normal urine; increased ingestion of protein, on the other hand, led to an increase in the non-fermentable fraction alone. C. R. HARINGTON.

Excretion of phosphate during water diuresis. R. E. HAVARD and G. A. REAY (Biochem. J., 1926, **20**, 99—101).—The rate of phosphate excretion is independent of the water rate, even when the urinary phosphate is below the level of the plasma phosphate. These results are discussed in connexion with some theories of kidney secretion. S. S. ZILVA.

Use of quinhydrone electrode for determination of p_H of fæces. C. S. ROBINSON (J. Biol. Chem., 1925, **66**, 811—812).—Determinations of the p_H of fæces by the use of the quinhydrone electrode of Biilmann (A., 1921, ii, 372) have been shown to agree within 0·2 p_H unit with the values obtained by the hydrogen electrode. C. R. HARINGTON.

Anæmia, urobilinuria, and intestinal hæmorrhage in rabbits in consequence of exclusive nutrition with cow's and goat's milk. G. BROUWER (Biochem. J., 1926, **20**, 105—107).—Severe anæmia developed in rabbits fed on cow's and on goat's milk. Urobilinuria and a loss of red blood corpuscles by capillary hæmorrhage into the intestinal cavity were observed. S. S. ZILVA.

Alkali content of the blood-serum of normal and diseased children. J. CSAPO (Biochem. Z., 1926, **167**, 38—42).—The total diffusible alkali in 1 c.c. of normal blood-serum corresponds with 4·8 c.c. of a 0·01*N*-solution. Combination with protein accounts for 3·4 c.c., with carbon dioxide for 1·4 c.c. of this amount. The alkalinity of pathological serum is less than normal only in tuberculosis, pleurisy, appendicitis, and pyelocystitis. The hydrogen carbonate concentration remains unaltered. It is suggested that the higher globulin content of the serum in these conditions leads to a retention of alkali in the diffusion thimble. E. C. SMITH.

Subcutaneous fat in the normal and sclerematous infant. H. J. CHANNON and G. A. HARRISON (Biochem. J., 1926, **20**, 84—92).—The analytical constants of the subcutaneous fat obtained from eight normal infants and one adult are compared with those obtained from four cases of sclerema neonatorum. In the normal cases, the iodine value is lowest at birth and increases to the adult value from the eighth to the twelfth month of life. There is a corresponding decrease of the m. p. with age. The saponification value is almost constant at 200. In the sclerema cases the fat had a higher m. p. and a slightly lower iodine value than normal. The raised m. p. is attributed to the presence of an excess of glycerides of the higher fatty acids—probably palmitic acid. Subcutaneous tissue in cases of sclerema contains an abnormal amount of cholesterol, calcium, and phosphorus. In the frozen sections of this tissue, sheaves of anisotropic crystals were observed. In this respect, and in their behaviour towards various solvents, these crystals were similar to tripalmitin obtained on slow crystallisation from ether at 0°. S. S. ZILVA.

Experimental calcæmia. P. ASTANIN (Biochem. Z., 1926, **168**, 231—238).—The effect on the blood calcium concentration of the oral or parenteral introduction of various calcium compounds was followed by de Waard's microchemical method (A., 1920, ii, 53). Normally only a transient hypercalcæmia resulted, which disappeared at a rate which was an exponential function of the height of calcæmia. R. K. CANNAN.

Effect of administration of calcium salts and of sodium phosphate on calcium and phosphorus metabolism of thyreoparathyroidectomised dogs. I. GREENWALD (J. Biol. Chem., 1926, **67**, 1—28).—Administration of calcium salts to thyreoparathyroidectomised dogs led to the retention of large amounts of calcium and phosphorus, the amount of calcium retained being about three times as much as the phosphorus; the greater part of the calcium and phosphorus retained was apparently deposited in the tissues as calcium phosphate. The effect of injection of sodium phosphate in producing tetany is apparently dependent on the concentration of calcium in the serum, since a parathyroidectomised dog in which the serum calcium was maintained at the normal level by administration of calcium salts, was as resistant to such injections as a normal animal, whilst it became much more sensitive when the serum calcium was allowed to fall. It is suggested that the calcium of the blood exists in the form of a small amount of ionic calcium in equilibrium with a large amount of an organic compound having physico-chemical properties resembling those of calcium citrate, and that the parathyroid hormone plays a part in the synthesis of this compound. C. R. HARINGTON.

Calcium of the blood-serum in experimental hypo- and hyper-calcæmia. A. R. MORITZ (J. Biol. Chem., 1925, **66**, 343—351).—Determinations of the relative amounts of diffusible and non-diffusible calcium by the author's method (A., 1925, i, 995) indicate that the hypocalcæmia which follows parathyroidectomy is accompanied by a relatively greater fall in the diffusible fraction; in the hypercalcæmia following injection of parathyroid extract no constant changes in the relationship of the two fractions were observed. C. R. HARINGTON.

Metabolism of the diabetic individual during and after muscular exercise. K. S. HETZEL and C. N. H. LONG (Proc. Roy. Soc., 1926, **B**, **99**, 279—306).—During short periods of muscular exercise, diabetic subjects show curves of oxygen intake and carbon dioxide output similar to those of normal men, although the maximum "oxygen debt" appears to decrease with the severity of the diabetes. For short periods of muscular exercise, not too long after a dose of insulin, the respiratory quotient of the excess metabolism is practically unity; for more prolonged periods the respiratory quotient is lower, whilst for any period of exercise where no insulin has been administered for a long time previously, the respiratory quotient of the excess metabolism is only slightly above the normal. The production and removal of lactic acid as shown by its concentration in the blood are the same as in normal individuals. Muscular exercise usually occasions a fall in the blood-sugar and blood-acetone concentrations, but not in the case of severe diabetics who have been without insulin for some time. W. O. KERMACK.

Carbon–nitrogen quotient of blood under normal and experimentally pathological conditions. L. GOMEZ (Biochem. Z., 1926, **167**, 424—432).—The total carbon and nitrogen of whole blood and blood filtrate after precipitation with tungstic acid have been determined for normal dogs and dogs which had experienced severe metabolic disturbance. The carbon and nitrogen contents of whole blood vary in different dogs and also in the same dog at different times, but the C : N ratio is constant at 3·5. For deproteinised blood, the value varies from 2 to 4 and the average value is 3. The ratio both for whole and for deproteinised blood is practically the same both after repeated bleeding, after poisoning

with phloridzin or phosphorus, and after pancreatectomy. P. W. CLUTTERBUCK.

Effect of pancreatectomy on the secretion of succus entericus. W. KOSKOWSKI and A. C. IVY (Amer. J. Physiol., 1926, **75**, 640—644).—Diet or starvation for 2—4 days does not affect the enzyme activity of the succus entericus. There is an increase in the content of invertase and a decrease in the amylase for a few days after pancreatectomy, followed by a return to normal. R. K. CANNAN.

Formation of lactic acid by depancreatised dogs. C. J. WEBER, A. P. BRIGGS, and E. A. DOISY (J. Biol. Chem., 1925, **66**, 653—669).—Both strychnine convulsions and exercise cause production of lactic acid in depancreatised dogs as in normal animals; prolonged starving of such dogs causes little or no depletion of the carbohydrate precursors of lactic acid which are present in the muscles. C. R. HARINGTON.

Blood diastases in depancreatised dogs. J. MARKOWITZ and H. B. HOUGH (Amer. J. Physiol., 1926, **75**, 571—578).—The diastase content of the blood of normal dogs is not constant. After complete removal of the pancreas there is a decrease within 20 hrs.; in partial pancreatectomy the decrease is slow. Insulin is without notable immediate effect, but depancreatised dogs kept alive with insulin have a normal blood-diastase activity. R. K. CANNAN.

Formation of deposits in gout and other diseases and the cause of swelling in beri-beri. N. R. DHAR (J. Physical Chem., 1926, **30**, 277—281).—Theoretical, in which the above are discussed in the light of researches on colloids. Sparingly soluble substances such as uric acid, calcium phosphate and oxalate are considered to remain in the body in the colloidal condition owing to the protective action of albuminous substances. Coagulation and crystallisation in the tissues then give rise to diseases such as gout, renal colic, oxaluria, lithiasis, etc.

Beri-beri is probably due to insufficient metabolism of carbohydrates owing to a deficiency of vitamin-*B*. L. S. THEOBALD.

Connexion between lipolytic power and cholesterol content of blood-serum in hypertonia. M. DÖRLE and H. VON WEISS (Biochem. Z., 1920, **167**, 395—400).—The increased metabolism in diabetes causes the lipolytic power of the blood-serum to be increased in spite of the decreasing effect of accompanying hypertonia. In luetic patients, decreased lipolytic power accompanies decreased blood pressure. In arteriosclerosis and essential hypertonia, lipolytic power is decreased or abolished, the cholesterol content being increased. In arteriosclerotic hypertonia, the lipolytic power under the influence of iodine therapy is increased, whereas the cholesterol content decreases. In those cases where iodine treatment fails and hypertonia remains, the cholesterol content increases and the lipolytic power decreases. P. W. CLUTTERBUCK.

Diazo- and urochromogen reaction of blood filtrate in renal insufficiency. E. BECHER (Deut. Arch. klin. Med., 1925, **148**, 10—18; from Chem. Zentr., 1925, II, 2016).—In severe renal insufficiency the filtrate, after treatment of blood with trichloroacetic acid, gives a definite diazo- and urochromogen reaction. Normal blood filtrate gives a slight yellow coloration with diazobenzenesulphonic acid in alkaline solution. This reaction is probably due to the presence in normal blood of tyrosine and histidine. In severe renal insufficiency the diazo-reaction is not due to mono- or di-hydric phenols, but aromatic hydroxy-acids may be concerned in it. G. W. ROBINSON.

Clinical and experimental studies on sodium benzoate. A. W. BRYAN (J. Clin. Invest., 1925, 2, 1—33).—Normally 70% of the benzoic acid administered by the mouth as sodium benzoate is excreted in the urine as hippuric acid in 2 hrs., or 85—90% in 3 hrs. In nephritis, but not in nephrosis, the excretion is reduced. Hepatic disease or experimental lesions affect the results only in so far as sufficient glycine may not be available for the synthesis. CHEMICAL ABSTRACTS.

Basal metabolism of some Orientals. G. MACLEOD, E. E. CROFTS, and F. G. BENEDICT (Amer. J. Physiol., 1925, **73**, 449—462).—The basal metabolism of Oriental women was 10·4% below the Harris and Benedict prediction standard. This is thought to be due to the specific low cell metabolism characteristic of Orientals. CHEMICAL ABSTRACTS.

Determination of energy values of foods and excreta. F. G. BENEDICT and E. L. FOX (J. Biol. Chem., 1925, **66**, 783—799).—The fact that the calorific value of oxygen (calories produced per 1000 c.c. of oxygen utilised in complete combustion), with respect to the different foodstuffs, varies only from 4·6 for proteins to 5·0 for carbohydrates, is utilised in the determination of the energy values of these materials by a method which eliminates the use of the bomb calorimeter. A known weight of the substance is burnt in a special combustion chamber connected with a respiration apparatus by which the oxygen utilised is measured. For approximate work, an average value of 4·825 is assumed as the calorific value of 1 litre of oxygen for a mixed diet of carbohydrates and fats. C. R. HARINGTON.

Glycolysis of embryonic tissue. E. NEGELEIN (Biochem. Z., 1925, **165**, 122—133).—Glycolysis (in absence of air) was most intense in a rat embryo of 0·47 mg. and decreased rapidly in embryos which were lighter or heavier than this. At the optimum, glycolysis is comparable with that of tumour cells (rat). The fœtal membranes behave similarly. Slight aërobic glycolysis occurs when embryos are suspended in Ringer solution or serum, but not in amniotic fluid.

Frog's retina glycolyses aërobically and anaërobically in Ringer solution or serum, but less intensely than the retina of the rat. C. RIMINGTON.

Effect of ions on liver and carbohydrate metabolism. I. Effect of electrolytes on hepatic secretion. II. Effect of electrolytes on carbohydrate metabolism. III. Effect of Ca and Na on glucogenetic function of the liver. N. HEIANZAN (Biochem. Z., 1925, **165**, 33—56, 57—80, 80—89).—I. Secretion of bile is inhibited by sodium, magnesium,

and calcium, and stimulated by potassium. The effect of sodium is not specific.

II. Hyperglycæmia is caused by calcium and sodium, but potassium and magnesium are without effect, as also is calcium in adrenalectomised animals. In animals with alimentary hyperglycæmia, when the ions magnesium, sodium, potassium are injected simultaneously with the sugar, a hyper- followed by a hypo-glycæmia occurs and the reverse with calcium, but when given prior to sugar, calcium raises, and sodium, potassium, magnesium lower the blood-sugar.

III. Calcium and sodium chlorides raise the blood-sugar of starved (glycogen-free) animals, but are without effect after phosphorus poisoning. Such livers still respond to adrenaline. The effect of ions involves the liver, but the presence of glycogen is not essential. C. RIMINGTON.

Carbohydrate metabolism of the central nervous system. III. Carbohydrate and glycogen content of the central nervous system of normal and narcotised animals, and of animals subjected to prolonged treatment with sodium bromide. S. UCHIDA (Biochem. Z., 1926, **167**, 9—20; cf. A., 1925, i, 1487).—Narcotics such as ether, chloroform, urethane, and morphine, which have a transitory exciting action on the central nervous system, cause considerable diminution in the glycogen and free carbohydrate of the brain. Protracted treatment with sodium bromide causes only a slight decrease, which can be referred to the poor condition of the animal. E. C. SMITH.

Function of the kidneys in the breakdown of β-hydroxybutyric acid. I. SNAPPER, A. GRÜNBAUM, and J. NEUBERG (Biochem. Z., 1926, **167**, 100—106; cf. A., 1924, i, 1141).—Kidneys perfused with defibrinated blood containing butyric acid produce no acetone, acetoacetic acid, or β-hydroxybutyric acid. β-Hydroxybutyric acid is removed when perfused without the appearance of acetone or acetoacetic acid. The lungs do not oxidise β-hydroxybutyric acid. E. C. SMITH.

Oxidation of acetoacetic acid and ester by hydrogen peroxide and its biochemical significance. P. W. CLUTTERBUCK and H. S. RAPER (Biochem J., 1926, **20**, 59—68).—The oxidation of the sodium derivative of acetoacetic acid or its ethyl ester in the cold by means of hydrogen peroxide yielded mainly α-hydroxyacetoacetic acid or αβ-dihydroxycrotonic acid. This compound gradually loses carbon dioxide and passes into acetylcarbinol. By subsidiary reactions, acetonylacetone, diacetylsuccinic, acetonylacetoacetic, acetic, glyoxylic, and oxalic acids are formed. The possible formation of carbohydrate from acetoacetic acid and also the possible origin of substituted pyrroles in the living organism are discussed in the light of the above results. S. S. ZILVA.

Lactic acid formation in smooth muscle in *rigor mortis*. I. E. MANGOLD and C. SCHMITT-KRAHMER (Biochem. Z., 1926, **167**, 1—8).—The mean lactic acid content of the smooth muscle of the pigeon's gizzard is 0·075%. This value increases to a maximum, mean 0·110%, 3 hrs. after death. The lactic acid production coincides with, and is the cause of, the contraction and hardening of the muscle after death. E. C. SMITH.

Muscle fatigue. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1926, **168**, 128—165).—There is an increase in the c_H of frog's muscle after fatigue or chloroform rigor which is to be accounted for by the parallel production of lactic acid. The p_H is determined in an ice-cold water extract of the muscle by means of the quinhydrone electrode. As a result of fatigue or rigor, there is an increase in the ash of the alcohol-soluble fraction of muscle roughly equivalent to the lactic acid production. The lactic acid appears to have rendered free an equivalent of fixed base, of which less than one-half is to be attributed to the liberation of free phosphate. The larger part is derived from the proteins (the water-insoluble fraction of the muscle). Contrary to Embden, it is found that the formation of lactic acid is coincident with contraction if moderate stimuli be employed. The hydrolysis of sodium hexosephosphate at the c_H of muscle leads to only a slight increase in c_H, accompanied by an increase in the buffer capacity. R. K. CANNAN.

Lactic acid changes in tetanus. G. EMBDEN, H. HIRSCH-KAUFFMANN, E. LEHNARTZ, and H. J. DEUTICKE (Z. physiol. Chem., 1926, **151**, 209—231).—The lactic acid content of isolated frog's muscle (in air or in hydrogen) is considerably lower immediately after a short tetanus than 5—30 sec. after. The muscle is dropped into liquid air at the required time, the powdered tissue extracted with ice-cold hydrochloric acid, the muscle proteins precipitated by Schenk's method, and the lactic acid in the filtrate determined by the method of Hirsch and Kauffmann. The relationship is discussed of this liberation of a relatively large quantity of lactic acid after the contraction period to the accepted explanation of the heat changes in muscle. H. D. KAY.

Phosphoric acid production in fatigued frog's muscle. G. EMBDEN and H. HENTSCHEL (Z. physiol. Chem., 1926, **151**, 167—202).—After a long period of stimulation of an isolated frog's muscle by repeated induction shocks, the inorganic phosphoric acid (which has been shown to be present momentarily at each contraction, but which is, in the unfatigued muscle, resynthesised at once into lactacidogen) begins to rise in quantity, and with increasing fatigue of the muscle remains in larger and larger amounts. The same phenomenon of incomplete reversibility is also observed after long tetanic stimulation. If the period of stimulation has not been too prolonged, the muscle is still capable, in oxygen, of at least partial resynthesis of the phosphoric acid into phosphoric ester. Muscles fatigued in air or in hydrogen contain greater amounts of free phosphoric acid than similar muscles stimulated for the same period in oxygen. H. D. KAY.

Influence of temperature on phosphoric acid in fatigued muscle. M. ALTMANN (Z. physiol. Chem., 1926, **151**, 203—208).—If the two gastrocnemii in the frog are maintained, one at 5°, and the other at 25°, and are both stimulated simultaneously until fatigued, the muscle at the higher temperature

contains a greater quantity of free phosphoric acid than that maintained at the lower temperature.
H. D. KAY.

Connexion between carbohydrate and phosphoric acid metabolism. I. Hydrolysis of hexosediphosphoric acid in the mammalian organism. O. FÜRTH and J. MARIAN (Biochem. Z., 1926, **167**, 123—155).—Parenteral administration of hexosediphosphoric acid to a dog fed on a diet of sucrose and lard resulted in the phosphoric acid being retained to the extent of 80% after the first injection and 46% after the second, whilst a fasting dog retained 63% and 22% after the first and second injections, respectively. No glycosuria followed the administration of 40 g. of hexosediphosphoric acid *per os*, and the normal sodium salt injected subcutaneously caused no irritation and was rapidly absorbed. Parenteral administration also had no ill effects, but guinea-pigs died after receiving 7·5—10 g. per kg. subcutaneously, owing to the toxicity of the phosphate formed on hydrolysis. The determination of sodium and phosphoric acid in the sodium hexosediphosphate gave results in accordance with the accepted constitution, but after acid hydrolysis, determination of the reducing sugar gave only 50% of the theoretical. An attempt to apply Hehner's method for the determination of glycerol to carbohydrates gave theoretical results in the case of dihydroxyacetone, dextrose, and lævulose, but with hexosediphosphate only 25% of the theoretical. E. C. SMITH.

Influence of exercise on the inorganic phosphates of the blood and urine. R. E. HAVARD and G. A. REAY (J. Physiol., 1926, **61**, 35—47).—Following short vigorous exercise, there is first a rise above the normal level of inorganic phosphate and then a fall below. In trained athletes, the rise is more pronounced and the fall below the normal may be suppressed. The changes are attributed to changes in the lactacidogen content of the muscles. The chloride excretion is depressed and the ammonia excretion increased in the same period, due probably to the fleeting acidosis associated with lactic acid production. R. K. CANNAN.

Maintenance values for the proteins of milk, meat, bread and milk, and soya-bean curd. M. S. ROSE and G. MACLEOD (J. Biol. Chem., 1925, **66**, 847—867).—Comparison of the relative efficiency of the above foods in maintaining a positive nitrogen equilibrium (in women), when they formed practically the sole source of protein in the diet, showed that, with an intake of protein of 0·5 g. per kg. bodyweight, the nitrogen balance was at almost all times positive. In the case of the soya bean, the fæcal nitrogen was 24% of the total nitrogen excreted; in no other case did it amount to more than 10—12%. The diets containing milk and bread and milk led, on the whole, to a larger retention of nitrogen than the meat diets. C. R. HARINGTON.

Blood changes during digestion. Urea formation. S. MORGULIS (J. Biol. Chem., 1925, **66**, 353—365).—A protein meal, subsequent to a period of fasting, causes, in dogs, an increase in the urea of the blood which precedes the increase in the amino-acids; the concentration of the latter may actually fall during the early stages of digestion. The blood of fasting dogs with an established Eck fistula contains very little urea but a normal amount of amino-acids. The results indicate the predominant importance of the liver in the process of urea formation.
C. R. HARINGTON.

Site of ammonia formation; *rôle* of vomiting in elimination of ammonia. S. BLISS (J. Biol. Chem., 1926, **67**, 109—140).—The observation of Nash and Benedict (A., 1922, i, 191) regarding the relatively large amounts of ammonia in the renal vein have been confirmed, but it has been further shown that the venous blood from other organs (*e.g.*, the pancreas) has a similarly high content of ammonia, and, further, that ligation of the renal blood-vessels is followed by an increase in the ammonia of the arterial blood; formation of ammonia cannot therefore be an exclusive function of the kidneys, as supposed by the earlier workers, but must occur in other organs as well. The failure of Nash and Benedict (*loc. cit.*) to observe significant increases in the ammonia of the blood following double nephrectomy was due to the considerable elimination of ammonia by the vomiting which occurs in the animals subjected to this operation. C. R. HARINGTON.

Metabolism of amino-acids and fatty acids. H. D. DAKIN (J. Biol. Chem., 1926, **67**, 341—350).—Administration of β-triphenylpropionic acid to rabbits resulted in the recovery of 55—72% of the unchanged acid from the urine; in this case at least, therefore, α-oxidation does not take place in the organism. α-Amino-β-dimethyl-*n*-butyric acid was excreted unchanged to the extent of 46%, whereas the isomeric leucine, under similar conditions, is 90% oxidised; this indicates the resistance to physiological oxidation of α-amino-acids containing no unsubstituted hydrogen atoms attached to the β-carbon atom, and supports the view that αβ-dehydrogenation may be the first stage in the oxidation of the amino-acids. *α-Carbamido-β-dimethyl-*n*-butyric acid* has m. p. 221°; *tert.-butylhydantoin* has m. p. 242—243° (decomp.). No oxidation of acrylic acid or of β-hydroxypropionic acid by muscle- or liver-tissue could be observed. The uramino-acids and hydantoins derived from leucine and phenylalanine were excreted for the most part unchanged, whilst the corresponding derivatives of glutamic and aspartic acids were almost entirely oxidised after administration to rabbits.
C. R. HARINGTON.

Influence of ternary food factors on nitrogen absorption during growth. E. F. TERROINE and A. M. MENDLER (Compt. rend., 1926, **182**, 413—416; cf. this vol., 197).—The nitrogen retention of growing pigs is increased by addition of ternary food factors; addition of sufficient carbohydrates such as starch or tapioca flour may increase this retention fourfold, whilst butter has a much smaller effect.
L. F. HEWITT.

Nitrogen and sulphur metabolism. H. E. C. WILSON (Biochem. J., 1926, **20**, 76—83).—Gelatin ingested during starvation can be retained in part for at least 6 days. Meat extractives ingested during

nitrogen starvation are in part retained and seem to exercise an inhibitory influence on nitrogen catabolism. The retained portion does not correspond in composition with muscle-tissue. Excess water ingestion increases the output of nitrogen in the urine by stimulating the catabolism of protein. The capacity of the tissues to retain protein also seems to be stimulated. Further evidence is adduced that in storage of protein the sulphur is retained first.

S. S. Zilva.

Nutrition of the white mouse. II. *Rôle* of certain sulphur compounds. III. Vitamin factors in the nutrition of mice. H. H. Beard (Amer. J. Physiol., 1926, **75**, 658—667, 668—681).—II. Taurine cannot replace cystine in the diet of mice. It is not merely sulphur, but cystine sulphur which is required by the organism. Cystine is the limiting amino-acid factor in caseinogen.

III. The requirement of the mouse for vitamin-*B* is in linear relation to the product of its weight, its surface, and the number of calories metabolised per day. R. K. Cannan.

Cholesterol. I. Synthesis of cholesterol in the animal body. F. S. Randles and A. Knudson (J. Biol. Chem., 1925, **66**, 459—466).—The total cholesterol in the bodies of white rats which have been kept, from the time of weaning, on a diet free from cholesterol, is not markedly different from that found in rats of the same age which have been kept on a normal diet. The organism of the rat is therefore apparently able to synthesise cholesterol (cf. Channon, A., 1925, i, 1001). C. R. Harington.

I. Cholesterol and phosphatide metabolism in pregnancy. II. Cholesterol and phosphatide distribution in some tissues of pregnant and non-pregnant rabbits. E. J. Baumann and O. M. Holly (Amer. J. Physiol., 1926, **75**, 618—631, 632—639).—I. There is little change in the blood lipins in pregnancy in dogs; in man there is an increase and in rabbits a decrease. Both in man and in the rabbit, the content in cholesterol and in phosphatides of the blood of the embryo is of the same magnitude as that of the young.

II. The increase in cholesterol and phosphatides in the mammary gland and elsewhere in human pregnancy is sufficient to account for the fall in blood lipins. R. K. Cannan.

Utilisation of minerals by ewes during the period of gestation. A. R. Winter (Amer. J. Physiol., 1925, **73**, 379—386).—In the early period of pregnancy, positive balances were obtained for nitrogen, sulphur, magnesium, phosphorus, sodium, and potassium, chlorine balances were variable, and 15 of 22 calcium balances were negative, the rations containing timothy hay or lucerne with or without bone meal. Chemical Abstracts.

Value of calcium phosphate as a supplement to the ration of dairy cows. J. B. Lindsey and J. G. Archibald (J. Agric. Res., 1925, **31**, 771—791).—A ration low in calcium was fed to dairy cows (Jerseys and Holsteins), with and without addition of calcium phosphate in the form of steamed bone meal. No effects definitely attributable to the calcium phosphate were observed, with the possible exception of an increase of the calcium content of the milk. Both rations apparently affected the milk production of the younger Jersey cows, but had no serious ill effects on the other animals. The experiment has been carried on for 2½ years.

C. T. Gimingham.

Mineral elements in animal nutrition. J. B. Orr (Brit. Assoc. Rep., 1925, 204—215).

Potassium in animal nutrition. III. Influence of potassium on excretion of sodium, chlorine, calcium, and phosphorus. H. G. Miller (J. Biol. Chem., 1926, **67**, 71—77).—Addition to the diet of rats of large amounts of potassium salts caused an immediate increase in the excretion of sodium and chlorine, which subsequently fell off, and a slight increase in the excretion of calcium and phosphorus. C. R. Harington.

Benzoylated amino-acids in the animal organism. I. Behaviour of hippuric acid following oral administration. W. H. Griffith **II. Hydrolysis of hippuric acid in the alimentary canal of the rabbit.** W. H. Griffith and P. B. Cappel (J. Biol. Chem., 1925, **66**, 671—681, 683—690).—I. The rate of excretion of hippuric acid, following oral administration of sodium hippurate to rabbits, was increased by the simultaneous administration of glycine or of protein containing much glycine; the absorption of sodium hippurate from an isolated loop of the intestine was slow.

II. Hippuric acid and benzoylalanine (but not α-benzamido*iso*butyric acid) were hydrolysed when introduced into the cæcum or the colon of rabbits; in conjunction with the results recorded above, this indicates that hippuric acid is first hydrolysed in the large intestine before absorption, the increased rate of excretion of hippuric acid caused by glycine being due to increased rate of re-synthesis from the latter and the benzoic acid derived by intestinal hydrolysis of the hippuric acid originally administered.

C. R. Harington.

Fate of creatine in the human organism. A. Chanutin (J. Biol. Chem., 1926, **67**, 29—41).—Oral administration of creatine to man is followed by retention of large amounts of the substance; after sufficiently prolonged intake of creatine, however, a definite increase in the excretion of creatinine occurs. Ingestion of creatine exerts a slight sparing effect on the nitrogenous metabolism.

C. R. Harington.

Fate of sugar in the animal body. I. Rate of absorption of hexoses and pentoses from the alimentary tract. C. F. Cori (J. Biol. Chem., 1925, **66**, 691—715).—The rates of absorption of various sugars have been determined by administration of known amounts to rats, and, after definite intervals, killing the animals and determining the total sugar remaining in the whole of the intestinal tract. In this way, the substances investigated have been arranged in the following (descending) order with respect to their rates of absorption: galactose,

dextrose, lævulose, mannose, xylose, arabinose. The rate of absorption of the hexoses was independent of the concentration of the sugar solution (from 25% to 80%) and was also independent of the amount remaining in the intestine (up to 70% absorption of the total amount of sugar); within these limits, the rate of absorption was constant for each sugar. The hypertonic sugar solutions administered were diluted in the stomach by excretion of water, but the skin was the only tissue to show signs of dehydration during the absorption of such hypertonic solutions. Amounts of dextrose up to 15 g. per kg. could be given to rats without producing glycosuria.

C. R. HARINGTON.

Ingestion of nitroanthraquinone. H. JOHN and V. FISCHL (Biochem. Z., 1926, **167**, 419—423).—When 20 g. of 1-nitroanthraquinone are fed to a number of guinea-pigs, none can be found in the fæces and only the following small amounts can be recovered from the urine: 0·87 g. as 1-aminoanthraquinone, 0·38 g. as 1-amino-4-hydroxyanthraquinone, 0·35 g. as 1 : 2 : 7-trihydroxyanthraquinone, and 0·03 g. as an unidentified aminohydroxyanthraquinone, m. p. above 320° (cf. A., 1925, i, 465).

P. W. CLUTTERBUCK.

Passage of chemical substances from the vascular system into the tissues. C. PAK (Arch. exp. Path. Pharm., 1926, **111**, 42—59).—Isolated organs were perfused at constant rate with a fluid containing the substance studied. From the difference in its concentration in the ingoing and outflowing fluids, the rate of absorption was determined. Ammonium chloride, urea, dextrose, dihydroxyphenylalanine, adrenaline, strophanthin, "verodigen" (a preparation of gitalin), and a number of alkaloids passed with equal ease into the tissues of the frog. The concentration in the tissues reached equilibrium with the perfusing fluid within a few hours, except in the case of the majority of the alkaloids, where considerable storage was inferred. Perfusion of the liver (frog and dog) with adrenaline resulted in long-continued absorption, due to destruction of the adrenaline by the liver-tissue. This was not observed with muscle of either warm- or cold-blooded animals.

R. K. CANNAN.

Behaviour and action of bile acids in the organism. A. ADLER (Z. ges. exp. Med., 1925, **46**, 371—424; from Chem. Zentr., 1925, II, 2002—2003).—Intravenous injection of 20 c.c. of 10% sodium dehydrocholate produces no harmful effect. The addition of increasing amounts of bile salts to blood-serum, urine, or bile does not produce a continuous decrease in surface tension; in some cases surface tension may be increased. Surface-active substances may cause increase or decrease in viscosity. Bile acids increase the viscosity of colloidal solutions of cholesterol, blood-serum, bile, and urine. Bile acids cannot be determined by methods depending on surface tension. Injection of bile salts in man is often unaccompanied by corresponding decrease in the surface tension of blood and urine. In individual cases, intravenous injection of bile acids may produce an increase in the surface tension of the blood and a decrease in that of the urine, and *vice versa*. Bile secretion is increased and the bile is richer in pigments. Injection of concentrated cholate solutions results in an increase in the bilirubin content of the urine together with a decrease in the bilirubin content of the bile. Liberation of bile constituents retained in the kidneys also occurs. Excretion of tetrachlorophenolphthalein in the bile is increased after injection of bile acids. Tetrachlorophenolphthalein alone causes increased flow of bile.

G. W. ROBINSON.

Relation between chemical constitution and taste of sweet substances. K. TÄUFEL (Biochem. Z., 1925, **165**, 96—101).—No generalisation is possible. The property of sweetness occurs in diverse chemical types; it may be physico-chemical. The sweetness of disaccharides is not an additive function of the sweetness of the constituent monosaccharides.

C. RIMINGTON.

Structural relationships of the cardiac poisons. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1926, **67**, 333—339).—Strophanthidin and those of its derivatives which still possess an unsaturated linking in the lactone ring (A., 1925, i, 1082) are characterised by their ability to reduce Tollens' reagent and to give a red colour with nitroprusside in alkaline solution; on saturation of this linking, both the power to give these reactions and the greater part of the toxicity disappear. The nitroprusside reaction also disappears after hydrolysis of the lactone. Similar observations were made on ouabain, on digitoxin, and, with regard to Tollens' reagent, on bufagin (cf. Abel and Macht, A., 1912, ii, 1193); it would therefore appear that the pharmacological action of these compounds may be connected with the presence of the unsaturated lactonic grouping.

C. R. HARINGTON.

Physiological action of histidine anhydride and of histidylhistidine [methyl] ester. T. HOSODA (Biochem. Z., 1926, **167**, 221—226).—The action of *l*-histidyl-*l*-histidine and its methyl ester, and of *l*-histidine anhydride on the isolated rabbit's intestine and uterus, and on the blood-pressure of the intact animal, has been investigated. Histidine anhydride has a slight action on the uterus at a concentration of 1 in 4000, histidylhistidine methyl ester a marked action at 1 in 20,000, but histidylhistidine is quite inactive at 1 in 1000. The masking of the free carboxyl group thus accentuates the physiological action. Subcutaneously 0·07 g. per kg. of histidine anhydride has no action on the blood-pressure.

E. C. SMITH.

Effect of histamine on blood chlorides. T. G. H. DRAKE and F. F. TISDALL (J. Biol. Chem., 1926, **67**, 91—100).—Injection into dogs of sub-lethal doses of histamine caused a reduction in the chloride content of the blood plasma; the degree of this reduction bore no definite relation to the degree of intoxication, nor was it due to loss of chlorides by increased gastric secretion.

C. R. HARINGTON.

Mechanism of intestinal secretion. IV. Action of known quaternary ammonium bases of meat extract on intestinal secretion. S. A. KOMAROV (Biochem. Z., 1926, **167**, 275—312).—Choline administered in doses of 30—35 mg./kg. has

no direct stimulatory or inhibitory action on intestinal secretion, the primary stimulatory effect being destroyed by a secondary inhibition caused by the entry of acid gastric juice into the duodenum. Stimulation with choline may occur even with doses of 1 mg./kg., but it is not so powerful as methylguanidine or carnosine. Carnitine also must be regarded as a subsidiary hormone stimulating intestinal secretion. The minimal stimulatory dose is about 0·05 g./kg., the total body content being 0·1 g./kg. It is much less powerful than methylguanidine, carnosine, or choline (cf. *ibid.*, 1924, **146**, 122; **147**, 221; **151**, 467). P. W. CLUTTERBUCK.

Pharmacological properties of pure *apo*-codeine. O. KRAYER (Arch. exp. Path. Pharm., 1926, **111**, 60—67).—No important difference was found between the pharmacological action of crystalline *apo*codeine and that of an amorphous commercial preparation. Quantitatively the former was some five times as active. R. K. CANNAN.

Effect of morphine on the concentration of ions in the blood plasma. M. CLOETTA and E. BRAUCHLI (Arch. exp. Path. Pharm., 1926, **111**, 254—262).—Although narcotics of the aliphatic series cause a decrease in the calcium and an increase in the potassium content of the blood plasma of dogs, yet no constant result was obtained after the administration of morphine. In both cases the sodium remained constant and the surface tension decreased very slightly. W. O. KERMACK.

Liberation of free phosphoric acid from surviving brain pulp and the influence of drugs. W. STAMM (Arch. exp. Path. Pharm., 1926, **111**, 133—148).—Brain pulp prepared in such a way as to make probable the survival of living cells shows during the first 3—6 hrs. rapid increases in non-coagulable nitrogen, and in free phosphoric acid when kept at 38° in Locke's solution. These increases are arrested by low temperature and are uninfluenced by the presence of oxygen. The phosphoric acid appears to be derived rather from the phosphatides of the brain than from lactacidogen. The effect on the liberation of free phosphoric acid of various drugs, chloroform, quinine, strychnine, scopolamine, atropine, nicotine, cocaine, caffeine, urethane, sodium bromide, morphine, and camphor, has been investigated. W. O. KERMACK.

Effects of narcotics on the composition of the cerebral cortex. A. TSCHERKES and H. GORODISSKY (Biochem. Z., 1926, **168**, 48—60).—Dogs were kept under deep anæsthesia with ether, chloroform, or chloral hydrate for 40—135 min. and then the nitrogen, phosphorus, cholesterol, and lipins of the grey matter were determined. The quantity of the unsaturated phosphatides was reduced, whilst the alcohol-soluble lipins were increased by the three anæsthetics. The most notable specific effect was the increase in cholesterol after chloral hydrate.
R. K. CANNAN.

Action of mixtures of gases. R. HOFER (Arch. exp. Path. Pharm., 1926, **111**, 183—205).—The effect of a mixture of carbon monoxide and hydrogen sulphide on white mice, and of carbon monoxide and hydrogen cyanide on cats, has been examined. An increase in the toxicity of the gases occurs when they are administered simultaneously.
W. O. KERMACK.

Partition problems. I. Organic lead compounds. R. EHRENBERG (Biochem. Z., 1925, **161**, 337—338).—Lead triethyl chloride and lead triphenyl chloride were injected into different rabbits. These were killed and the organs etc. analysed for lead. No lead was found in the blood after lead triphenyl chloride, whilst it was present in this fluid after the ethyl compound. A noteworthy amount was deposited in the brain and cord in both cases.
H. I. COOMBS.

Effect of excessive ingestion of calcium on calcium content of tissues with and without application of ultra-violet light. W. DENIS and R. C. CORLEY (J. Biol. Chem., 1925, **66**, 609—617).—No increase in the calcium content of the tissues of rabbits was observed following the daily oral administration of calcium chloride or calcium lactate, whether or not the animals were simultaneously irradiated with ultra-violet light.
C. R. HARINGTON.

Sensitisation by porphyrins, especially by putrefaction porphyrin, with respect to light rays and *X*-rays. H. KÄMMERER and H. WEISBECKER (Arch. exp. Path. Pharm., 1926, **111**, 263—280).—Putrefaction porphyrin is particularly powerful in sensitising animals to sunlight, but neither it nor any of the other porphyrins investigated sensitises animals or blood-cells with respect to *X*-rays.
W. O. KERMACK.

Physiological action of light. VI. Alterations in cell electrophoretic potential produced by direct irradiation of the blood *in vivo*. I. S. FALK and C. I. REED (Amer. J. Physiol., 1926, **75**, 616—617).—There is a small but definite decrease in the negative electrophoretic potential of the red blood-cells. R. K. CANNAN.

Enzymic breakdown and synthesis of carbohydrates. H. VON EULER and K. MYRBÄCK (Svensk Kem. Tidskr., 1925, **37**, 173—184; from Chem. Zentr., 1925, II, 1875—1876).—Synthesis of glycogen is not a reversal of enzymic hydrolysis through the stages dextrose → maltose → dextrin (or polyamyloses) → glycogen. This is inferred from unpublished investigations by Sjöberg and also from the view that blood-sugar, the degradation product of glycogen, has not the structure and configuration attributed to α- and β-1 : 4-glucose; it should therefore be termed "bioglucose." The enzyme systems hitherto used in attempts to synthesise glycogen from dextrose contain no enzyme capable of changing 1 : 4-glucose into "bioglucose." The primary enzymes concerned in the hydrolysis of starch or glycogen are bioglucosidases, which may be separable into α- and β-forms. The amylobiase of Pringsheim is identical with β-bioglucosidase. It is supposed that glycogen and starch are not attacked by 1 : 4-α-glucosidase (maltase) or by the corresponding

β-glucosidase. The action of emulsin on starch is due to the presence of a bioglucosidase. In a system containing β-glucosidase only, this enzyme attacks glycogen with formation of biodiglucose (γ-diglucose). Bioglucose may be transformed into 1 : 4-glucose without the action of an enzyme, but di- and tri-amyloses are only formed by enzymic action. Hexose-phosphate and lactic acid probably play a part in the synthesis of carbohydrates. It was shown experimentally that a carcinoma of great fermentative power produced no fermentation of pyruvic acid. The formation of acetaldehyde in animals and plants is probably not due to carboxylases.

G. W. Robinson.

Action of catalase in autotrophic plants. M. Gračanin (Biochem. Z., 1926, **168**, 429—442).—The activity of the catalase of germinating seeds increases to a maximum—generally on the fourth or fifth day. In dicotyledons, the catalase is chiefly localised in the embryo and cotyledons, and in the monocotyledon *Zea mays*, in the embryo and endosperm. In all the seeds examined, the testa contained only small amounts of catalase, and it is therefore thought that the catalase has some distinct function in the germinating seed. After the fifth day, the activity of the catalase in the cotyledons decreases, but rises in the roots to a practically constant value and also rises quickly in the stalks to approximately the same level as in the cotyledons. In the fully developed plant the catalase is chiefly in the leaves and roots. H. I. Coombs.

Activity and iron content of highly active catalase preparations. S. Hennichs (Ber., 1926, **59**, [*B*], 218—225; cf. A., 1924, i, 697).—Fresh horse liver is extracted with an equal quantity of distilled water and the extract treated with half its volume of alcohol (or with toluene), whereby a considerable quantity of inactive matter together with an inhibitory substance is precipitated. The clear solution is treated with an equal volume of alcohol, and the precipitated substance is immediately dissolved in water. Further purification is effected by adsorption with aluminium hydroxide and kaolin and elution with disodium hydrogen phosphate. The "activity" of the catalase—(reaction constant)/(dried residue in 50 c.c. of the reaction mixture)—is thereby raised to 25,000. The iron content of catalase preparations of "activity" 10,872—25,000 varies only between 3·33% and 4·12%, whilst from 11·33% to 12·09% of ash is present. The products are no more sensitive towards hydrocyanic acid than Senter's hæmase (A., 1903, ii, 662) with much lower activity. Their behaviour does not afford any support to Warburg's hypothesis that the action of hydrocyanic acid on the respiratory process consists in combining with catalytically active iron.

H. Wren.

Enzymes and light. VIII. L. Pincussen. Catalase. I. F. Seligsohn (Biochem. Z., 1926, **168**, 457—463).—Blood catalase is more active in dilute than in strong solutions, but is destroyed more quickly by irradiation in the former than in the latter. Similarly, at the optimum p_H (6·81), it is destroyed most rapidly by irradiation. The addition of a salt diminishes the activity of the catalase, but protects it from the action of light. The case of potassium iodide is complicated by the destructive action of the iodine liberated by the light, and this effect was also observed when "alival," $[CH_2I{\cdot}CH(OH){\cdot}CH_2{\cdot}OH]$, was added. H. I. Coombs.

Alterations in the enzyme activity of the blood. L. Pincussen. II. Factors governing the alteration of catalase. F. Seligsohn. III. The influence of radiation on catalase. L. Pincussen (Biochem. Z., 1926, **168**, 464—473, 474—480).—II. When 0·5 c.c. of a 1 : 100 pilocarpine solution or 0·5 c.c. of a 1 : 1000 adrenaline solution was injected into a rabbit the results were uncertain, but with 1 c.c. a distinct rise in the activity of the catalase in the blood was observed with the pilocarpine and a fall with the adrenaline. In the last case, change of diet influenced the result. Insulin and adrenaline act in the same sense and mutually strengthen each other's effect. Injection of potassium cyanide in non-lethal doses did not markedly affect the catalase of the blood (cf. A., 1925, i, 94).

III. The activity of the blood-catalase of the rabbit, kept in the dark, is slightly greater than when the animal is exposed to light, especially if a sensitiser be given. Experiments carried out at high and low altitudes appear to give the same results.

H. I. Coombs.

Catalase property of hæmoglobin. A. Kultjugin (Biochem. Z., 1926, **167**, 238—240).—Solutions of repeatedly crystallised oxyhæmoglobin show no catalase activity. Hæmoglobin precipitated from solutions of erythrocytes by chloroform is inactive, whilst the filtrate, free from hæmoglobin, rapidly destroys hydrogen peroxide. There is no proportionality between the catalase activity of blood and its oxyhæmoglobin value, and therefore no connexion between the blood-pigment and the enzyme.

E. C. Smith.

Loss of catalase activity of blood on keeping. A. Kultjugin (Biochem. Z., 1926, **167**, 241—244).—On keeping for 2½ hrs. the catalase activity of human, rabbit's, and guinea-pig's blood falls 3·3, 5·4, and 14·4%, and for 5 hrs., 5·4, 11·3, and 23·8%, respectively. E. C. Smith.

Peroxydase function of oxyhæmoglobin. A. Bach and A. Kultjugin (Biochem. Z., 1926, **167**, 227—237).—The peroxydase content of blood is proportional to, and may be calculated from, the oxyhæmoglobin value. A second determination of the peroxydase by the guaiacol method is unnecessary. Oxyhæmoglobin must be regarded as a peroxydase, since it differs in properties, such as thermolability, and sensitivity to acids, only quantitatively from the plant peroxydases. E. C. Smith.

Poisoning of lipase by quinine and atoxyl. P. Rona and K. Gyotoku (Biochem. Z., 1926, **167**, 171—181).—The lipase of the mucous lining of the stomach of the rabbit and dog, and of the pancreas of the rabbit, ox, sheep, and pig, purified by the method of Willstätter, Haurowitz, and Memmen (A.,

1925, i, 201), is slightly less sensitive to atoxyl and quinine than the crude lipase, and rabbit's liver lipase is much less sensitive. Pig's stomach lipase is, however, much more sensitive when pure. A mixture of the enzymes behaves as the sum of its constituents, hence the protective accompanying substances must be very closely associated with the enzyme.

E. C. SMITH.

Yeast maltase. VI. R. WILLSTÄTTER and E. BAMANN (Z. physiol. Chem., 1926, **151**, 242—272).—Properly buffered, yeast maltase has an optimum p_H at 6·75—7·25. The kinetics of the action of maltase on maltose depends in a marked degree on the purity of the enzyme preparation. Using maltase purified by adsorption on alumina, the product of the reaction time and the amount of enzyme is found to be constant for the same amount of hydrolysis. Addition of alumina, in insufficient quantity to remove the whole of the maltase, to an impure maltase solution (yeast autolysate) completely alters the shape of the hydrolysis–time curve. A maltase unit is that amount of enzyme which, acting on 2·5 g. of maltose hydrate in 50 c.c. of solution at 30° and p_H 6·8, will hydrolyse 50% of the sugar in 1 min. Methods of determining the maltase content of yeast and of yeast preparations are given. Contrary to the usually accepted statement, maltase is more readily separable from yeast than is invertase. Fresh yeast is treated with finely-powdered diammonium phosphate and after 1 hr. the liquid resulting is diluted with ten times the volume of water (calculated on the dried yeast). After 5—8 hrs., the maltase is quantitatively in solution. A similar result may be obtained by treating pressed yeast with ethyl acetate, diluting with water, and neutralising with ammonia. On keeping for 1 day, 95—100% of the maltase of the yeast is found in solution. Maltase is far less stable than invertase, but may be kept at 0° for a week without diminution in activity. The activity of most preparations actually increases at first, reaching a maximum value between the second and fifth day after preparation. Subsequently the activity begins to fall off.

H. D. KAY.

Maltase. VII. Separation of maltase and invertase. R. WILLSTÄTTER and E. BAMANN (Z. physiol. Chem., 1926, **151**, 273—285).—The action of a series of hydrogels on the mixture of maltase and invertase which occurs in yeast autolysates has been studied. Kaolin adsorbs maltase much more readily than invertase, but destroys it rapidly, and only from 14 to 20% of the adsorbed enzyme can be recovered. Aluminium hydroxide also adsorbs the maltase preferentially, but gives much better yields on elution. Using an autolysate from a yeast rich in invertase, a single adsorption with an aluminium hydroxide gel is sufficient to free the invertase practically completely from maltase, leaving some 80% of the invertase in the unadsorbed residue. An adsorbate containing both maltase and invertase may be freed from the latter enzyme by elution at 0° with potassium dihydrogen phosphate solution, which leaves the maltase still adsorbed. Subsequent elution with diammonium phosphate gives a maltase preparation free from invertase.

H. D. KAY.

Effect of high concentrations of neutral substances on the action of peptase. A. BLAGOVESTSCHENSKI (Biochem. Z., 1926, **168**, 6—13).—The inhibition of the action of trypsin on peptone by high concentrations of dextrose, sucrose, or sodium chloride varied as $\sqrt{\rho^3}$, where ρ was the molar concentration of the added substance. The protein-sparing action of carbohydrate may find an explanation in this general phenomenon.

R. K. CANNAN.

Influence of arsenic and antimony compounds on enzyme activity. III. Peptic hydrolysis of caseinogen. J. A. SMORODINCEV and N. P. RIABOUSCHINSKI (Biochem. Z., 1926, **168**, 73—76; cf. A., 1924, i, 472).—The inhibition of the peptic hydrolysis of caseinogen by arsenate, arsenite, and potassium antimony tartrate is not due to a change in the p_H of the mixtures.

R. K. CANNAN.

Perhydridase of the colostrum and milk of the cow. D. MICHLIN (Biochem. Z., 1926, **168**, 36—47).—Using Bach's nitrate method of determining the reducing activity of milk, it has been shown that the activity appears before the end of the colostrum period and persists in milk of all periods of lactation. There was no relation between the reducing activity of milk and the fat content.

R. K. CANNAN.

Plant proteases. II. Activation and inhibition of plant proteases by hydrocyanic acid. III. Substrate and optimum p_H for proteolysis. R. WILLSTÄTTER, W. GRASSMANN, and O. AMBROS (Z. physiol. Chem., 1926, **151**, 286—306; 307—318).—II. Plant proteases show marked differences in their behaviour in presence and absence of hydrocyanic acid. Some are rendered more active and some less active in its presence. Papain attacks egg-albumin only when hydrocyanic acid is present; after denaturation of the protein, however, the presence of hydrocyanic acid is unnecessary for hydrolysis by this enzyme. The action of bromelin on gelatin, and on peptone derived from albumin, is also accelerated by the presence of hydrocyanic acid. Hydrogen sulphide increases the peptolytic activity of both enzymes. Bromelin and papain are closely related, possibly even identical, but the protease of the pumpkin has widely different properties. Both hydrocyanic acid and hydrogen sulphide inhibit its activity. In its adsorption relationships it also differs from papain, the latter being adsorbed by alumina in weakly alkaline, the former in weakly acid solution.

III. Carica protease (papain) without activator or in presence of hydrocyanic acid has optimum p_H, when acting on gelatin, which is practically at the isoelectric point of the substrate, about p_H 5·0. The same correspondence is observed in the hydrolysis of peptone derived from egg-albumin (optimum p_H 5·0—5·2, isoelectric point 4·8) and of fibrin (optimum p_H 7·1—7·3, isoelectric point 7·2). Bromelin resembles papain in this respect, hydrolysing gelatin at an optimal rate between p_H 4·5 and 5·0, and peptone at 5·0. The proteolytic enzyme from the pumpkin is very different in its behaviour, namely, in its specificity, its adsorption relationships and its sensitiveness to alcohol, on the one hand, and the

optimal p_H of its proteolytic activity on the other. With peptone as substrate, the optimal p_H is sharp at 6·3, whilst gelatin is most rapidly attacked in weakly alkaline solution. Pumpkin protease either (*a*) is accompanied by impurities which strongly modify its properties, or (*b*) belongs to a class of plant proteases quite different from that to which bromelin and papain belong. H. D. KAY.

Synthetic action of plant proteases. A. BLAGOVESTSCHENSKI (Biochem. Z., 1926, **168**, 1—5).—There was a decrease, over an experimental period of 4 weeks, in the amino-nitrogen of a mixture of powdered seeds of *Phaseolus Mungo*, L., and a glycerol solution of leucine or glycine, in the presence of toluene. In the case of leucine, a crystalline material resembling leucineimide was extracted. R. K. CANNAN.

Primeverosidase and primeverase, enzymes of almond emulsin. M. BRIDEL (Bull. Soc. Chim. biol., 1926, **8**, 67—70).—See A., 1925, i, 1438.

Enzyme from seeds of *Rhamnus*, rhamnodiastase. M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1926, **8**, 35—39).—See this vol., 201.

Tyrosinase-tyrosine reaction. IV. Identity of tyrosinase from different sources. H. S. RAPER and H. B. SPEAKMAN (Biochem. J., 1926, **20**, 69—72).—Preparations of tyrosinase from the potato, the mealworm (*Tenebrio molitor*), and *Agaricus dryophilus* produce a red compound from tyrosine which has the same properties in each case. The action of tyrosinase originating from the mealworm or from the potato on quinol, phenol, *p*-cresol, resorcinol, or pyrocatechol is the same and the p_H range of the activity of these two preparations is also the same. S. S. ZILVA.

Occurrence of urease in blood-cells, blood plasma, and tissues of *Limulus*. L. LOEB and O. BODANSKY (J. Biol. Chem., 1926, **67**, 79—90).—In the muscle-tissue, blood plasma, amœbocytes, and unfertilised eggs of *Limulus*, but in no other crustacean, was found an urease, which was destroyed by heating at 70—80° for 30 min.; the enzyme could be extracted from the amœbocyte tissue by the blood-serum, but by no other fluid. The presence of urease in this species may account for the toxic effects of the injection of urea. C. R. HARINGTON.

Ultrafiltration of urease solutions. M. JACOBY (Biochem. Z., 1926, **167**, 21—24).—Jack-bean urease can be removed from solution by ultrafiltration. The size of the particles is variable, being dependent, not on the enzyme itself, but on the colloidal complex with which it is associated. No separation can be effected between urease and auxourease, since they are both bound in the one complex, but inhibitory substances are found in the ultrafiltrate. E. C. SMITH.

Influence of beryllium on formation of enzyme. F. LEHR (Biochem. Z., 1926, **168**, 166—174).—In suitable concentration beryllium chloride increases the urease activity of *Bacillus proteus* suspended in a phosphate mixture. Higher concentrations inhibit. In aqueous suspension, only inhibition is observed. The acceleration cannot be duplicated in suspensions of the pulverised bacteria or in the case of jack-bean urease preparations, so that it must be attributed to a stimulation of the living cells to produce more of the enzyme. This distinguishes the effects of calcium and of beryllium in stimulating urease activity. R. K. CANNAN.

Effect of hydrogen cyanide on alcoholic fermentation. O. WARBURG (Biochem. Z., 1925, **165**, 196—202).—Living yeast and maceration juice are similarly affected. Inhibition is caused by 0·01*N*-hydrogen cyanide, although a concentration of 0·001*N* is practically without effect. The phenomenon is not due to narcosis, but probably to a specific chemical action. C. REMINGTON.

Effect of hydrogen sulphide on chemical processes of the cell. E. NEGELEIN (Biochem. Z., 1925, **165**, 203—213).—Such processes as respiration and fermentation of yeast, respiration, carbon dioxide and nitrate assimilation in *Chlorella* are similarly affected by hydrogen sulphide and by hydrogen cyanide. All processes are completely inhibited except fermentation, which is unaffected. In the case of *Chlorella*, respiration is increased by these substances. C. RIMINGTON.

Alcoholic fermentation in presence of hydrogen sulphide and hydrogen cyanide. C. NEUBERG and G. PERLMANN (Biochem. Z., 1925, **165**, 238—246).—Both substances have an inhibiting effect on zymase, but do not destroy the enzyme. Possibly other activators are involved. C. REMINGTON.

Growth of yeast in wort. O. LUDWIG (Biochem. Z., 1926, **167**, 384—394).—The increase in the number of cells during the growth of yeast is obtained by counting, and a number of tables and curves give the cell count together with the probable errors of each determination. The growth curves are unsymmetrical and possess a series of maxima. Robertson's growth formula cannot, therefore, be applied. P. W. CLUTTERBUCK.

Dehydrogenations produced by resting bacteria. IV. Theory of the mechanism of oxidations and reductions *in vivo*. J. H. QUASTEL (Biochem. J., 1926, **20**, 166—194).—Certain substances can act towards methylene-blue as donators or acceptors of hydrogen in the presence of bacteria, but will not do so *in vitro* without being activated by organisms. The author argues that this activation as well as the actual reduction takes place on the cell surface of the organism. The mechanism of activation is ascribed, not to any specific "hydrogen transportase," but to the existence of electrical fields caused by the differential grouping of molecules on the surface of the bacterium and to the polar properties of the activated substances. Extending this theory based on the electrical and polar properties of molecules, the mechanism of oxidation and reduction *in vivo* is interpreted in various biological processes—*e.g.*, β-oxidation, asymmetric oxidation of the double linking, the difference in the activation of *cis*-

and *trans*-isomerides, the oxidation of propionic acid, and the mode of oxidation of branched chains.

S. S. ZILVA.

Simulation of living creatures. HERRERA (Compt. rend., 1926, **182**, 462; cf. this vol., 244).—When a 14% solution of sodium hydroxide in water coloured with rhodamine is dropped into a solution of olive oil in petroleum, the drops simulate the appearance and movements of amœbæ and infusoria, the phenomenon being ascribed to diffusion currents, surface-tension effects, and osmosis.

L. F. HEWITT.

Hydrogen sulphide production by anaërobic spore-bearing bacteria. M. C. KAHN (J. Bact., 1925, **47**, 439—447).—No essential correlation is observed between the native protein-digesting ability and the hydrogen sulphide-producing properties of the organisms. CHEMICAL ABSTRACTS.

Lactic acid fermentation. II. A. I. VIRTANEN, H. KARSTRÖM, and R. BÄCK (Z. physiol. Chem., 1926, **151**, 232—241).—Glyceraldehyde, dihydroxyacetone, methylglyoxal, and pyruvic acid are neither fermented nor utilised as sources of carbon by typical lactic acid bacteria (*Streptococcus lactis* and *B. casei* ε). Dried preparations of these bacteria also fail to produce lactic acid from the above compounds. On the other hand, the trioses lose their reducing power much more rapidly in presence of the dried bacteria. Carboxylase is absent from lactic acid bacteria. The fermentation of dextrose by *S. lactis* is unaffected by the presence of calcium sulphite. H. D. KAY.

Fermentation of α-ketoglutaric acid by *Bacterium xylinum*. R. IWATSURU (Biochem. Z., 1926, **168**, 34—35).—Succinic acid was isolated in amount corresponding with 30—70% of the theoretical yield. The participation of a carboxylase is inferred. R. K. CANNAN.

Indole. W. L. KULP (J. Bact., 1925, **10**, 459—471).—The Böhme–Ehrlich, Goré, and Gnezda tests for indole are apparently satisfactory. A good medium for indole production by bacteria should contain free tryptophan. Indole-negative organisms do not use indole, nor can they be induced to produce it by continued subculture in a tryptophan medium. Satisfactory p_H for growth of a bacterial species is also favourable for indole production by that species. Indole production is delayed in proportion to the amount of carbohydrate present, but media containing small quantities can be used if sufficient buffer is added. CHEMICAL ABSTRACTS.

Effects of polarised light on bacterial growth. S. S. BHATNAGAR and R. B. LAL (Nature, 1926, **117**, 302).—Preliminary experiments with *Vibrio cholerœ* and *Bacillus typhosus* indicate that bacterial life is favourably affected by polarised light as compared with ordinary light of equal intensity.

A. A. ELDRIDGE.

Growth of micro-organisms on irradiated, lipin-containing substrates. H. VON EULER (Biochem Z., 1925, **165**, 23—28).—A medium containing arachis oil is more favourable to the growth of *Penicillium glaucum* if previously irradiated by ultra-violet light. *Rhizopus chinensis* behaves similarly on a lecithin-containing substrate. There is an optimum duration of irradiation. Prolonged exposure produced in the medium factors inhibiting the growth of an organism isolated from butter.

C. RIMINGTON.

Insulin and co-zymase. A. I. VIRTANEN and H. KARSTRÖM (Ber., 1926, **59**, [*B*], 45—53).—The observation that insulin can replace co-zymase in the activation of *B. casei* ε, and hence can function as co-zymase, renders probable that it functions similarly in the organism promoting the degradation of sugars by activating the formation of hexosephosphate. The sugar content of the blood of rabbits is very appreciably increased by the wash-water containing co-zymase from lactic acid bacteria. Again, as in the case of co-zymase (cf. Embden and Lehnartz, A., 1924, i, 903), the blood-sugar is raised when insulin and calcium or fluorine ions are simultaneously injected. This result is attributed to stabilisation of hexosediphosphate, the amount of which in the blood increases markedly. As the dextrose combines with phosphoric acid, the glycogen becomes hydrolysed and the total blood-sugar (dextrose and hexosediphosphate) increases. Insulin is regarded as the co-zymase of blood. It is assumed that the active component of insulin is identical with that of co-zymase and that the difference lies in the admixed material.

The fermenting power per cell of *B. casei* ε is the same in the presence or absence of insulin, which therefore does not activate fermentation by the living organism. Insulin has no marked effect on the growth of the bacteria. Similarly, the co-zymase of yeast does not increase the fermenting power per cell of living *B. casei* ε, whence it appears that the ferment already contains the optimal amount of co-zymase, thus accounting also for the inactivity of insulin. On the other hand, yeast co-zymase promotes the growth of the cell, and hence increases the total production of lactic acid; the action is attributed partly to the buffering effect of the wash-waters, partly to their content of growth factors.

H. WREN.

Interaction of insulin, muscle-tissue, and dextrose. A. D. BARBOUR (J. Biol. Chem., 1926, **67**, 53—58).—No effect on the rotatory power of dextrose could be observed on incubating solutions of the latter with muscle tissue and insulin (cf. Lundsgaard and Holbøll, A., 1925, i, 208).

C. R. HARINGTON.

Inactivation of insulin by dextrose. Genesis of diabetes. J. R. MURLIN (Science, 1925, **62**, 332—334).—Incubation of insulin with dextrose, but not with lævulose, *in vitro*, considerably reduces its activity. The genesis of diabetes by failure of the liver or pancreas is briefly considered.

A. A. ELDRIDGE.

Destructive action of acids, alkalis, and enzymes on insulin. H. A. SHONLE and J. H. WALDO (J. Biol. Chem., 1925, **66**, 467—474).—The loss of activity of insulin brought about by the action of dilute acid or alkali or of trypsin is irreversible;

the rate of destruction of insulin runs parallel with the rate of hydrolysis of the "primary protcose" fraction of the protein material present. C. R. HARINGTON.

Insulin and micro-organisms. L. B. WINTER and W. SMITH (J. Physiol., 1925, **60**; Proc. Physiol. Soc., v.).—When lactose is substituted for dextrose in the culture medium of the coliform bacillus which has lost its property of forming an insulin-like substance by pure culturing, activity is immediately regained, but is again lost after some months, when it is not regained by the use of different sources of nitrogen or other sugars. A. A. ELDRIDGE.

Action of insulin on the domestic fowl. G. J. CASSIDY, S. DWORKIN, and W. H. FINNEY (Amer. J. Physiol., 1926, **75**, 609—615).—The blood of normal fowls contains 0·2% of reducing substance, of which 15% is not fermentable by yeast. Insulin produces hypoglycæmia, but there are no convulsions. R. K. CANNAN.

Carbohydrate metabolism of the mouse after injection of sugar solutions and of insulin. III. E. BISSINGER and E. J. LESSER (Biochem. Z., 1926, **168**, 398—420).—The proportion of the quantity of a dose of sugar which is burnt in the animal body, as measured by the respiratory quotient, to the quantity which disappears, as measured by chemical analyses, was studied. Glycogen analyses were also carried out and all the analyses were done on whole animals. When dextrose was injected into starved mice, about 30% of the dose disappeared in 30 min., and this sugar was not converted into an acid-hydrolysable product intermediate between dextrose and glycogen, but, the authors think, was probably converted into hexosediphosphate. When insulin is injected with the sugar into the starved animals, the processes of combustion and conversion into glycogen are accelerated. H. I. COOMBS.

Influence of insulin, administered orally and subcutaneously, in phloridzin diabetes. O. H. GAEBLER and J. R. MURLIN (J. Biol. Chem., 1925, **66**, 731—781).—Subcutaneous injection of insulin into completely phloridzinised dogs causes a decrease in the excretion of dextrose and a rise in the respiratory quotient; dextrose exerts a sparing effect on the protein metabolism, as indicated by a decreased excretion of nitrogen, in phloridzin diabetes; this sparing effect is enhanced by simultaneous administration of insulin. C. R. HARINGTON.

Insulin and phloridzin diabetes. II. T. P. NASH, jun. (J. Biol. Chem., 1925, **66**, 869—900).—Administration of dextrose to completely phloridzinised dogs led to a decrease, both in the blood and urine, of total non-protein nitrogen, inorganic phosphates, and ketones; creatinine was little altered. The general condition of the animals improved. Comparison of the above results with those obtained when insulin was administered simultaneously with the dextrose shows no constant difference, but whereas the recovery of dextrose from the urine, when administered alone, amounted to more than 90%, it was reduced to an average of 72·5% in those experiments in which insulin also was given. This reduction in the output of dextrose, under the influence of insulin, was associated with an increased storage of glycogen. The urinary nitrogen excretion was also reduced 30—65%. C. R. HARINGTON.

Relation of secretin formation to the entrance of acid chyme into the small intestine—properties of secretin. J. MELLANBY and A. ST. G. HUGGETT (J. Physiol., 1926, **61**, 122—130).—Secretin exists preformed in the mucosa of the small intestine. There is no evidence that it originates from a precursor under the influence of the gastric hydrochloric acid. Secretin is soluble in water, dilute alkali and acid, and 75% alcohol or acetone. It is destroyed by proteolytic enzymes, but not by heat (100°) or nitrous acid. It is precipitated by saturation with ammonium sulphate, but not by half saturation. Secretin possesses the properties of a secondary albumose. R. K. CANNAN.

Increased urinary lactic acid in avitaminosis and the influence of insulin on this increased output. L. ROSENWALD (Biochem. Z., 1926, **168**, 324—334).—In avitaminosis in dogs there is a relatively increased excretion of lactic acid which is only a part of the increased incompletely oxidised carbon of the urine. Insulin decreases the output of lactic acid, but this soon rises again. In avitaminosis, the oxidative phase of carbohydrate metabolism is mainly affected. H. I. COOMBS.

Sources of error in the technique employed for the biological assay of fat-soluble vitamins. H. CHICK (Biochem. J., 1926, **20**, 119—130).—An important source of error in the biological method of estimating the fat-soluble vitamins-*A* and -*D* consists in the variation in the reserves of these two vitamins which may be present in the young rats employed. These reserves depend on the diet on which the young rats are reared. Usually the reserve of vitamin-*D* is low in comparison with that of vitamin-*A*. Great irregularities are avoided if materials rich in vitamin-*D*, such as egg-yolk, cod-liver oil, summer "pasture-fed" cow's milk, are used sparingly in the diet of the breeding rats. The degree of illumination to which test rats are usually submitted in the animal house is of slight importance. Results previously obtained concerning the presence of vitamin-*A* are discussed in the light of the latest conception of the antirachitic vitamin-*D*. S. S. ZILVA.

Maintenance of a standardised breed of young rats for work on fat-soluble vitamins. H. H. SMITH and H. CHICK (Biochem. J., 1926, **20**, 131—136).—A description of the diet and general management for breeding rats for nutritional work on fat-soluble vitamins. The use of dried milk prepared from the winter milk supply is advocated (see preceding abstract). S. S. ZILVA.

Effect of deficiency of vitamin-*A* on nitrogenous metabolism. A. F. MORGAN and D. F. OSBURN (J. Biol. Chem., 1925, **66**, 573—594).—In young rats on a normal diet, the proportion of the urinary nitrogen in the form of allantoin is lowest when growth is most rapid; in rats on a diet deficient in

vitamin-*A*, on the other hand, the lowest excretion of allantoin is observed during the periods of most rapid loss of weight. The uric acid excretion is in all cases inversely proportional to that of allantoin. The relationships in adult rats are similar to those observed in young rats on a complete diet. The results are explained on the hypothesis that deficiency of vitamin-*A* causes impairment of the normal capacity of the organism to synthesise purines from non-purine precursors, with the result that, in animals suffering from such a deficiency, some substances, which are normally excreted as allantoin, are utilised in the body for re-synthesis of purines; the uric acid is thought to represent the ultimate oxidation product of these purine fragments which cannot be so re-synthesised. C. R. HARINGTON.

***B*-Avitaminosis, glycæmia, and glycogen reserves.** L. RANDOIN and E. LELESZ (Bull. Soc. Chim. biol., 1926, **8**, 15—29).—See A., 1925, i, 751.

Vitamin-*B* of lemon rind. S. G. WILLIMOTT (Biochem. J., 1926, **20**, 31—36).—Vitamin-*B* is present in appreciable amounts in the rind of the fresh lemon. S. S. ZILVA.

Use of colloidal ferric hydroxide sol for adsorbing the vitamins-*B* and -*D*. R. ZAJDEL and C. FUNK (Biochem. J., 1926, **20**, 26—30).—Untrustworthy results were obtained in preparing the yeast growth-promoting vitamin by Eddy, Kerr, and Williams' adsorption method (A., 1925, i, 342). This method also gave negative and inconsistent results in the preparation of vitamin-*B*. The degree of adsorption probably depends on the presence of casual impurities in the extracts. S. S. ZILVA.

Water-soluble vitamin content of the velvet bean. W. D. SALMON and E. R. MILLER (J. Agric. Res., 1925, **31**, 793—799).—Pigeons on a diet of polished rice were protected against polyneuritis by the addition of 2 g. of velvet beans per day. Pigeons suffering from polyneuritis recovered on receiving raw velvet beans or alcoholic or acetic acid extracts. Alcohol-extracted beans had no protective action. Rats thrived on a ration containing velvet beans as the sole source of vitamin-*B*, provided the beans did not constitute more than about 20% of the diet. C. T. GIMINGHAM.

Nutritional requirement of the chicken. VI. Vitamin-*C*. E. B. HART, H. STEENBOCK, S. LEPKOVSKY, and J. G. HALPIN (J. Biol. Chem., 1925, **66**, 813—818).—Not only did chickens fed on a diet free from vitamin-*C* not develop scurvy, but their livers contained sufficient vitamin-*C* to cure guinea-pigs suffering from scurvy when administered in a daily dose of 3 g. C. R. HARINGTON.

Effect of orange juice on calcium, phosphorus, magnesium, and nitrogen retention, and on urinary organic acids of growing children. M. S. CHANEY and K. BLUNT (J. Biol. Chem., 1925, **66**, 829—845).—The addition of 600—700 c.c. of orange juice per diem to a constant basal diet caused, in growing children, a considerable increase in the retention of calcium and phosphorus, a smaller increase in the retention of magnesium and nitrogen, and a gain in weight. The organic acids of the urine showed an increase equivalent to about 7% of the citric acid of the orange juice. C. R. HARINGTON.

Antirachitic substances. II. Action of *n*-butyl nitrite on activated cholesterol and vitamin-*D*. C. E. BILLS (J. Biol. Chem., 1925, **66**, 451—457).—Natural cod-liver oil and a solution of irradiated cholesterol in cod-liver oil were both rendered physiologically inactive by prolonged keeping in the cold or by heating in the boiling water-bath for 1 hr. in presence of *n*-butyl nitrite. C. R. HARINGTON.

Fat-soluble vitamin. XXVI. Effect of irradiation on antirachitic properties of milk. H. STEENBOCK, E. B. HART, C. A. HOPPERT, and A. BLACK (J. Biol. Chem., 1925, **66**, 441—449).—The antirachitic properties of cow's and goat's milk were increased 8- to 10-fold by irradiation of the milk with ultra-violet light, and to a somewhat less extent by irradiation of the whole animals. C. R. HARINGTON.

Vitamins. XI. Inorganic blood phosphorus and bone ash in rats on normal, rachitic, and irradiated rachitic diets. R. A. DUTCHER, M. CREIGHTON, and H. A. ROTHROCK (J. Biol. Chem., 1925, **66**, 401—407).—A marked fall in the inorganic phosphorus of the blood and in the percentage of ash in the bones was observed in rats which were kept on a diet lacking the antirachitic factor; irradiation of the diet partly abolished this effect, but a slight fall in both blood phosphorus and bone ash was still observed on comparison with rats kept on a complete diet. C. R. HARINGTON.

Antirachitic value of fresh spinach. H. CHICK and M. H. ROSCOE (Biochem. J., 1926, **20**, 137—152).—The leaves of spinach are a rich source of vitamin-*A*. When this vegetable is grown in the winter, spring, or autumn in the open, it possesses no antirachitic properties. Slight antirachitic potency was observed in spinach grown in midsummer. Spinach leaves irradiated with ultra-violet rays become powerfully antirachitic. S. S. ZILVA.

Antirachitic value of winter spinach. M. A. BOAS (Biochem. J., 1926, **20**, 153—165).—The addition of cod-liver oil to the diet causes an improvement in the general health of the rat and an increase in the rate of growth of both the skeleton and the whole body. There is also an improvement in the degree of calcification of the skeleton, since there is a rise in the amount of calcium per unit increase in body-weight. Fresh leaves of winter-grown spinach cause an even greater improvement in the well-being of rats and in the rate of growth; the weight of the skeleton is not, however, proportionally increased. It is concluded that the vitamin-*D* content of winter spinach is negligible compared with its content of vitamin-*A*. Of the total calcium excretion of the rat, 95—98% is found in the fæces. This partition is independent of the amount of fat-soluble vitamins in the diet. The presence of both cod-liver oil and spinach in a diet deficient in fat-soluble vitamins causes an increase in the amount of phosphorus excreted in the urine at the expense of that excreted in the fæces. S. S. ZILVA.

Antagonistic action of alkaline-earth ions on plant plasma. VII. H. KAHO (Biochem. Z., 1926, **167**, 25—37; cf. A., 1925, i, 217).—The alkaline-earth salts, acting in concentrations and for a length of time sufficient to coagulate the plasma proteins, show a similar anion effect to that of the alkali salts. The order of permeability and coagulant action of the cations is $Mg > Ba > Sr > Ca$, and of the anions $CNS > Br > NO_3 > OAc > Cl > SO_4$ (the last in the case of magnesium only). The action of the alkaline-earth salts in neutralising the toxic action of the alkali salts depends on their inhibition of the abnormal penetrating power of the latter, and is inversely proportional to their own penetrating power. The order of the effect of the ions is therefore the reverse of the above series. E. C. SMITH.

Effect of temperature on the coagulating action of alkali salts on plant plasma. H. KAHO (Biochem. Z., 1926, **167**, 182—194; cf. preceding abstract).—Salts which penetrate with difficulty (chloride, acetate, sulphate, citrate, tartrate, and nitrate of potassium and sodium) become decreasingly effective with fall of temperature from 36° to 0°. The relatively more penetrating salts (thiocyanate, iodide, bromide, and nitrate) have a minimum effect at 9—13°, increasing with rise or fall of temperature. Since different types of cell differ in their permeability to certain salts, *e.g.*, chlorides and nitrates, the latter may fall into either of the above groups, according to the substrate used. E. C. SMITH.

Formation of carbamide and a substance giving the same colour reaction as formaldehyde with phenylhydrazine, by heating plant juices. R. FOSSE (Compt. rend., 1926, **182**, 175—177; cf. A., 1925, ii, 162).—Fresh juices extracted by pressure from green leaves etc. do not give a colour reaction with phenylhydrazine and ferricyanide, and do not contain appreciable amounts of carbamide, but after warming for a short time the colour reaction produced by formaldehyde or glyoxylic acid is shown, and considerable amounts of carbamide are found. It is suggested that hydrolysis of a ureide accounts for these results. L. F. HEWITT.

Manganese and plant growth. J. S. MCHARGUE (Ind. Eng. Chem., 1926, **18**, 172—175).—Manganese was found to be indispensable for plant growth, and is particularly concerned in the synthesis of chlorophyll; the chlorotic leaves of plants deprived of manganese had a smaller content of starch and sugar than normal, and in such plants growth soon ceased altogether. The cultures were made in purified quartz sand in acid-proof stoneware jars. A considerable time (about 6 weeks) must be allowed to elapse for the exhaustion of the manganese, which in the case of mature seeds is localised in the pericarp and germ. D. G. HEWER.

Physical and chemical factors in the growth of asparagus. E. B. WORKING (Univ. Arizona Agric. Exp. Sta. Tech. Bull., 1925, **5**, 1—124).—The rate of growth increases with rise of temperature; an improvement in the salt balance of the soil induces more rapid growth at the same temperatures, the result being obtained by the addition of sodium salts in medium or low concentration. The amino-acids present in the young stalk are favourable to high imbibitional swelling of a protoplasm containing a high percentage of pentosan. CHEMICAL ABSTRACTS.

Influence of alcohol on the growth of seedlings. R. PEARL and A. ALLEN (J. Gen. Physiol., 1926, **8**, 215—231).—Soaking the dry seeds of the cantaloupe (*Cucumis melo*) for 3 hrs. in solutions of ethyl alcohol (2—16% by volume) causes a decrease in the number of seeds which germinate as compared with seeds soaked in distilled water. If the germinated seeds are grown in distilled water in the dark, the total growth is 9—35% greater in the case of the alcohol-soaked than in the water-soaked seeds. This is not an osmosis effect, since soaking the dry seeds in dextrose solutions isotonic with the alcohol solutions causes no such increased growth. It is, perhaps, due to an elimination by the alcohol of the constitutionally weak and defective seeds. C. P. STEWART.

Influence of light and temperature on the germination of seeds in the absence of calcium. R. CERIGHELLI (Compt. rend., 1926, **182**, 483—485; cf. this vol., 99).—Light appears to have no effect on the growth of the plant, temperature appears to have no effect on the growth of the root, whilst 11° is the optimum temperature for the growth of stalk of young pea plants grown in the absence of calcium salts. In every case growth is superior in plants grown in the presence of calcium salts. L. F. HEWITT.

Translocation of food materials of the wheat seedling. L. E. YOCUM (J. Agric. Res., 1925, **31**, 727—744).—The changes in composition of the seeds, plumules, and roots of wheat seedlings up to 25 days after sowing have been studied. The amount of sugar in the seed increases rapidly during the first 6 days, and then decreases; the seedlings become dependent on photosynthesis after 12 days. Nitrogen moves rapidly from the seed to the plumules and roots during the first 3 days; at 6 days, the whole plant contains about the same percentage as the original seed and after that the percentage is always higher. There is a very rapid intake of mineral elements by the wheat seedling; the amount present is increased as early as the third day and the maximum ash content of plumules and roots is reached in 12—15 days. The concentration of the cell sap, as measured by f. p. determinations, decreases until the twelfth day, and then increases; this closely follows the changes in water, sugar, and ash contents of the plants. C. T. GIMINGHAM.

Acetaldehyde fixation in alcoholic fermentation of higher plants. J. BODNÁR, C. SZEPESSY, and J. FERENCZY (Biochem. Z., 1925, **165**, 16—22).—In the presence of sodium sulphite, the anaërobic respiration of peas gives rise to acetaldehyde, the quantity being greater when dextrose is present. Alcohol and carbon dioxide are also produced in theoretical proportions, but the quantities are less than in the absence of sulphite. C. RIMINGTON.

Acetaldehyde as an intermediate product of plant respiration. G. KLEIN and K. PIRSCHLE (Biochem. Z., 1926, **168**, 340—360).—Acetaldehyde was proved to be present in strongly respiring organs (buds and seedlings) and also in roots and leaves etc. of many different plants. The acetaldehyde was isolated by means of sulphite or, better, by "dimedon" (dimethyldihydroresorcinol) and was also determined in many cases by means of a hydrogen sulphite–iodine titration method. H. I. COOMBS.

Formaldehyde as an intermediate product of carbon dioxide assimilation. G. KLEIN and O. WERNER (Biochem. Z., 1926, **168**, 361—386).—Formaldehyde was isolated from various plants by means of "dimedon" (dimethyldihydroresorcinol). The compound formed by the action of dimedon on the formaldehyde was obtained in comparatively good yield and could be easily characterised by means of its m. p. Careful controls were carried out on the chemicals used, plants in the absence of light, chlorophyll-free tissues, etc.—all with negative results. Narcosis with phenylurethane completely inhibited the formation of formaldehyde, as also did the presence of hydrogen cyanide. The absence of formaldehyde in these control experiments proves that the formaldehyde is an intermediate product in the assimilation of carbon dioxide by the plant.

H. I. COOMBS.

Synthesis of starch in plants in the presence of calcium and sodium salts. W. S. ILJIN (Ecology, 1925, **6**, 333—351).—When leaves of plants are immersed in dilute solutions of maltose or dextrose containing varying amounts of calcium or sodium chloride, different concentrations of the salts are required to stop the formation of starch in different plants. Species growing on lime endure high concentrations of calcium chloride, but show low tolerance to sodium chloride; plants growing on soils low in lime are very susceptible to calcium chloride. Sodium chloride is best tolerated by halophytes.

CHEMICAL ABSTRACTS.

Diurnal quantitative variations in carbohydrates of leaves of green plants. P. P. STANESCU (Compt. rend., 1926, **182**, 154—156; cf. A., 1924, i, 354).—The various carbohydrates (mono-, di-, and poly-saccharides) may vary independently, inversely, or in a parallel manner. In general, the disaccharides vary most widely in amount, the total carbohydrates decrease in the evening, and in many cases the monosaccharides increase in quantity during the night. In *Polyanthes tuberosa* the mono- and disaccharides show large variations, the polysaccharides remaining practically constant; in *Medicago sativa* exactly the reverse is the case, and in *Acer Negundo*, *Urtica dioica*, *Carpinus Betulus*, and *Rhus typhina*, the polysaccharides vary slightly and the other carbohydrates remain practically constant.

L. F. HEWITT.

Effect of concentration of potassium salts in soil media on the carbohydrate metabolism of plants. Diastatic activity of the nasturtium. D. T. ENGLIS and H. A. LUNT (Soil Sci., 1925, **20**, 459—463).—Additions of potassium chloride (0·2, 1, and 5 g. per 4-gallon pot) to nasturtium plants grown in sand decreased the diastatic activity of the leaves and stems, as determined by a modification of the method of Brown and Morris. With plants grown in peat, 1 g. of potassium chloride gave the highest activity and 0·2 g. the lowest. The diastatic activity appeared to be correlated rather with general favourable growing conditions than with the amount of potassium present. C. T. GIMINGHAM.

Nitrogen : base ratio in Leguminosæ and Gramineæ. A. RIPPEL and O. LUDWIG (Ber. deut. bot. Ges., 1925, **43**, 537—543).—Broad beans and oats were grown in sand with and without addition of combined nitrogen, and the plants were analysed at the time of flowering. The "nitrogen equivalent" of the bases was obtained by calculating the amount of nitrogen required to combine as nitrate with the potassium, calcium, and magnesium present, allowance being made for the bases combined as phosphates and sulphates. The difference between the "nitrogen equivalent" of the bases and the nitrogen found by analysis is expressed as a percentage excess of nitrogen. With broad beans, this figure is much higher when combined nitrogen is withheld than when it is given; it is still greater in oats grown normally with nitrogen, whereas nitrogen-starved oats show a large excess of bases. C. T. GIMINGHAM.

Proteins. O. LOEW (Ber., 1925, **58**, [*B*], 2805—2807).—Basing his arguments mainly on the work of E. Schulze, published mainly in agricultural yearbooks, the author points out that the protein which is formed in the cells of growing plants is not indifferent, like a reserve protein in the seeds or technical protein, but is an extremely labile substance which generally is converted as rapidly as it is formed into nucleoproteins, chloroplast, and cytoplasm. It is therefore not permissible to reach conclusions with regard to the mode of formation of labile protein in plants from the structure of the stable modification.

H. WREN.

Variation of protein content of maize. IV. H. B. ARBUCKLE and O. J. THIES, jun. (J. Elisha Mitchell Sci. Soc., 1925, **41**, 64—69; cf. A., 1925, i, 1518).—The protein content of maize is affected by climate, but scarcely at all by the composition of the soil. Variation in different ears of the same variety is ascribed to variation in inheritance.

CHEMICAL ABSTRACTS.

Phosphorus metabolism of higher plants. I. Enzymic conversion of inorganic phosphoric acid into organic combination. J. BODNÁR (Biochem. Z., 1925, **165**, 1—15).—Pea-meal contains an enzyme capable of forming organic compounds—probably esters—from added phosphoric acid. It is inactivated by heat or methyl alcohol.

C. RIMINGTON.

Plastid pigments. I. Absorption spectra of plastid pigments in living tissue. W. LJUBIMENKO (Bull. Acad. Sci. Russie, 1918, [6], 1811—1834; from Chem Zentr., 1925, II, 407—408).—The author has compared the absorption spectra of living leaves of fifty species of plants with the absorption spectra

of α- and β-chlorophyll in ethereal solution. Variations occur in that the red half, and occasionally the whole of the spectrum, is displaced either towards the red or the violet, the intervals between the bands remaining unchanged. Numbering the absorption bands from the red end of the spectrum, the intensity decreases in the order I=X>VII>III>IV>VI. The other bands are still weaker. Band V of β-chlorophyll and band IX of both α- and β-chlorophyll were not found. Data are given for the wave-lengths of the different bands. G. W. ROBINSON.

Influence of formaldehyde on the alkaloid synthesis of *Lupinus luteus*, L. T. SABALITSCHKA and C. JUNGERMANN (Biochem. Z., 1926, **168**, 387—397).—When lupin seeds were allowed to germinate in an atmosphere containing formaldehyde, the alkaloid content of all parts of the seedlings (14 days) was lower than in the absence of formaldehyde. Seedlings 3 weeks old which were grown in an atmosphere containing formaldehyde for 1 week had an alkaloid content very close to that of similar normal seedlings (cf. this vol., 99, 208). H. I. COOMBS.

Absolute and percentage alkaloid content of single parts of the seedling and young plant in *Strychnos nux vomica*, L., during germination. T. SABALITSCHKA and C. JUNGERMANN (Biochem. Z., 1926, **167**, 479—490).—Both the absolute amount and the percentage of alkaloid decrease during germination up to the 47th day, but both increase from the 47th to the 121st day. Decomposition or utilisation of alkaloid in the early stage, and synthesis of alkaloid in the later stage, preponderate, the nitrogen for the synthesis being derived from the reserve protein of the seed. A series of curves indicates the variations in alkaloid content of the stems, roots, and leaves individually.

P. W. CLUTTERBUCK.

Reproductive organs of plants. Chemical composition of spores of *Aspidium filix-mas* (male fern). A. KIESEL (Z. physiol. Chem., 1925, **149**, 231—258).—The dry substance of the spores contains 17—25% of oil containing lecithin, cholesterol, and a hydroxyphytosterol. The saponifiable portion yields formic, acetic, oleic, linoleic, cerotic, palmitic, and hydroxy-fatty acids. Cerotic acid is also found in relatively large amount in the first ether extract of the spores. The amount of glycerol found corresponds with 44% only of the fatty acids, which are probably also combined with sterols before saponification. Free choline occurs in the spores in traces. Sucrose is present to some 2%. About 9% of their dry weight is protein; by acid hydrolysis of the protein-containing residue remaining after ether and alcohol extraction of the spores, a mixture of amino- and other acids is obtained from which leucine, tyrosine, and azelaïc acid have been isolated, and which contains also alanine, aminovaleric acid, and *l*-proline, but no basic amino-acids. H. D. KAY.

Glucosides in plants hydrolysable by rhamnodiastase. M. BRIDEL and C. CHARAUX (Bull. Soc. Chim. biol., 1926, 8, 40—49).—See this vol., 201.

Application of rhamnodiastase to study of fresh roots of *Polygonum cuspidatum*, Sieb. and Zucc. A new glucoside, polydatoside. M. BRIDEL and C. BÉGUIN (Compt. rend., 1926, **182**, 157—158; cf. this vol., 201).—When invertase is allowed to act on an extract of 100 g. of the cortex of fresh roots of *Polygonum cuspidatum*, Sieb. and Zucc., the rotation increases by +1·33°, and reducing sugar corresponding with 0·83 g. of dextrose is produced. When rhamnodiastase is allowed to act on the same fresh extract the rotation decreases by −0·22°, and reducing sugar corresponding with 0·086 g. of dextrose is formed. The new glucoside, *polydatoside*, indicated by the preceding results, is extracted from the cortex by alcohol and purified by crystallisation from a mixture of acetone and ether. The glucoside has m. p. 153—154°, contains 11·4% of water, has $[\alpha]_D$ −57·9° (in ethyl-alcoholic solution), and on hydrolysis by sulphuric acid yields 42·2% of dextrose (calculated on the anhydrous glucoside), and *polydatogenol*, subliming without melting at 245—250°, slowly assuming a red tint on treatment with ammonia.

L. F. HEWITT.

***Chlorocodon Whiteii*: its constituents and their pharmacological actions.** W. J. DILLING (J. Pharm. Exp. Ther., 1926, **26**, 397—411).—The following constituents have been extracted from the roots of *Chlorocodon Whiteii*: a yellow, volatile oil with a strong coumarin-like odour (1·2%); a brown, non-volatile solid, m. p. 48—50° (indefinite) (2·8%); a resin (0·7%); a glucoside (0·045%); impure dextrose (20%). The pharmacological actions of the volatile oil, of the solid m. p. 48—50°, and of the glucoside are described (see Goulding and Pelly, Proc. Chem. Soc., 1908, 62; 1911, 235).

W. O. KERMACK.

Calcium oxalate monohydate and trihydrate in plants. A. FREY (Vrtljschr. naturf. Ges. Zurich, 1925, **70**, 1—65; from Chem. Zentr., 1925, II, 1366—1367).—The occurrence of a metastable calcium oxalate trihydrate and a stable monohydrate is considered on the basis of the phase rule and chemical and physical investigations. In plants, both monohydrate and trihydrate occur at different temperatures, and the system must therefore have one degree of freedom. This is attained by the disappearance of the metastable trihydrate. The other constituents occurring in plants, with the exception of acids, have no effect on the system. The equilibria are, however, affected by the partial pressure of water vapour. Calcium oxalate trihydrate is metastable above 0°, *i.e.*, over the whole physiological range of temperature, and has the tendency to form the monohydrate. The transformation is monotropic, and takes place in osmotically dilute, although, with reference to calcium oxalate, supersaturated solutions. The solubility of the trihydrate is increased by hydrogen ions or oxalate ions, and decreased by addition of calcium ions or increase of viscosity. From an examination of a number of plants it is concluded that the trihydrate occurs where the sap has a low osmotic pressure, whilst the monohydrate occurs with saps of high osmotic pressure. In cells

containing the trihydrate, calcium ions and plant mucilages are found. The various theories relating to the occurrence of these hydrates in plants are discussed. The excretory function is secondary in the formation of calcium oxalate crystals in plants.
G. W. ROBINSON.

Mineral content of pasture grass and its effect on herbivora. W. ELLIOT, J. B. ORR, and T. B. WOOD. **I. General report.** W. ELLIOT. **II. Effect of addition of mineral salts to the ration of sheep.** W. ELLIOT and A. CRICHTON. **III. Analyses of samples of pastures from various areas of the British Isles.** W. GODDEN. **IV. Seasonal variations in the mineral content of pastures.** E. M. CRUICKSHANK. **V. Effect of fertilisers on the mineral content of soils.** W. GODDEN.—See B., 1926, 251.

Sulphate content of the leaf-tissue fluids of Egyptian and Upland cotton. J. A. HARRIS, C. T. HOFFMAN, and W. F. HOFFMAN (J. Agric. Res., 1925, **31**, 653—661).—The sulphate content of the leaf-tissue fluid of Upland cotton (Meade and Lone Star varieties) is significantly greater than that of Egyptian cotton (Pima). W. O. KERMACK.

Nitrogenous components of yeast nucleic acid. P. A. LEVENE (J. Biol. Chem., 1926, **67**, 325—327).—Cytidinephosphoric acid was recovered unchanged after heating for 2 hrs. at 100°, and after dissolving in 5% ammonia and re-precipitation with acetic acid; this leads the author to criticise the view of Jones and Perkins (A., 1925, i, 487) regarding the ease of de-amination of cytosine.
C. R. HARINGTON.

Leaf-cell cytoplasm. I. Soluble proteins. A. C. CHIBNALL and C. E. GROVER (Biochem. J., 1926, **20**, 108—118).—"Soluble" proteins, *i.e.*, proteins which are uncombined and pass readily into solution when the cytoplasm is extracted with water, were prepared from the leaves of eleven herbaceous plants and one ligneous plant. They possess the properties of glutelins. They have an isoelectric range from p_H 4·0 to 5·0, in which their solubility is at a minimum. Below p_H 4·0, they are slowly soluble, the solubility increasing with decrease of p_H to 2·5, beyond which they are again precipitated. In such an acid solution the proteins are sensitive to the presence of salts, but not all to the same degree. Above p_H 5·0, they become increasingly soluble with increase of p_H and can be precipitated from solution by salts usually employed in the precipitation of proteins. The leaf-cell sap was in all cases alkaline in respect to the above isoelectric range, so that the proteins were present in the cytolysed cells as anions. "Soluble" protein could not be prepared from the leaves of herbaceous plants having a leaf-cell sap which was not alkaline with respect to the isoelectric point of these proteins. S. S. ZILVA.

Alcohol-soluble protein from polished rice. W. F. HOFFMAN (J. Biol. Chem., 1925, **66**, 501—504).—By extraction with hot 70% alcohol there was obtained from polished rice 0·12% of a protein of the elementary composition C 55·92, H 6·49, N 16·22, S 1·14%; it approximated in composition, therefore, to the alcohol-soluble proteins of the maize family. The nitrogen distribution of the protein from rice differs from that of other typical proteins of this class in that the ammonia nitrogen is much less, and the arginine nitrogen greater in amount.
C. R. HARINGTON.

Constitution of the dihydroxyquinolinecarboxylic acid from the hydrolysis of rice husks. II. Y. SAHASHI (Biochem. Z., 1926, **168**, 69—72).—The acid (cf. A., 1925, i, 1520) is concluded to be 2 : 6-dihydroxyquinoline-4-carboxylic acid, which passes readily into the isomeric *o*-iminoquinone. Methylation gave a dimethyl derivative containing one methoxyl and one *N*-methyl group. This is oxidised to methoxy-*N*-methylisatin. Concentrated nitric acid gave 3-nitro-2-hydroxypyridine-4 : 5 : 6-tricarboxylic acid. Acetylation introduced two acetyl groups, whilst benzoylation gave a monobenzoyl derivative corresponding with the tautomeric form.
R. K. CANNAN.

Pectins of the sugar-beet. F. EHRLICH and R. VON SOMMERFELD (Biochem. Z., 1926, **168**, 263—323).—Beet parings from the sugar factory were washed many times with water at 55—60° to remove any remaining sugar. At this temperature, the pectin did not go into solution, but at 80° or above the pectin was converted into soluble hydropectin and yields of 25—30% were obtained. By treatment with 70% alcohol, a soluble fraction—araban (25—35%)—and an insoluble fraction—calcium and magnesium pectates (65—75%)—were obtained. Araban is a mixture of different anhydrides of arabinose and when hydrolysed with dilute sulphuric acid a yield of 90% of pure, crystalline arabinose could be obtained, but no other carbohydrate. The purest samples of araban gave analyses which corresponded with the formula $2C_5H_{10}O_5 - H_2O$ or $3C_5H_{10}O_5 - 2H_2O$. The calcium and magnesium pectates gave an ash of mixed carbonates of 5·7%, of which 40% was calcium and 60% magnesium. The free acid was obtained from the mixture of salts, by treatment with hydrochloric acid, as a snow-white powder and was found to be a comparatively strong acid. By careful hydrolysis digalacturonic acid *a*, $C_{12}H_{16}O_{12},H_2O$, and digalacturonic acid *b*, $C_{12}H_{16}O_{12}$, were obtained (cf. A., 1917, i, 321). By hydrolysis and other methods, pectic acid was found to contain galacturonic acid, galactose, arabinose, and also acetyl and methoxyl groups. Analyses for these substances, elementary analyses, and a mol. wt. determination agreed well with a formula 4 mols. galacturonic acid+2 mols. methyl alcohol+3 mols. acetic acid+1 mol. arabinose+1 mol. galactose−10 mols. water=$C_{43}H_{62}O_{37}$ for pectic acid. H. I. COOMBS.

Action of mercury compounds on rust spores of wheat. J. BODNÁR and A. TERÉNYI (Chem.-Ztg., 1926, **50**, 109—110).—The amount of mercury adsorbed by the spores from solutions of salts was

greatest in the case of mercuric acetate; none was adsorbed from mercuric cyanide. The course of germination in calcium nitrate solution and in soil was followed in each case. Spores treated with mercuric chloride or bromide do not afterwards germinate, but those treated with a salt which dissociates readily in water germinate late. Mercury is less active than copper in killing the spores.

S. I. Levy.

Micro-determination of the hydrogen-ion concentration of capillary blood. C. J. Martin and E. H. Lepper (Biochem. J., 1926, **20**, 37—44).—A drop of blood is introduced into a tube of 2·5 mm. internal bore and about 7·5 cm. long, containing saline and phenol-red. After sealing both ends and mixing the contents, the tube is centrifuged to separate the corpuscles and the colour of the mixture of saline and plasma is compared with that of phosphate standards. The error of this method is $\pm 0{\cdot}03$ p_H unit. The correction necessary to convert the p_H at the ordinary temperature to that of the blood is discussed. S. S. Zilva.

Discrepancy between electrometric and colorimetric determinations of c_H according to the salt-content of the solution. E. H. Lepper and C. J. Martin (Biochem. J., 1926, **20**, 45—58).—Comparative p_H determinations by the electrometric and colorimetric methods were carried out on varying mixtures of phosphates and on sodium hydrogen carbonate with and without the addition of varying concentrations of sodium chloride, phenol-red being used as indicator. Coincidence was obtained only when the concentration of the sodium was the same as that of the phosphate solutions used for colorimetric comparisons. Serum diluted to 1 in 30 with 0·85% sodium chloride contains approximately the same concentration of sodium ions as the standard phosphate solution, which explains why the colorimetric and electrometric results obtained by various workers under these conditions are identical.

S. S. Zilva.

Titrimetric double hydrogen or quinhydrone electrode systems for determination of p_H: applications to urine and blood. G. H. Meeker and B. L. Oser (J. Biol. Chem., 1926, **67**, 307—317).—The use of the potentiometer and standard cell in the electrometric determination of p_H is avoided by the employment of two half-cells, one containing the fluid under investigation and the other a known buffer solution; the latter is titrated with a second known buffer solution until the potential in it balances that in the unknown cell, of which the p_H can then be calculated from that of the final buffer mixture. The method has been applied to hydrogen and quinhydrone electrodes; with the latter, satisfactory determinations have been made of the p_H of urine and blood, in both cases after dilution. C. R. Harington.

Colorimetric determination of p_H of cerebrospinal fluid. I. McQuarrie and A. T. Shohl (J. Biol. Chem., 1925, **66**, 367—374).—The importance is emphasised of avoiding changes in the tension of carbon dioxide when investigating the p_H of cerebrospinal fluid; determinations by the method of Hastings and Sendroy (A., 1924, ii, 869), with special precautions to avoid this error, show that the p_H of the cerebrospinal fluid and of the blood-serum is normally the same within the limits of experimental error. C. R. Harington.

Nephelometry of blood lipins. G. Blix (Biochem. Z., 1926, **167**, 313—320).—Critical investigation of the nephelometric method of Bing and Heckscher for the determination of fat in "primary ether extracts" (cf. A., 1924, i, 1258; A., 1925, i, 995) shows it to be untrustworthy. Nephelometric methods are suitable more for the determination of single blood lipins than for the determination of groups of lipins or total lipins of blood. P. W. Clutterbuck.

Weight analysis of the protein groups of human blood plasma and salt plasma. W. Starlinger (Biochem. Z., 1926, **168**, 423—428).—The agreement between determinations of cell volume of blood and the same blood citrated (1 of isotonic sodium citrate to 9 of blood) was within the experimental error. Also the quantitative comparison of the precipitating action of ammonium sulphate in plasma-serum and suitably recalcified citrate serum shows good agreement. H. I. Coombs.

Determination of labile serum globulins. G. Leendertz (Biochem. Z., 1926, **167**, 411—418).—In order to obtain a narrowly prescribed fraction of the grossly dispersed serum proteins, a refractometric method is worked out for the determination of the globulin precipitated by acetic acid. The quotient labile globulin/serum protein gives the percentage proportion of the globulin precipitable by acetic acid to the total serum protein. P. W. Clutterbuck.

Electrometric titration in physiological fluids. III. Blood-sugar method. E. Mislowitzer (Biochem. Z., 1926, **168**, 217—226).—Bertrand's method is so modified that the amount of reduced iron produced by the oxidation of the cuprous oxide (*i.e.*, by the addition of the acid ferric sulphate solution) is determined electrometrically by titration with standard potassium bromate solution. The method applied to blood filtrates requires about 1—2 c.c. of blood. R. K. Cannan.

Determination of sugar in blood. W. F. Duggan and E. L. Scott (J. Biol. Chem., 1926, **67**, 287—305).—A critical study of the methods of Benedict (A., 1918, ii, 247), Folin and Wu (A., 1920, ii, 337), Shaffer and Hartmann (A., 1921, ii, 417), and Hagedorn and Jensen (A., 1923, ii, 265, 440) for the determination of dextrose, indicates that the last three of these methods are suitable for concentrations of dextrose similar to those met with in blood; certain emendations are suggested to the table of Shaffer and Hartmann, indicating the relation between the amount of sodium thiosulphate used in the titration and the amount of dextrose present. The method of Benedict is criticised on the ground that increase either in the amount of dextrose present

or in the amount of picric acid used is liable to give fictitiously high results. C. R. HARINGTON.

Correction of Folin–Wu blood-sugar values. B. L. OSER and W. G. KARR (J. Biol. Chem., 1926, **67**, 319—323).—From a series of determinations on known solutions of dextrose a curve has been constructed relating the colorimetric ratios observed by the method of Folin and Wu (A., 1920, ii, 337) to the actual concentrations of dextrose; tables are given showing directly the concentration of dextrose in mg. per 100 c.c. corresponding with a given colorimetric reading. C. R. HARINGTON.

Hagedorn's blood-sugar method. E. VON FAZEKAS (Biochem. Z., 1926, **168**, 175—177).—Modifications are proposed involving the method of precipitation of the proteins, the composition of the solutions, and the time of reduction. R. K. CANNAN.

Precipitation of dextrose by Salkowski and Van Slyke's methods. E. BISSINGER (Biochem. Z., 1926, **168**, 421—422).—Dextrose can be recovered quantitatively from the precipitate formed with copper sulphate and calcium hydroxide. The precipitate is dissolved in acetic acid and the metals are removed, when the dextrose can be determined by Bertrand's method. H. I. COOMBS.

Measurement of blood for micro-analysis without a torsion balance by means of a pipette. Z. ERNST and ST. WEISS (Biochem. Z., 1926, **168**, 443—447).—The author suggests a modification of Bang's methods; a special pipette for measurement of the blood is described, the torsion balance and filter-paper being dispensed with. H. I. COOMBS.

Determination of iron in blood, tissues, and urine. F. S. FOWWEATHER (Biochem. J., 1926, **20**, 93—98).—The organic matter is destroyed with sulphuric acid and hydrogen peroxide, acetone and 3*M*-ammonium thiocyanate are then added, and the solution is made up to a definite volume. It is then compared colorimetrically with standard solutions of ferrous ammonium sulphate also containing acetone. S. S. ZILVA.

Electrometric titration in physiological fluids. II. Determination of iron. E. MISLOWITZER and W. SCHAEFER (Biochem. Z., 1926, **168**, 203—216).—The iron of blood may be determined by reducing the ash of blood with titanous chloride and titrating electrometrically the reduced iron with standard potassium bromate solution. R. K. CANNAN.

Iron in nutrition. II. Determination of iron in biological material. C. A. ELVEHJEM and E. B. HART (J. Biol. Chem., 1926, **67**, 43—51).—The incinerated material is dissolved in hydrochloric acid and the phosphates are removed from the solution with ammonium molybdate; the boiling solution is treated with excess of potassium hydroxide and the precipitate filtered off and re-dissolved in hydrochloric acid; the iron is then converted completely into the ferric condition by addition of potassium permanganate, and finally determined colorimetrically by the thiocyanate method. This method is applicable to such biological material as milk, which contains relatively little iron and much phosphorus. C. R. HARINGTON.

Micro-determination of amylase. W. ENGELHARDT and M. GERTSCHUK (Biochem. Z., 1926, **167**, 43—53).—A method is described for the determination of amylase in 0·06 c.c. of blood, urine, or saliva by digestion with starch and determination of the sugar formed by Hagedorn and Jensen's method. Duplicate determinations differ by not more than 10—15%. The optimum p_H for blood-amylase lies between 6·3 and 6·8, the optimum sodium chloride concentration being 0·1%. Dextrose formation from starch is directly proportional to the enzyme concentration. E. C. SMITH.

Determination of gases in blood by vacuum extraction and manometric measurement. III. Gasometric determination of methæmoglobin. D. D. VAN SLYKE (J. Biol. Chem., 1925, **66**, 409—414).—Determinations are made by the method of Van Slyke and Neill (A., 1924, ii, 872) of the combining capacity of blood for carbon monoxide before and after treatment with an ammoniacal solution of sodium hyposulphite; the latter reagent reduces any methæmoglobin which may be present to hæmoglobin, which then combines with carbon monoxide; the difference of the two determinations therefore indicates the amount of methæmoglobin in the original sample. C. R. HARINGTON.

Quantitative determination of dihydroxyacetone. W. R. CAMPBELL (J. Biol. Chem., 1926, **67**, 59—69).—Dihydroxyacetone, when boiled with phosphomolybdic acid, reduces the latter 180 times as rapidly as does dextrose. This fact makes possible the colorimetric determination of dihydroxyacetone in presence of dextrose. By this method it was not possible to detect any considerable amount of dihydroxyacetone in normal human blood except after oral administration of the substance. C. R. HARINGTON.

Colorimetric determination of phosphorus. C. H. FISKE and Y. SUBBAROW (J. Biol. Chem., 1925, **66**, 375—400).—The method of Bell and Doisy (A., 1920, ii, 769) for the colorimetric determination of phosphorus has been modified by the substitution of 1-amino-β-naphthol-6-sulphonic acid for the quinol used by the earlier workers as a reducing agent for the phosphomolybdic acid. This gives a much more rapid reduction in the cold than is the case with quinol, with consequent diminution of the errors due to other substances present, which, on prolonged heating, may produce interfering colours. Details are given of the application of the modified method to the determination of phosphorus in blood, urine, and organic matter in general. C. R. HARINGTON.

Determination of uric acid in blood. A. IONESCU, I. BIBESCU, and D. POPESCU (Bul. Soc. Chim. România, 1926, **7**, 65—72).—The protein is

precipitated with trichloroacetic acid, and the filtrate treated with solutions of phosphotungstic acid and sodium carbonate, when a blue colour is immediately produced owing to reduction of the tungstic acid. The mixture is then titrated with alkali ferricyanide solution until the blue colour is destroyed by re-oxidation to the tungstic salt. Theoretically 2 mols. of ferricyanide are equivalent to 1 mol. of uric acid, but the ferricyanide solution should be standardised against a known uric acid solution in the presence of trichloroacetic acid. The method is unaffected by other substances usually present in the blood, and avoids the errors of purely colorimetric methods. Tests show that normally whole blood and serum contain 0·15 g. and 0·05 g. of uric acid per 1000 g., respectively. W. HUME-ROTHERY.

Micro-determination of lactic acid and lactates in pure solution. K. HANSEN (Biochem. Z., 1926, **167**, 58—65).—Lactic acid is quantitatively oxidised to acetic acid at 70° by potassium dichromate in acid solution. The excess of dichromate is titrated with sodium thiosulphate. In pure solution, 1 mg. of lactic acid may be determined by this means to within 2%. E. C. SMITH.

Clarification by charcoal of urine containing sugar. I. M. KOLTHOFF (Biochem. Z., 1926, **168**, 122—127).—" Norit " and Merck's medicinal charcoal adsorb appreciable amounts of dextrose and sucrose. In the clarification of urine prior to sugar determinations, loss may be avoided if only the minimum amount of charcoal necessary almost to remove the colour be used. R. K. CANNAN.

Determination of water-soluble excreta of aquatic animals. E. LENK (Biochem. Z., 1926, **168**, 61—68).—The change in the electrical conductivity of sea-water containing fish was used as a measure of the rate of excretion of water-soluble materials after feeding. The temperature coefficient of this rate was 1—1·21 for the rise from 10° to 20°, and 1·18—1·44 for the rise from 15° to 25°.
R. K. CANNAN.

Determination of calcium in tissues, fæces, and milk. R. C. CORLEY and W. DENIS (J. Biol. Chem., 1925, **66**, 601—608).—The material to be analysed is heated in the autoclave at 180° for 2 hrs. with 0·1*N*-sodium hydroxide; the solution is then acidified and filtered. Calcium is precipitated from the filtrate as oxalate and the precipitate separated and dissolved in dilute sulphuric acid; potassium permanganate is added in slight excess to remove traces of organic matter; the calcium is then re-precipitated by ammonium oxalate, the precipitate is separated and titrated with 0·01*N*-potassium permanganate. Results obtained by this method compare favourably with those obtained by incineration of the organic matter. C. R. HARINGTON.

Determination of the distribution of fat in animal tissues. R. VLADESCO (Compt. rend. Soc. Biol., 1925, **93**, 755—756; from Chem. Zentr., 1925, II, 2180).—The animal tissue (10 g.) is heated with concentrated nitric acid (20 c.c.) and water (5 c.c.) until it is completely dissolved. The solution is then cooled and filtered through a tared filter paper, on which the fat is retained and may be weighed after drying to constant weight. During the heating with nitric acid and subsequent cooling the mixture should be shaken continuously to prevent aggregation of the fat globules. G. W. ROBINSON.

Micro-determination of nitrogen. A. KULTJUGIN and H. IVANOVSKI (Biochem. Z., 1925, **165**, 118—121).—The use of quartz-glass in Bang's iodometric method (A., 1913, ii, 446) may be avoided by nesslerising the distillate. C. RIMINGTON.

Determination of protein nitrogen. E. VOIT (Z. Biol., 1926, **84**, 153—168).—Of the proteins tested, only albumins and globulins were precipitated by the addition to their solutions of 4 volumes of 95% alcohol acidified to tropæolin-OO. Acidified alcohol saturated with sodium sulphate completely precipitated all proteins and metaproteins tested, partly precipitated proteose solutions, but did not remove peptones, polypeptides, or amino-acids. The method has been applied to the determination of protein and non-protein nitrogen in various animal products. Determinations are recorded of the solubility of sodium sulphate in alcohol (78 and 85 vol.%) in the presence of varying concentrations of hydrochloric and sulphuric acids. R. K. CANNAN.

Determination of extractive nitrogen. F. WEBER (Z. Biol., 1926, **84**, 169—180).—For animal and vegetable materials, except those containing gliadin, the method of Voit (preceding abstract) is preferable to that of Stutzer (cf. A., 1906, ii, 820).
R. K. CANNAN.

Calcium pectate method for the determination of pectin. A. M. EMMETT and M. H. CARRÉ (Biochem. J., 1926, **20**, 6—12).—Pectin can be determined accurately by precipitation with 4 volumes of alcohol containing the amount of hydrochloric acid required to make the resulting mixture 0·1*N*. After keeping over-night the precipitate is filtered, washed with acidified alcohol, and dissolved off the filter-paper with hot water. It is then hydrolysed with sodium hydroxide and determined as calcium pectate, the precipitate being washed free from chlorides and reboiled with water three times before being filtered through a Gooch crucible and dried at 100°. The application of the method to the determination of pectin in the presence of oxalates or other substances giving insoluble calcium salts is satisfactory. Weaker acids, such as acetic acid, can also be employed providing a sufficiently large concentration of hydrogen ions is ensured. Precipitation of pectin by neutral 95% alcohol is untrustworthy. S. S. ZILVA.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

MAY, 1926.

BIBLIOTECA POLITECNICA

General, Physical, and Inorganic Chemistry.

Measurement of the fine structure of hydrogen lines with the Lummer-Gehrcke plate. P. H. VAN CITTERT (Ann. Physik, 1926, [iv], **79**, 94—96).—A reply to the criticisms of Gehrcke (this vol., 101) regarding the author's work on this subject (A., 1925, ii, 909). J. S. CARTER.

New series in the secondary hydrogen spectrum. W. E. CURTIS (Phil. Mag., 1926, [vii], **1**, 695—700).—An examination of Kimura and Nakamura's work on the influence of the electrodeless discharge on the secondary spectrum of hydrogen (A., 1923, ii, 594) has led to the allocation of 18 lines in the region 5989—5597 Å. to three series, consisting, respectively, of 7, 6, and 5 lines. Other characteristics of the lines in question confirm the suggested arrangement for two of the series, but leave the third somewhat uncertain. A. B. MANNING.

Nitrogen in the sun and stars. F. E. BAXANDALL (Nature, 1926, **117**, 483—484).—A correction of statements made by Saha (this vol., 221) concerning the occurrence of the line 3995 Å. and the non-occurrence of other nitrogen lines in the stellar spectra. A. A. ELDRIDGE.

Stripped oxygen, O VI, the *pp'*-group in O V, and new aluminium lines in the extreme ultra-violet. I. S. BOWEN and R. A. MILLIKAN (Physical Rev., 1926, [ii], **27**, 144—149).—The "lithium doublet" of stripped oxygen, O VI, has been located at 1031·98, 1037·69 Å., and the *pp'*-group of O V has been obtained in the fourth order as a sextuplet, the ratio p_1p_2/p_2p_3 being 2·27. Fifteen new faint lines of Al II and Al III between 1250 and 500 Å. are tabulated. Extrapolation yields the following values of ionisation potentials: N V, 97·39; O VI, 137·35; F VII, 184·07; Cl VII, 113·73 volts. A. A. ELDRIDGE.

Spectrum of ionised oxygen (O II). A. FOWLER (Proc. Roy. Soc., 1926, **A**, **110**, 476—501).—New measurements of the lines of the spectrum of singly ionised oxygen, O II, have been made in the region 6750—1850 Å., 90 lines being assigned to the doublet and 68 to the quadruplet system, whilst particulars of about 400 lines are given. On the supposition that three of the doublet p terms form a Rydberg sequence, with $4R$ for the series constant, the value 93,952 has been assigned to the term $2p_2$. The values of other terms are derived from the observed wave-numbers and a value of about 240,000 is deduced for the $1s$ term, corresponding with an ionisation potential of 30 volts, in fair accordance with the value, 31 volts, deduced from stellar spectra. This value for the $1s$ term is provisional, as the $1s$—$2p$ lines which lie in the extreme ultra-violet have not yet been identified. The spectrum of singly ionised oxygen shows, as anticipated, a close similarity to that of neutral nitrogen, the wave-numbers of several of the groups of oxygen lines being approximately double those of the corresponding groups in the nitrogen spectrum. F. G. SOPER.

Spectrum of neon in the extreme ultra-violet. T. LYMAN and F. A. SAUNDERS (Proc. Nat. Acad. Sci., 1926, **12**, 92—96).—A more detailed account of work described by the authors (A., 1925, ii, 911) and subsequently confirmed by Hertz (*ibid.*, 723). Two neon lines of great intensity occur at 743·73 and 735·95 Å. A number of others occur between these and the helium line at 584 Å. The series relationships of the lines have been determined and the average value of the $1p$ term has been calculated by adding to the wave-number of each line the appropriate term as given by Paschen. This value is 173,930 and corresponds with an ionisation potential of 21·47 volts, in agreement with that of 21·5 volts determined by Hertz (*loc. cit.*). A. E. MITCHELL.

Intermittent glow-discharge of neon. F. M. PENNING (Physikal. Z., 1926, **27**, 187—196; cf. A., 1920, ii, 581; 1924, ii, 585).—Four types of striated discharges have been observed with neon, and the intermittent form resembling that of air studied by Geffcken (*ibid.*, 1925, **26**, 241) has been examined more closely. According to this author, the time t between flashes is given by $t = C(V_s - V_0)/i$, in which i is the current, V_s the flashing voltage, and V_0 the minimum running voltage. This expression does not agree with experiment. The revised form $t = C(V_{max.} - V_{min.})/i$, in which the voltages are the maximum and minimum values during a single period, leads to better agreement, although $t_{obs.}$ (90—20×10^{-4} sec.) remains from 11 to 20% greater than $t_{calc.}$ (80—15×10^{-4} sec.). The residual discrepancies are ascribed to gradual disappearance of the discharge, and experiments with varying current strengths afford an approximate guide to the course of the diminution. The light phenomena have been analysed by means of a stroboscope and rotating mirror and an interpretation of the results is advanced. The failure to observe negative striations at the moment of flashing,

the formation of a continuous discharge, and the transition from continuous to intermittent forms have also been investigated. Kaufmann's formula (Ann. Physik, 1900, [iv], **2**, 174) for the latter is inapplicable. The phenomena are discussed theoretically. R. A. MORTON.

New lines in the arc spectrum of scandium at normal pressure. S. PIÑA DE RUBIES (Anal. Fís. Quím., 1926, **24**, 41—46; cf. A., 1925, ii, 829).—The wave-lengths and intensities of 60 new lines of the arc spectrum of scandium are given. A complete list is given for all lines between 2232 and 3717 Å. G. W. ROBINSON.

Spark between carbon rods impregnated with a mixture of oxides of molybdenum, titanium, and vanadium as the source of a closely-spaced line spectrum in the visible region. (MISS) M. EPPLEY (J. Franklin Inst., 1926, **201**, 333—335).—A source of closely-spaced line spectra between 6678 and 3990 Å., in which the lines are of very nearly equal intensity, is described. Such a spectrum has the advantage that strong lines need not be over-exposed in order to ensure the appearance of weak lines, and a 26-minute exposure with a slit width of 0·03 mm. can be used. The spark between carbon electrodes coated with a fused mixture of the oxides of vanadium, titanium, and molybdenum in the following proportions is used: V_2O_5 8, MoO_3 5, TiO_3 2 parts by weight. The lines in this spectrum are identified by photographing on it the spark spectrum of an alloy of the following composition: cadmium 35, zinc 35, lead 73, tin 30 parts by weight. C. J. SMITHELLS.

Doublet $K\beta_1$ [of manganese and chromium]. N. SELJAKOV and A. KRASNIKOV (Nature, 1926, **117**, 554—555; cf. A., 1925, ii, 914).—The ratio of the intensities of the lines $K\beta_1$ and $K\beta'$ in the absorption spectrum remains the same as in the emission spectrum, and there is no trace of any new absorption line in the same region. The lines are always present or absent together. Contrary to Sommerfeld's view, the authors still regard the combination of the lines $K\beta_1$ and $K\beta'$ as a "relativity doublet."
A. A. ELDRIDGE.

Spectra of exploding wires. R. DÉOHÊNE (J. Phys. Radium, 1926, [vi], **7**, 59—64).—The spectra obtained during the explosion of copper, nickel, and silver wires by means of electric discharges of varying tensions have been studied. Emission and absorption rays have been detected on a continuous background, the intensity of which increases with the number of explosions for a particular tension, but decreases with the weight of the wire. The continuous spectrum is the ordinary spectrum of the metal, the absorption and emission rays being due to the portions of it absorbed and unabsorbed by the vapour of the metal, respectively. It is concluded that, in general, rays absorbed at low tensions are arc rays, whereas rays which appear as dark bands at low tensions but are absorbed only at high tensions are spark rays. J. GRANT.

Arc spectrum regularities for ruthenium. W. F. MEGGERS and O. LAPORTE (J. Washington Acad. Sci., 1926, **16**, 143—154).—The lowest term in the ruthenium spectrum previously regarded by the authors (A., 1925, ii, 1101) as a quintuplet-D term is in reality, as indicated by Sommer (Naturwiss., 1925, **13**, 840), a quintuplet-F term. Hence all the quantum numbers given are to be increased by one unit. Eighteen multiplets are presented which have been selected as representative of quintuplet, triplet, and inter-system combinations of P, D, F, and G terms. The Zeeman patterns of 34 ruthenium arc lines between the limits 3428 and 4522 Å., most of which involve the low ^5F term, have been photographed. The majority of lines are very complex in the magnetic field and difficult to resolve. Nine lines between 3727 and 4200 Å. are tabulated, the observed and calculated Zeeman effects being in fair agreement. Assigning the value zero to $^5F_5$, the lowest energy level of the normal atom, the relative values of the levels combining to give the various multiplets are tabulated. The interval rule is not obeyed. From the terms recognised in the arc spectrum the following electron configurations are indicated: $7d$ and $1s$; $6d$ and $2s$; $8d$; $7d$ and $1p$. The last electron arrangement accounts for all the higher levels so far examined. J. S. CARTER.

Separation of the various orders of spectra of cadmium. F. ESCLANGON (J. Phys. Radium, 1926, [vi], **7**, 52—58).—The spectra emitted when cadmium contained in a fused silica tube is excited by high-frequency currents at temperatures ranging from 330° to 450° have been studied spectrographically by the method of Bloch (A., 1923, ii, 350). By varying the tensions of the discharge for fixed temperatures it has been possible to classify the rays emitted according to the degree of ionisation of the atom. Thus for wave-lengths of 3695·5—2306·6 Å. rays due to Cd I, Cd II, Cd III, and Cd IV have been graded according to their intensities. New rays for Cd III and Cd IV have been noted, the latter being always short. Long rays may be due to Cd I, Cd II, or Cd III or their combinations. Rise in temperature decreases, but increase in the exciting current increases the lengths of the rays. In general, the results agree with those of previous workers (cf. A., 1925, ii, 334).
J. GRANT.

***K*-Series emission spectra for the elements from tantalum (73) to bismuth (83).** B. R. STEPHENSON and J. M. CORK (Physical Rev., 1926, [ii], **27**, 138—143).—Accurate measurements have been made of the K lines for tantalum, tungsten, osmium, iridium, platinum, gold, thallium, lead, and bismuth; values of $\sqrt{\nu/R}$ plotted against the atomic number give practically straight lines. There is good correspondence between values of $\Delta(\nu/R)$ for $K\alpha'$—$K\alpha$ and $L\beta$—$L\alpha'$; $\Delta\lambda$ for $K\alpha'$—$K\alpha$ is practically constant at 4·85 X. A. A. ELDRIDGE.

Reflexion by a crystal of its own characteristic radiation. W. DUANE (Proc. Nat. Acad. Sci., 1926, **12**, 140—143; cf. following abstract).—It is believed that slightly more radiation was reflected at the bromine $K\alpha$ line in the second order than in its immediate neighbourhood. A possible explanation is put forward. J. S. CARTER.

Selective reflexion of *X*-rays by crystals of potassium bromide. S. K. ALLISON (Proc. Nat. Acad. Sci., 1926, **12**, 143—144).—In a previous paper with Duane (A., 1924, ii, 720) certain irregularities were noted at points corresponding with wave-lengths of the bromine *K*-series lines and interpreted as indicating reflexion by the crystal of its own characteristic spectrum. These measurements are now regarded as untrustworthy. J. S. CARTER.

Absorption of *X*-rays of wave-length down to 0·08 Å. S. J. M. ALLEN (Physical Rev., 1926, [ii], **27**, 266—276).—A confirmation and extension of previous results (*ibid.*, 1924, [ii], **24**, 1); mass absorption coefficients have been measured for "paraffine," carbon, sulphur, aluminium, iron, nickel, copper, zinc, palladium, silver, tin, barium, tungsten, platinum, gold, lead, bismuth, thorium, and uranium, for wave-lengths from 0·56 to 0·08 Å. The computed values of the mass-scattering coefficients increase in general with the atomic number, becoming approximately unity for tungsten, platinum, gold, lead, and bismuth. A. A. ELDRIDGE.

Dependence of intensity of *X*-ray spectral lines on the voltage of excitation. H. STUMPEN (Z. Physik, 1926, **36**, 1—17).—Intensities were measured by means of the ionisation chamber. Up to about 4·5 times the voltage required for initial excitation, the intensity increases as the square of the voltage; above that limit, the increase is not so great. The intensity of the *L* lines increases again more rapidly when the voltage necessary to excite the *K* radiation is reached. E. B. LUDLAM.

Light quanta and photo-electric emission. C. G. BARKLA (Nature, 1926, **117**, 448).—The ionisation produced by a heterogeneous beam of *X*-rays in a gas or the electronic emission from a metal plate is abruptly and considerably increased either by adding radiations of higher frequency to, or eliminating those of lower frequency from, the beam. The *J* electron emission is an effect of the radiation as a whole. When an aluminium wedge is placed in the path of a heterogeneous beam of *X*-rays, a spectrum of radiations varying in average wave-length is transmitted, capable of showing both *J*-absorption lines and *J*-absorption edges by the ionisation method. A. A. ELDRIDGE.

Infra-red spectrometer and a glass-quartz universal spectrograph. C. LEISS (Z. Physik, 1926, **36**, 60—72).—For use down to 15 μ, the spectrometer consists of one (or two) rock-salt prisms and a Wadsworth mirror. Rotation of the system is effected by means of an endless screw with micrometer head. The two slits are symmetrical and adjustable by means of rotating rings. The spectrograph is designed so that simple manipulation enables it to be used either for the ultra-violet or the visible region. A convenient diaphragm is described for obtaining comparison spectra in coincidence, and also a method of using the apparatus for absorption spectra. E. B. LUDLAM.

Spectroscopic phenomena of the high-current arc. A. S. KING (Astrophys. J., 1925, **62**, 238—264).—In the high-current arc (1000 amp. at 100 v.), the high-temperature lines are intensified, widening phenomena are developed, reversals are numerous, and a continuous spectrum appears in the ultra-violet. Band spectra are absent in emission, but may appear in absorption. The spectra examined were those of iron (2800—8400 Å.), selected regions of titanium, magnesium, calcium, copper, and aluminium; certain lines of sodium, gallium, oxygen, and nitrogen are described. The degrees of widening, usually unsymmetrical, are given for 920 iron lines (4250—8400 Å.). The selection of lines suitable for wave-length standards is discussed, and the high-current arc is compared with other sources in respect of the tendency towards displacement. A. A. ELDRIDGE.

Possible explanation of the relativity doublets and anomalous Zeeman effect by means of a magnetic electron. F. R. BICHOWSKY and H. C. UREY (Proc. Nat. Acad. Sci., 1926, **12**, 80—85).—The hypothesis of the spinning electron postulated by Uhlenbeck and Goudsmit (this vol., 215) is extended and applied to the separation of multiplet spectral terms. The electron is assumed to be a charged magnetic doublet with a magnetic moment of one-half of a Bohr magneton. In accordance with the experimental results of Stern and Gerlach, the theory requires the allocation of half-quantum numbers for the *s*-orbits. The formulæ obtained differ but slightly from those of Landé and Sommerfeld. On the basis of the theory, the spectrum of helium should be similar to that of the alkaline earths in comprising a singulet and triplet series of lines. The hypothesis cannot account for the fine structure of the hydrogen and helium lines. A. E. MITCHELL.

Distribution of energy between the modified and the unmodified rays in the Compton effect. Y. H. WOO (Physical Rev., 1926, [ii], **27**, 119—129).—Measurements were made of the intensity of scattered *X*-rays from cylinders of paraffin, wood, and graphite, and plates of aluminium and sulphur. Values of the ratio increase as the atomic number decreases; for a given element they increase with the angle of scattering in the order, but not the proportion, predicted by Jauncey's theory. Experiments with lithium indicate that the Compton effect is due to true scattering, and that the unmodified line occurs when the energy imparted to the electron during the process of scattering is insufficient to eject it from the atom. A. A. ELDRIDGE.

Volta effect. C. G. BEDREAG (Ann. sci. Univ. Jassy, 1926, **13**, 346—359).—The Volta effect is shown to be closely associated with the sub-grouping of the electrons in the outer shell of the atoms, but is also modified by the formation of molecules and by the surface layer, which is analogous to the layer causing ordinary surface tension, but is only of the thickness of one atom or molecule. The work done by an electron in passing across this layer is a function of the constitution of the atom, and the Volta effect for two substances is the algebraic sum of the work of passage across the two layers in contact. The observed effect, however, is complicated by the

thermo-electrical, photo-electrical, and chemical effects which may co-exist. E. B. LUDLAM.

Ratio e/m in metals. T. V. IONESCO (Ann. sci. Univ. Jassy, 1926, **13**, 274—277).—An expression for e/m in terms of the current produced in a ring of the metal is obtained by means of an alternating magnetic field, uniform and perpendicular to the plane of the ring. E. B. LUDLAM.

Critical ionisation potentials by positive-ion impact. W. J. HOOPER (J. Franklin Inst., 1926, **201**, 311—331; cf. Franck, A., 1924, ii, 715).—The author has repeated experiments of previous investigators with apparatus designed to distinguish between ionisation and other spurious effects of positive-ion impact. Evidence is obtained (*a*) that the so-called ionisation current is due to a secondary electron emission from the walls of the chamber, (*b*) that it is produced by the impact of positive ions, (*c*) that either there is no ionisation of hydrogen by positive ions up to 925 volts or that it is so small at pressures below 0·012 mm. as to be masked by secondary phenomena, and (*d*) that at higher pressures ionisation by positive ions might be an important factor within this range of potentials. C. J. SMITHELLS.

Variations in the photo-electric sensitivity of platinum. L. A. DUBRIDGE (Proc. Nat. Acad. Sci., 1926, **12**, 162—168; cf. Herrmann, A., 1925, ii, 947; Woodruff, this vol., 3).—Experiments in which a platinum strip was heated at high temperatures (1200—1500°) in the highest attainable vacuum for varying periods of time show that even after such treatment the metallic surface is still slightly sensitive to radiation from a quartz mercury arc, and still gives a measurable photo-electric emission. The removal of gas from the platinum is accompanied by a shift in the long wave-length limit to a final value between 1943 and 1973 Å. The variation of the photo-current with the temperature of the platinum filament was investigated. During the initial stages of outgassing, the current varies widely and irregularly with temperature. After prolonged heating (100 hrs.), the photo-current increases with temperature in a regular manner. The possible explanations of the temperature effect are reviewed. J. S. CARTER.

Low-voltage discharges in helium. W. H. MCCURDY and P. DALTON (Physical Rev., 1926, [ii], **27**, 163—172).—Measurements were made of the potential distribution and of the mean energy and concentration of the electrons in helium at 0·095, 0·5, and 2·9 mm. pressure. A. A. ELDRIDGE.

Diffusion of electrons. G. GLOCKLER (Proc. Nat. Acad. Sci., 1926, **12**, 178—180).—Mathematical. The average number of collisions which an electron makes when diffusing a distance a through a gas, when no field is acting on the electron, is $3a^2/2\lambda^2$, λ being the mean free path of the electron. The number of impacts is thus independent of the velocity.
J. S. CARTER.

Magnetic moment of the orbit of the valency electron of the solid alkali metals. L. C. JACKSON (Nature, 1926, **117**, 449).—The contribution to the magnetic susceptibility of the valency electrons for the solid state is of the order: potassium, $+14{\cdot}5\times10^{-6}$; rubidium, $+22{\cdot}8\times10^{-6}$; cæsium, $+29{\cdot}4\times10^{-6}$. These values are much smaller than would be expected for a normal n_1 orbit, but are of the order to be anticipated for the residual moment of nearly completely compensated shared orbits. Also the closest distance of approach of the atoms in the lattice (2·25 Å. for potassium) falls between the values for the major axis of the n_1 orbit (3·2 Å.) and the radius of the rare gas core (1·55 Å.). A. A. ELDRIDGE.

Motion of the spinning electron. L. H. THOMAS (Nature, 1926, **117**, 514).—Theoretical considerations lead to the disappearance of the discrepancy in Uhlenbeck and Goudsmit's idea of the spinning electron (this vol., 215), in which the precession of the spin axis in an external magnetic field required to account for Zeeman effects seemed to demand doublet separations twice those observed.
A. A. ELDRIDGE.

Spinning electrons and the structure of spectra. R. DE L. KRONIG (Nature, 1926, **117**, 551).—The views of Uhlenbeck and Goudsmit (this vol., 215) are criticised. A. A. ELDRIDGE.

Analogue of Clapeyron's law in the case of evaporating electrons. J. DROSTE (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 900—904).—Mathematical. It is shown that Richardson's equation for the equilibrium between a hot metal and the electrons it emits is applicable also to the equilibrium in an arbitrarily shaped, evacuated enclosure the walls of which all consist of the same metal. M. S. BURR.

Emission of electrons under the influence of intense electric fields. RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD. (B. S. GOSSLING) (Phil. Mag., 1926, [vii], **1**, 609—635).—The discharge obtained in highly exhausted tubes using a cathode with a sharp edge or points has been investigated. The discharge is ascribed to the emission of electrons from the metal surface of the cathode under the influence of intense external electric fields (Lilienfeld's "autelectronic discharge," Physikal. Z., 1922, **23**, 506). The cathode consisted of a loop of fine tungsten wire, or of a wire point, and the anode generally of a nickel disc. The tube was connected in series with a high resistance to a source of high potential, and attempts were made to determine the relation of current to voltage. The visible phenomena accompanying the discharge were very varied, and the variation of current with voltage at times exhibited irregularities difficult of explanation. When, however, the conditions were steady, a linear relation was observed between the logarithm of the current and the square root of the voltage. Currents ranging from 10^{-9} to 10^{-4} amp. and occasionally higher were obtained with a voltage range from about 4000 to 25,000. Heating the cathode filament between determinations displaced the characteristic curve towards the higher voltages, but in general left the slope of the curve unaltered. Some of the apparently spontaneous displacements of the characteristic curve were due to the presence of small amounts of sodium salts or similar substances. The steady autelectronic dis-

charge was practically independent of the temperature of the cathode. Where such a temperature effect exists, it is probably a secondary phenomenon due to the progressive elimination of some impurity in the tube. It shows itself as a simple displacement of the current–voltage curve. Estimates of the current density and of the surface field at the cathode during discharge gave values of 10^6 amp./cm.^{2} (minimum) and 5×10^5 to 5×10^6 volts/cm., respectively. The average value of the gradient of the characteristic curve ($d\log_e I/df^{1/2}$, where I is the current and f the potential gradient) was 0·017, which may be compared with 0·0013, the corresponding gradient for a general thermionic emission. The results are discussed in the light of Schottky's theory (Z. Physik, 1923, **14**, 63). A. B. Manning.

Universal constant of thermionic emission. P. W. Bridgman (Physical Rev., 1926, [ii], **27**, 173—180).—With certain assumptions, it is shown theoretically that an emission formula of the type $I = AT^2e^{-\phi_0/T}$ demands that A shall have Dushman's universal value. The relevant condition is considered with respect to the divergences obtained experimentally for coated metals.

A. A. Eldridge.

Electronic phenomena at the surface of metals. C. E. Mendenhall (J. Franklin Inst., 1926, **201**, 269—278).—Recent work by Dowling on contact electromotive force, Welo and DuBridge on photo-electricity, and Farnsworth on emission of electrons under electronic bombardment is reviewed in connexion with the structure of metal surfaces. The general conclusion is that there are two changes produced by thermal ageing of a surface in a high vacuum: outgassing, which in itself is complex, and tends to reduce the number of secondary electrons; and a change in surface structure due to crystallisation, which tends to increase the number, and develop the characteristic features of the secondary electron curve. The combination of these effects is probably responsible for the variable results that have been obtained and for the difficulty of obtaining stable limiting surface conditions. C. J. Smithells.

Thermo-electric effects and heat capacity of electrons in metals. E. D. Eastman (J. Amer. Chem. Soc., 1926, **48**, 552—562).—The apparent heat capacity of electrons, C, is compared with their partial molal heat capacity, $\overline{C}$ (a physical entity), and the possible relative magnitudes of these quantities are discussed. Consideration of the available data shows that the Thomson effect, σ, is not equal to C, so that C and c_v cannot be calculated from thermo-electric data. On the assumption that the Soret effect (variation in composition due to a temperature gradient) has no significant influence on σ, it is shown that for the alkali metals, silver, gold, etc., σ and $\overline{C}$ are less than C; for magnesium $\sigma=\overline{C}$, nearly; and, with an extra assumption, $\overline{C}$ is greater than C for aluminium, lead, and platinum. These results are interpreted as indicating that an increase in the ratio of electrons to atoms increases the inter-atomic constraints in the metals of the first group and decreases them in the metals of the last group. It is suggested that the introduction of extra electrons into the atoms causes the formation of stable groups and configurations with the other electrons with a consequent "tightening" effect. S. K. Tweedy.

Mobility of gaseous ions. M. Laporte (Compt. rend., 1926, **182**, 620—622).—By a modification of a method previously described (*ibid.*, 1921, **172**, 1028), it is shown that in wet and dry air, oxygen, and nitrogen, in carbon dioxide under different pressures, and in argon, ions of various mobilities between two definite sets of limits exist. The values found by other observers are within these limits.

S. K. Tweedy.

Limitations of the theoretical equations for the mobilities of gaseous ions. L. B. Loeb (J. Franklin Inst., 1926, **201**, 279—299).—A review of recent experimental work on the mobility of gaseous ions. The independence of the mobility and inertia of the ion leads to the assumption of a change in diameter of the ion in explaining the ageing effects found by Erikson. These changes in diameter must, however, be small. Evidence for clustering of ions is derived from the author's recent work. An attempt is made to explain the differences in positive and negative ion mobilities by a study of the structure of the molecule in a qualitative way, and leads to the conclusion that further quantitative progress requires a knowledge of the law of force between molecules and ions at close approach. C. J. Smithells.

Atomic weight of uranium lead and the age of an especially ancient uraninite. T. W. Richards and L. P. Hall (J. Amer. Chem. Soc., 1926, **48**, 704—708).—Uranium lead from a specimen of the oldest Pre-Cambrian mineral yet found ($1·5\times10^9$ years) has an atomic weight of 206·07. Correction for the thorium content of the mineral reduces this to 206·02, but it appears probable that the atomic weight of pure uranium lead is less than this. S. K. Tweedy.

Rock-lead, ore-lead, and the age of the earth. A. Holmes (Nature, 1926, **117**, 482).—The assumption that ordinary lead has been wholly derived from the radioactive elements during their terrestrial history, leading to an estimate of 3200×10^6 years as the age of the earth, is unjustified, since it should lead to a value of less than 207 for the atomic weight of ordinary lead. It is considered that the value 1600×10^6 years is of the right order, and hence approximately half the lead of igneous rocks is of radioactive origin. Further, the ore-lead of mineral veins cannot be a concentration of the lead of igneous rocks, but presumably originated either in the ancestral sun or during the events attending the birth of the solar system. In the latter case, uranium and thorium must have originated or become radioactive at about the same time. If in the former case it was of radioactive origin, it must have been generated during a period in which the average ratio of uranium to thorium was 6 : 16·2, whereas the terrestrial ratio indicates a ratio greater than 6 : 15. A determination of the atomic weight of lead separated

from a representative collection of igneous rocks would appear desirable. A. A. ELDRIDGE.

Anomalous scattering of α-particles. P. DEBYE and W. HARDMEIER (Physikal. Z., 1926, 27, 196—199).—The scattering of α-particles by magnesium and aluminium is markedly less than the values deduced on the assumption that the nuclei and particles may be regarded as point-charges obeying the inverse square law of force (cf. A., 1925, ii, 1109). The phenomena are probably due, not to the breakdown of the simple law of force, but to attendant circumstances. When the nucleus is exposed to strong electric fields, its structure is not perfectly rigid, and, like the atom, it may exhibit a mobility given by its polarisability a (electric moment of the nucleus in unit field). In such a deformable nucleus, the supplementary attractions decrease with the fifth power of the distance. The polarisability of an atom is of the dimensions of volume and of the order 10^{-24} cm.^{3}, likewise for the nucleus it should be of the order 10^{-36} cm.^{3} The orbit of an α-particle has been calculated on this basis, and a curve reproducing experimental data is obtained when values of $1{\cdot}30\times10^{-36}$ and $0{\cdot}96\times10^{-36}$ are taken for aluminium and magnesium, respectively. The conception of polarisability is developed so that the conditions (distance, energy, velocity) for the capture of an α-particle by the nucleus are plausibly defined. R. A. MORTON.

Natural β-ray spectrum of radium-*D*. L. F. CURTISS (Physical Rev., 1926, [ii], 27, 257—265).—The following values are obtained for the intensity, $H\rho$, and energy (volts$\times10^{-5}$), respectively, of the five lines (the fifth being new) of the natural β-ray spectrum of radium-*D*; the radium-*B* line, $H\rho=660{\cdot}9$, being taken as the standard: (1) 50, 594·3, 0·3033; (2) 3, 600·3, 0·3092; (3) 25, 709·1, 0·4268; (4) 10, 735·2, 0·4576; (5) 1, 742·5, 0·4663. The energy of the γ-ray, which is emitted after the disintegration, is $0{\cdot}467\times10^5$ volts. A. A. ELDRIDGE.

High-frequency rays of cosmic origin. R. A. MILLIKAN (Science, 1925, 62, 446—448).—Renewed investigations have unambiguously demonstrated the existence of non-homogeneous radiation of cosmic origin, and having a penetrating power such that it is completely absorbed only after passage through the equivalent of 6 ft. of lead. The frequencies $(4—6{\cdot}7)\times10^{-4}$ Å. do not extend into the X-ray region; the rays pass through space in all directions, and with equal intensity day or night, stimulating, on striking matter, softer rays of approximately the frequency predicted by the theory of the Compton effect. The computed frequency corresponding with the formation of helium from hydrogen corresponds closely with the highest frequency rays observed. The computed frequencies of these rays also correspond closely with the energy involved in the capture of an electron by a positive nucleus. A. A. ELDRIDGE.

Origin of high altitude radiation. V. F. HESS (Physikal. Z., 1926, 27, 159—164).—Misleading statements in recent papers of Hoffmann (A., 1925, ii, 1110) and Millikan (cf. preceding abstract) are corrected. Hoffmann's criticism of the usual method of calculating the ionising action of a radioactive substance uniformly dispersed in an absorbing medium is unfounded. Even were it true, it would constitute no argument against the existence of high altitude radiation. Běhounek's absorption experiments (Physikal. Z., 1926, 27, 8), although open to criticism, seem to show that at sea level no appreciable radiation of greater penetrating power than the γ-rays of radium-*C* exists. The existence of highly penetrating rays at heights from 4 km. upwards is proved by the absorption experiments of Kolhörster and Millikan. The latter's observation that these rays give rise to a secondary radiation of about the same hardness as the γ-rays of radium-*C* explains the course of the absorption curves obtained by Hoffmann and Běhounek. A. B. MANNING.

Free path of protons in helium. A. J. DEMPSTER (Proc. Nat. Acad. Sci., 1926, 12, 96—98).—The results described previously with hydrogen (A., 1925, ii, 1020) have been obtained with protons which had been accelerated through 4500 volts. Similar experiments have been made with helium. At comparatively low pressures, all the ions except the hydrogen atoms were much reduced in intensity and disappeared at a pressure that had little influence on the proton bundle. As the pressure increased, the bundle broadened, but with 930 volts accelerating potential protons were observed as a definite group of rays with a pressure of 0·53 mm. At this pressure, the mean free path for a rapidly moving particle, assuming the kinetic gas theory value for the diameter of the helium atom, is 1·4 mm. The protons must therefore have passed through at least 120 atoms without appreciable alteration of their direction or velocity. Rays were obtained with an acceleration of only 14 volts with pressures up to 0·03 mm., when they make seven collisions in their path. No indications of loss of energy by the protons when passing through the atoms were obtained. Thus protons with the velocities used pass freely through helium atoms with only slight changes in their velocity or direction.
A. E. MITCHELL.

Interference of canal-rays. E. RUPP (Ann. Physik, 1926, [iv], 79, 1—34).—A detailed account of investigations of the interference possibilities of canal-rays from hydrogen and mercury in which a number of points of primarily physical interest are considered. Interference is possible only between light quanta from one and the same atom. The maximum path differences corresponding with interference for H_β and the mercury line 546 μμ are 15·2 and 62 cm., respectively. J. S. CARTER.

Relationship between atomic volume and atomic number. C. DEL FRESNO (Anal. Fís. Quím., 1926, 24, 47—61).—From theoretical considerations, it is deduced that within the same group in the periodic system and with increasing atomic number, the differences in atomic volume corresponding with equal increases in atomic number, for elements of consecutive periods, increase with atomic number. When the differences in atomic number of consecutive elements of the same group are unequal, the greater

atomic volume difference corresponds with the smaller atomic number difference and *vice versa*. Barium, radium, and arsenic form exceptions to this rule.
G. W. ROBINSON.

Radiation and the disintegration and aggregation of atoms. G. E. M. JAUNCEY and A. L. HUGHES (Proc. Nat. Acad. Sci., 1926, **12**, 169—173; cf. this vol., 221).—Postulating that in all interactions between radiation and matter, the following principles are satisfied: conservation of matter, charge, and momentum; reversibility of the process; velocities not to exceed that of light, the ways in which protons and electrons can produce a quantum by mutual annihilation are considered mathematically. This is possible by collision of two electrons and one proton or by collision of two protons and one electron, radiation of wave-lengths $2{\cdot}6\times10^{-5}$ and $1{\cdot}95\times10^{-5}$ Å., respectively, being produced. The ways in which four protons and two electrons can come together to form a quantum and a helium nucleus are considered. In general, the radiation produced has a wave-length of the order 4×10^{-4} Å. If, however, an electron moving with a velocity almost that of light collides with four protons and one electron all at rest, the wave-length produced is 8×10^{-4} Å. J. S. CARTER.

Correspondence principle and doublet spectra. J. KUDAR (Physikal. Z., 1926, **27**, 107—111).—A theoretical discussion of the difficulties attending the relativistic interpretation of optical and X-ray spectra from the side of the correspondence principle. The "real" relativistic quantum process (azimuthal quantum number k changes by 1) corresponds with a "virtual" magnetic quantum process (azimuthal quantum number K remains unchanged), the latter process corresponding with the classico-mechanical conception; *i.e.*, the real doubling of the (relativistic) quantum state of the electron responsible for light-emission corresponds with the virtual doubling of the (magnetic) quantum state of the core (cf. Landé, A., 1924, ii, 511, 711). R. A. MORTON.

Test of the correspondence principle based on the prediction of the absolute intensities of spectral lines. R. C. TOLMAN and R. M. BADGER (Proc. Nat. Acad. Sci., 1926, **12**, 173—174).—As the classical theory permits the calculation of absolute rates of energy emission, it is possible to test the correspondence principle by calculating the absolute intensities of spectral lines. The work of Czerny (A., 1925, ii, 1024) on the far infra-red spectrum of hydrogen chloride provides information as to the intensities of lines 8, 9, and 10 in the pure rotational spectrum. The necessary measurements of the dielectric constant have been made by Zahn (A., 1924, ii, 809), whilst the electric moment of the rotating molecules has been calculated by Pauling (this vol., 225). A rather complex calculation, details of which are promised later, leads to the values 5·6, 6·8, and $10{\cdot}6\times10^{16}$ c.g.s.u. for the respective Einstein absorption coefficients B_{ij} of these lines. The corresponding theoretical values calculated from the correspondence principle are 11·9, 11·8, and $11{\cdot}6\times10^{16}$ c.g.s.u., respectively. Considering experimental difficulties and mathematical complexities the agreement is held to be satisfactory. J. S. CARTER.

Quantum mechanics and a preliminary investigation of the hydrogen atom. P. A. M. DIRAC (Proc. Roy. Soc., 1926, **A**, **110**, 561—579).—The orbital motion of the electron in the hydrogen atom is examined mathematically on certain proposed general equations of motion, and an expression is obtained for the transition frequencies which is similar to a Rydberg equation. The general equations of motion have been developed from the point of view (Heisenberg, Z. Physik, 1925, **33**, 879) that if x and y are two functions of the co-ordinates and momenta of a dynamical system, then in general xy is not equal to yx. Equations which satisfy quantum conditions are given (cf. Proc. Roy. Soc., 1925, **A**, **109**, 642) by which $xy—yx$ can be calculated.
F. G. SOPER.

Dynamics of the helium atom. V. TRKAL (Z. Physik, 1926, **36**, 194—214; cf. A., 1923, ii, 478, 479).—A mathematical investigation of the dynamics of the helium atom model for the "singular" case in which the sum of the squares of distances between electrons and the nucleus is constant. By means of an analogy with hydrogen, the Hamiltonian functions for the three-body problem of the helium atom are used to connect the energy of the atom with quantum numbers and frequencies. R. A. MORTON.

Theory of light emission in the Rutherford-Bohr atom. J. PALACIOS (Ann. Physik, 1926, [iv], **79**, 55—80).—An amplification of work previously published elsewhere (A., 1925, ii, 835).
J. S. CARTER.

True absorption of light. T. BIALOBJESKI (Ann. Physique, 1926, [x], **5**, 215—264).—A theory of the transformation of light into heat in passing through an absorbing medium is developed. A part of the energy of radiation of a light wave becomes irregularly diffused throughout the medium through which it is passing, as a result of the heterogeneity of the medium. In the case of a gas, the heterogeneity arises from the fluctuations of density accompanying the molecular motion. The varying pressure exerted by the diffused waves on the molecules performs a positive amount of work which reappears as energy of molecular motion, that is, as heat. The mathematical and physical bases of the theory, and its development from the point of view of the quantum hypothesis, are discussed. A. B. MANNING.

Mechanics of light-quanta. K. SCHAPOSCHNIKOV (Z. Physik, 1926, **36**, 73—80).—A theoretical discussion of collisions between light-quanta and electrons. E. B. LUDLAM.

Systematic relations between electronic structure and band-spectrum structure in diatomic molecules. I. R. S. MULLIKEN (Proc. Nat. Acad. Sci., 1926, **12**, 144—151).—From a consideration of the structure of known band spectra, taking into account the occurrence of nearly integral and half-integral rotational quantum numbers, "missing lines" near the band-origins, occurrence of P, Q, and R branches, and the nature of the electronic multiplicity, certain postulates for the interpretation

and prediction of the structure of band spectra are put forward. J. S. CARTER.

Systematic relations between electronic structure and band-spectrum structure in diatomic molecules. II. The ZnH, CdH, and HgH molecules and their spectra. R. S. MULLIKEN (Proc. Nat. Acad. Sci., 1926, **12**, 151—158).—An application of the postulates (preceding abstract) to the spectra of ZnH, CdH, and HgH investigated by Kratzer (Ann. Physik, 1923, [iv], **71**, 89), Hulthén (A., 1925, ii, 470), and Ludloff (*ibid.*, 1113). Kratzer's equation for the representation of bands is criticised, and it is suggested that the added linear term, the theoretical justification of which is questionable, should be suppressed. Predicted first lines are in agreement with experiment where data are most trustworthy. The stabilities of molecules in their various excited states and their electronic configurations are discussed. According to the postulates, a structure essentially the same as in the HgH bands is to be expected for the transition $^2P_{1,2} \rightarrow {}^2S$ for all molecules; and for $^2S \rightarrow {}^2P_{1,2}$ a structure differing only in respect to the missing lines.

J. S. CARTER.

Electronic states of the helium molecule. R. S. MULLIKEN (Proc. Nat. Acad. Sci., 1926, **12**, 158—162).—A study of the helium bands leads to the designation $2S—mP$ (m=3, 4, 5 . . .) for the "main" and "second" series bands. The relatively intense "main" series is emitted by a molecule composed in its least excited state of two atoms in metastable $2S$ "doublet" states, and the weaker "second" series by a molecule composed of two metastable $2S$ singulet atoms. The additional bands at 6400, 4546, and 5730 Å. (Curtis, A., 1922, ii, 330; Kratzer, *ibid.*, 1923, ii, 595) are discussed and evidence is put forward to show that the first two bands correspond with a transition of the type $xP—mS$ and the third with $xP—mD$. The various electron levels and transitions now known for the helium molecule are presented in the form of an energy-level diagram. J. S. CARTER.

Alternating intensities in band lines. J. C. SLATER (Nature, 1926, **117**, 555—556).—The alternating intensities of the bands of neutral and ionised nitrogen, and of oxygen, may be connected with the difficulty of assigning the proper period in quantising the rotation of a symmetrical system. Thus the anomalous intensities should depend on the properties of the states, and not of the transitions. In every case examined, the lines starting or ending at a given rotational state are either all strong or all weak.

A. A. ELDRIDGE.

Structure of the bands 4511 and 4123 in the spectrum of carbon monoxide. O. JASSE (Compt. rend., 1926, **182**, 692—694).—The bands in the spectrum of carbon monoxide can be arranged in series, P, Q, and R, and the equation $R(m)-Q(m)=Q(m+1)-P(m+1)$ holds. The bands 4511 and 4123 have a more complex structure than those of Hulthén (A., 1925, ii, 470), but they belong to the same series.

W. THOMAS.

Ultra-violet absorption spectra of aqueous solutions of sulphur dioxide and some of its derivatives. F. H. GETMAN (J. Physical Chem., 1926, **30**, 266—276; cf. Wright, J.C.S., 1914, **105**, 673; Garrett, *ibid.*, 1915, **107**, 1324; Schaefer, Niggemann, and Koehler, A., 1915, ii, 389).—The extinction coefficients of aqueous solutions of sulphur dioxide, sodium sulphite, sodium hydrogen sulphite, and potassium metabisulphite have been studied and curves showing the logarithms of the molecular extinction plotted against corresponding wave-lengths are given. In agreement with Baly and Bailey (J.C.S., 1922, **121**, 1813) and others, it is found that aqueous solutions of sulphur dioxide show a characteristic absorption band at 276 μμ, attributed to hydrated sulphur dioxide (SO_2,H_2O). For solutions of the same concentration, the extinction curve can readily be reproduced provided that oxygen and carbon dioxide are excluded. Freshly-prepared solutions of potassium metabisulphite give a characteristic band at 263 μμ, and this is regarded as evidence of the existence of the undecomposed salt in solution. On keeping, this band is replaced by that of sulphur dioxide at 276 μμ. Freshly-prepared solutions of sodium hydrogen sulphite show end absorption only, but on keeping in the light, if oxygen be present, photo-oxidation of the ion HSO_3' occurs with the simultaneous development of the band at 276 μμ. The absorption coefficient increases up to a maximum in 30 days. No band at 257 μμ was obtained with solutions of either sodium hydrogen sulphite or potassium metabisulphite, as is claimed by Baly and Bailey (*loc. cit.*). Light is essential to the oxidation of hydrogen sulphite solutions; the presence of sucrose retards this oxidation. Solutions of sodium sulphite do not show selective absorption.

Baly's relationship (A., 1915, ii, 714) connecting ultra-violet frequencies with a fundamental frequency in the infra-red is applicable to the bands at 263 and 276 μμ found for potassium metabisulphite and the hydrated sulphur dioxide, respectively.

Beer's law does not apply to aqueous solutions of sulphur dioxide or its derivatives.

L. S. THEOBALD.

Constitution and absorption spectra of ferro- and cupri-nitricoxide salts. W. MANCHOT and E. LINCKH (Ber., 1926, **59**, [*B*], 406—411; cf. Manchot and co-workers, A., 1907, ii, 93; 1910, ii, 414; 1914, ii, 567).—The absorption spectra have been determined for constant thickness and varying concentration of solution. The optical behaviour of ferronitricoxide sulphate, selenate, and chloride in aqueous solution is identical, the coloured cation, $FeNO'$, being uninfluenced by the optically indifferent anions. Cl', SO_4'', and SeO_4''. The spectra of the green solutions of ferronitricoxide chloride in alcohol, esters (acetic, benzoic, or malonic), or hydrochloric acid are completely similar, so that hydrogen chloride may replace alcohol or ester in the anionic complex which causes the colour. On the other hand, the spectra of the red solutions of ferronitricoxide sulphate in concentrated sulphuric acid or of ferronitricoxide chloride in pyridine denote a different structure of the coloured component.

Solutions of cuprinitricoxide salts in concentrated sulphuric acid, alcohol, or ethyl acetate have closely similar absorption spectra, which nearly resemble those of the green type of ferronitricoxide salts. It appears probable that the colour is due entirely to the compound CuX_2,NO, and that the solvent takes no part in the formation of the complex. Copper compounds analogous to the brown ferronitricoxide salts do not appear to exist, thus explaining the observations that aqueous solutions of copper salts do not absorb nitric oxide and that the production of cuprinitricoxide salts is greatly restricted by the presence of water. The red ferronitricoxide salts have no counterpart among copper compounds. H. WREN.

Constitution and absorption spectra of ferronitrososulphide compounds (Roussin's salts) and their relationship to the dissociating ferronitricoxide salts. W. MANCHOT and E. LINCKH (Ber., 1926, **59**, [*B*], 412—418).—The absorption spectra of Roussin's salts, belonging to the red series [$Fe(NO)_2S{\cdot}K$ and $Fe(NO)_2S{\cdot}SO_3K$, in water; $Fe(NO)_2S{\cdot}Et$ in alcohol], are closely similar to one another, but differ completely from those of the brown, green, or red ferronitricoxide salts (cf. preceding abstract). They are formed by an irreversible reaction, the absorption of 2 mols. of nitric oxide being independent of the partial pressure of the latter; during their decomposition there is no evidence of the production of compounds containing a smaller proportion of nitric oxide. Their formation depends on the presence of the thiol group. The most probable constitution is $RS{\cdot}Fe(NO)_2{\cdot}Fe(NO)_2{\cdot}SR$. In confirmation of Bellucci's formulation,

$$\left[\begin{matrix}Fe(NO)_2S\\Fe(NO)_2S\end{matrix}\!\!>\!Fe\!<\!\begin{matrix}Fe(NO)_2S\\NO\end{matrix}\right]K,$$

for the black series of Roussin's salts (cf. A., 1907, ii, 29, 472; 1908, ii, 499, 593), it is observed that the absorption spectra of these compounds dissolved in water are closely analogous to those of the brown, dissociating ferronitricoxide salts. Further, they are readily produced when potassium ferronitrosulphide is treated with an aqueous solution of ferrous sulphate in an atmosphere of nitric oxide. The formation of the red from the black salts is necessarily accompanied by partial decomposition, whereby iron is eliminated in combination with nitric oxide and is subsequently oxidised, with consequent formation of nitrous oxide or ammonia, according to conditions. Direct conversion of the red into the black series cannot be achieved, and is not in any case possible if the potassium atom of the compound $Fe(NO)_2SK$ is replaced by a non-mobile group unless a portion of the molecule is destroyed. H. WREN.

Absorption spectrum of tin vapour in the ultra-violet. R. V. ZUMSTEIN (Physical Rev., 1926, [ii], **27**, 150—156).—The arc spectrum of tin between 1950 and 2170 Å. has been explored, 12 new lines being observed. Values of the wave-length, frequency, and intensity are tabulated, together with known values from 6000 to 2190 Å. and 1756 to 1950 Å.; 53 lines (38 of which are new) at which absorption by the vapour was observed are also indicated. The results are in general agreement with McLennan, Young, and McLay's table of frequency differences (A., 1925, ii, 454). A new table, revised to envisage the absorption experiments and the new arc lines, is given. A. A. ELDRIDGE.

Infra-red absorption spectra of organic derivatives of ammonia. III. Di- and tri-phenylamine. IV. Mono-, di-, and tri-benzylamine. F. K. BELL (J. Amer. Chem. Soc., 1926, **48**, 813—817, 818—823; cf. this vol., 222).—III. Infra-red absorption curves for molten diphenylamine (at 65°) and triphenylamine (145°) are figured. In the region 2·8—3·4 μ, the same qualitative differentiation is observed between aniline and di- and tri-phenylamines as between aniline and the alkylanilines, whilst the intensity of the benzene band at 3·3 μ is not increased with increasing phenylation of the ammonia (cf. Lecomte, A., 1924, ii, 641). In the region 3·0—10·0 μ, the curves for di- and tri-phenylamine are decidedly similar.

IV. Infra-red absorption spectra of mono-, di-, and tri-benzylamine, the first two at the ordinary temperature, the last at 105°, are figured. The same general qualitative differentiation is observed in these three compounds as that previously recorded between corresponding amines of the aryl and aryl–alkyl types. The absorption spectrum of monobenzylamine suggests the predominance of the alkyl structure. In tribenzylamine, the aryl structure is most marked, whilst the dibenzylamine curve is intermediate. In the cases of di- and tri-benzylamine, both the benzene band at 3·3 μ and the methyl band at 3·5 μ are present, indicating the probability of the presence of these two bands in all aryl–alkyl derivatives, although a broad band at 3·4 μ could not be resolved in the case of monobenzylamine. A new band, characteristic of the benzene nucleus, was located at 5·1 μ.

F. G. WILLSON.

Absorption spectra of mesityl oxide. R. A. MORTON (J.C.S., 1926, 719—720).—Mesityl oxide reacts completely with sodium hydrogen sulphite solution, giving a practically quantitative yield of the double compound. The ketone regenerated from the hydrogen sulphite compound was identical with the original product in respect to b. p. and absorption spectrum in the liquid state, and in alcoholic solution. The substance exhibits four distinct absorption bands, the maximum wave-length absorbed being at 3240 Å. The pure liquid shows the same frequency of maximum absorption as the vapour. Thus the reported isolation by Harries (A., 1899, i, 566; 1904, i, 427) of a form of mesityl oxide inactive towards sodium hydrogen sulphite has not been confirmed. A. E. MITCHELL.

Infra-red absorption of the N—H linking. E. O. SALANT (Proc. Nat. Acad. Sci., 1926, **12**, 74—80).—Di-*n*-propylamine, di-*n*-butylamine, di*iso*amylamine, diphenylamine, dibenzylamine, and hydrazobenzene show absorption from 2·9 to 3·1 μ, whilst tri-*n*-propylamine, tri-*n*-butylamine, tri*iso*amylamine, triphenylamine, tribenzylamine, and azobenzene do not. An absorption band in the region of 3 μ is therefore characteristic of the N—H linking. In the solid state, diphenylamine has the absorption band at 2·89 μ instead of between 3 and 3·1 μ. This shift of the band is attributed to the linking of the nitrogen

to the unsaturated carbon atom, and not to any influence of the physical state. A. E. MITCHELL.

Absorption spectra and tautomerism. I. Keto-enol tautomerism. Ethyl acetoacetate, acetylacetone, and α-benzoylcamphor. R. A. MORTON and W. C. V. ROSNEY (J.C.S., 1926, 706—713).—Measurements of the absorption spectra of ethyl acetoacetate, acetylacetone, α-benzoylcamphor, and a large number of derivatives, have been made. The results are in agreement with those of Grossmann (Z. physikal. Chem., 1914, **109**, 305), with the addition that it is shown that thin films of ethyl acetoacetate exhibit an absorption band at 2430 Å., and that ethyl dialkylacetoacetates exhibit one in the region of 2800 Å. The results indicate that keto-enol tautomerides exhibit the same wave-length of maximum absorption, but show extinction coefficients of a different order of magnitude. A. E. MITCHELL.

Absorption spectra and tautomerism. II. Ethyl mesityloxidoxalate, formylphenylacetate, and diacetylsuccinate. R. A. MORTON and E. ROGERS (J.C.S., 1926, 713—718).—An examination of the absorption spectra of ethyl mesityloxidoxalate, ethylformylphenylacetate, and ethyl diacetylsuccinate, has shown that these are different in type from those exhibited by keto-enol tautomerides (cf. preceding abstract). The reversible α ⇌ β isomerism of ethyl mesityloxidoxalate resembles ring-chain tautomerism rather than keto-enol tautomerism. The metallic derivatives appear to be co-ordinated compounds. The ratio of the absorptive powers of the two isomerides of ethyl formylformate is 1 : 1·2, which, taken in conjunction with the work of Errera and Henri (A., 1925, ii, 1137), indicates that these are *cis-trans* isomerides. Similar results for ethyl diethylsuccinate indicate that its isomerides are of the *cis-trans* type. A. E. MITCHELL.

Valency. V. Absorption spectra of halogen and sulphonic derivatives of camphor. Origin of the ketonic absorption band. T. M. LOWRY and G. OWEN (J.C.S., 1926, 606—622).—Quantitative data are given for the general and selective absorption of twenty halogen and sulphonic derivatives of camphor. These show that whilst the general absorption is influenced to a large extent by the introduction of a negative group in any position in the molecule, the selective absorption is influenced by a halogen atom only when this is in the α-position. The effect of a halogen atom or a sulphonic group in the more remote β- and π-positions is negligible. The ketonic absorption band is attributed to an activation of the valency electron of the double linking uniting carbon and oxygen. A. E. MITCHELL.

Valency. VI. General and selective absorption of halogen derivatives of methane. Origin of general absorption. T. M. LOWRY and (MISS) R. R. SASS (J.C.S., 1926, 622—630).—Quantitative data for nine halogen derivatives of methane are given. The general absorption of the chloro- and bromo-derivatives increases progressively from chloroform to carbon tetrabromide. Methyl iodide produces a band which increases in intensity and wave-length on passing to methylene iodide and to iodoform, where the absorption becomes selective and the crest is resolved into two maxima. The ultra-violet absorption band of methyl iodide is explained on the relative weakness of the band between carbon and iodine and the small energy quanta required to activate it. It is suggested that the general absorption of the halogen derivatives of methane and of camphor (cf. preceding abstract) and the increase in general absorption due to α-substitution of negative atoms is due to activation of a single linking, analogous to the activation of the double linking of the carbonyl group (*loc. cit.*). The close resemblance between the absorption spectra of iodoform and potassium iodide observed by Crymble, Stewart, and Wright (A., 1910, ii, 470) has been confirmed. A. E. MITCHELL.

Band series in infra-red absorption spectra of organic compounds. I. J. W. ELLIS (Physical Rev., 1926, [ii], **27**, 298—313).—The nature of the absorption curves characteristic of various organic liquids suggests that the origin of the different absorption bands may be traced to different atoms, or pairs of atoms, as absorbing centres. The frequencies of a series of outstanding bands, attributed to vibrations between atoms of a carbon–hydrogen pair, correspond with the expression $\nu_n \times 10^{-12} = 47{\cdot}37n - 0{\cdot}783n^2$, where $n = 1, 2, \ldots 10$. For a carbon–carbon linking, the frequencies of many bands are expressed by $\nu'_n \times 10^{-12} = 10{\cdot}71n$, where $n = 1, 2, \ldots 28$. Practically all the bands, up to 7 μ, observed in the spectra of the simple hydrocarbons, are accounted for by combinations of low-frequency members of these two series, $\nu_c = \nu_m + \nu'_n$. A. A. ELDRIDGE.

Fluorescence of mercury vapour. H. NIEWODNICZAŃSKI (Nature, 1926, **117**, 555).—The fluorescence radiation excited by an aluminium spark in mercury vapour, the mercury being contained in sealed tubes or in tubes connected to a mercury-vapour pump, remains unchanged if the entire tube is kept at a constant temperature, and is not increased by local cooling. The results are not in agreement with those of Wood and van der Lingen (A., 1922, ii, 245; cf. Proc. Roy. Soc., 1921, **A**, **99**, 362). Besides the bands and lines observed by these authors, the line 4358 Å. was found, appearing at 200° and having a maximum intensity at 230—270°. The line 2537 Å. appears at 130° and has a maximum intensity at 230°. A. A. ELDRIDGE.

Difference of the fluorescence and absorption spectra of uranyl salts. G. H. DIEKE and A. C. S. VAN HEEL (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 953—954).—The frequency interval between the spectral groups of the fluorescence spectrum of a uranyl salt is larger than that between the analogous groups in the absorption spectrum. This difference varies slightly for different salts, and is explained by supposing that the frequency interval of the fluorescence bands corresponds with the change of oscillation energy in the non-excited state, and that of the absorption bands to the difference between the energy levels in the excited state. M. S. BURR.

Monochromatic excitation of fluorescence [in uranyl salts]. A. C. S. VAN HEEL (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 955—957).—Examination of uranyl calcium phosphate (autunite) and of uranyl potassium sulphate at the temperatures of liquid air and liquid hydrogen has shown that pronounced fluorescence cannot be excited by light which has not exactly the same wave-length as one of the absorption lines. Numbering the fluorescence bands towards the red 1, 2, 3, etc., and the absorption bands towards the violet 1′, 2′, 3′, etc., band 1 is the same as band 1′. No fluorescence is excited by light of wave-length of fluorescence band 2. Light of wave-length of the reversible band 1 or 1′ excites the two fluorescence bands 2 and 3, but it is uncertain whether 1 emits or not. On excitation by band 2′, the fluorescence of bands 2 and 3 increases, the reversible band and a band still more towards the red, possibly 4, emit. Photographic observations were made in liquid air, but only visual ones in liquid hydrogen.

M. S. BURR.

Luminescence of solids. J. EWLES (Proc. Leeds Phil. Lit. Soc., 1925, **1**, [i], 6—10).—A theory of luminescence is developed according to which the necessary impurity, usually a coloured salt or a rare earth, is present in a state of solid solution, the atoms being incorporated in the crystal lattice of the "solvent." These incorporated atoms, linked with solvent atoms by electrostatic binding forces, constitute the radiating systems. Excitation may be by light, *X*-rays, or cathode rays, and for photo-excitation there exist definite excitation wave-lengths characteristic of the impurity. Atoms of impurity absorb the excitation waves, the absorbed energy causing an alteration of their electronic configuration (*e.g.*, an electron jumps from one orbit to another). As a result of the change in the external force field, the linked solvent atoms are displaced into a new and unstable configuration, which when excitation ceases returns to the original state with emission of energy in the form of luminescence. Consideration of the spectroscopic nature and of the direction of polarisation of the luminescent radiation supports this view. Cathode rays excite no considerable light emission until the rays attain a considerable velocity. For the slower rays, only soft "impulse" radiation results, which is absorbed largely by the solvent before reaching an impurity nucleus, light emission not commencing to any notable extent until a speed corresponding with an *X*-ray excitation quantum for the impurity is reached. Phosphorescence differs from luminescence in that it necessitates the ejection of an electron. Since the atom is more or less permanently ionised, the structure may resolve itself into a metastable configuration from which it will only return, possibly by a number of quantum jumps through stationary states, with emission of luminescence, on recovery of the lost electron. The fact that the intensity of luminescence passes through a maximum with increasing concentration of active impurity is explained by assuming that the emission is proportional to the number of impurity atoms present in a state of solid solution, and that there is a fairly low limiting concentration beyond which the impurity does not go into solid solution. The excess atoms cannot therefore form centres of emission, but can nevertheless absorb the exciting radiation and possibly also the emitted luminescent radiation. There is thus increased absorption and decreased emission. A necessary condition of the theory outlined is that the solvent must be transparent to some of the frequencies absorbable by the impurity in the state of solid solution.

J. S. CARTER.

Photographic spectra of triboluminescence. D. M. NELSON (J. Opt. Soc. Amer., 1926, **12**, 207—215).—The spectrum of triboluminescence can be photographed if a circular piece of suitable material is rotated (2000 revolutions/min.) and a wire brush or carborundum is pressed against a point a little below the slit of a spectrograph. The light from sphalerite gives a continuous spectrum in the yellow, with a duration of 0·02 sec. Chlorophane yields a similar spectrum consisting of a narrow yellow band. The spectrum obtained from a powdered synthetic zinc sulphide is wider and extends over into the green. The colours of triboluminescence, phosphorescence, and fluorescence spectra appear to be the same, with no essential difference in the case of the luminescent powder. The character of the brush does not affect the colour of the light, but exerts some influence on the intensity.

R. A. MORTON.

Triboluminescence. W. PERSCHKE (Compt. rend., 1926, **182**, 630—632).—The triboluminescence of zinc sulphide containing varying small quantities of manganese is uninfluenced by the action of red heat for 1—6 hrs. and by variation in the rate of cooling.

S. K. TWEEDY.

Samarium phosphors. M. TRAVNIČEK (Ann. Physik, 1926, [iv], **79**, 237—260; cf. A., 1925, ii, 354).—Intimate mixtures of traces of samarium oxide with oxides of the alkaline-earth metals (with or without sulphur) and a little alkali fluoride yield brilliant phosphors on fusion. The basis may be the oxides, sulphides, or sulphates, and the type atom oxygen or sulphur. Intense illumination with ultra-violet light results in a persistent afterglow which may be resolved spectroscopically into three groups of bands: (*a*) two or three double bands about 40—60 Å. wide in the region 640—670 μμ, (*b*) a doublet in the orange-red consisting of two bright lines less than 10 Å. wide and flanked on either side by weaker satellites, (*c*) a third group in the green-yellow similar in structure to (*b*). The discontinuities in the spectrum are connected with the property which samarium shares with other rare earths of exhibiting an absorption spectrum in solution or in the solid state consisting of very narrow bands. Comparable lines in the spectra yielded by different alkaline-earth phosphors exhibit shifts depending on the mol. wt. of the substance used as a basis.

In the sulphide phosphors, the lines move towards the blue as the mol. wt. of the sulphide increases, whilst the shift is in the opposite direction for the oxide phosphors. The relative intensities of single lines vary with the method of excitation. The spectra emitted from fused mixtures of calcium and strontium sulphides do not consist of the superposed spectra of

the individual phosphors as do the spectra of the mixed phosphors, but intermediate stages are observed. The effect of temperature on the duration of the afterglow and the influence of diluting the phosphors with inactive materials have been studied. The displacements of bands from red to violet in the sulphide and sulphate phosphors are connected with increasing heats of formation for the compounds in the order magnesium, calcium, strontium, and barium; and decreasing heats of formation of the oxides are accompanied by the reverse displacements. Tomaschek's mechanism for the phosphorescence is supported. R. A. MORTON.

Comparison of the energy and the ionisation produced in air by *X*-rays of different wave-lengths. H. KULENKAMPFF (Ann. Physik, 1926, [iv], **79**, 97—142).—The conditions for accurate determinations of the energy of *X*-rays by means of a thermopile and galvanometer are discussed in detail and data given for rays of varying hardness. Simultaneous measurements of the ionisation effected in a definite length of air allow the fraction of the total energy which is absorbed to be evaluated. The radiations employed were largely, but not strictly, monochromatic, since the complete emission of various metals used as anticathodes was passed through filters transmitting selectively the $K\alpha$ lines concerned. The amount of energy necessary for the formation in air of an ion-pair is independent of the wave-length within the range 0·56—2 Å. and corresponds with 35±5 volts/ion-pair. R. A. MORTON.

Increased conductivity of solid dielectrics on exposure to *X*-rays. C. ROOS (Z. Physik, 1926, **36**, 18—35).—Paraffin, ebonite, and amber show typical saturation values. The increase in conductivity is the same for rhombic as for monoclinic sulphur and does not reach a saturation value. The conductivity increases directly as the hardness of the *X*-rays. E. B. LUDLAM.

Dielectric constants of solutions of electrolytes. H. SACK (Physikal. Z., 1926, **27**, 206—208).—The expression $D=D_0[1-(D_0-D_1)n4\pi r^3/3D_0]$, in which D is the dielectric constant of a dilute solution, D_0 that of the solvent, D_1 that of a sphere of solute of radius r, and n the number of such spheres per c.c., leads to reasonable values of r for sugar solutions, but not for solutions of electrolytes. The discrepancy is due to the dipolar nature of the water molecule. In the neighbourhood of ions, orientation occurs within the sphere of influence of the ions. The phenomena are discussed theoretically and the expression $D=80(1-3{\cdot}0c)$, in which c is the molar concentration, is shown to be in good agreement with the ionic "sphere of influence" of the univalent aqueous salt solutions for which it is applicable. R. A. MORTON.

Dielectric constant and molecular weight of bromine vapour. L. PAULING (Physical Rev., 1926, [ii], **27**, 181—182).—Bramley's value for the dielectric constant of bromine vapour (A., 1925, ii, 802) is probably incorrect, and his conclusion that the vapour has the formula $(Br_2)_6$ is invalid. A. A. ELDRIDGE.

Dielectric constant of natural and synthetic mixtures. K. LICHTENECKER (Physikal. Z., 1926, **27**, 115—158).—A summary of work in the past fifty years, with an extensive bibliography. An historical section is followed by a comparison of formulæ connecting the dielectric constants of mixtures. The following matters are considered among others: refractive indices of mixtures, refractive index, and pressure (density) changes; dielectric constants and pressure (density), temperature, variations; dielectric constants of liquids under high pressures; the doubly-refracting and other properties of anisotropic mixtures. R. A. MORTON.

Association, adsorption, and dielectric constant. C. T. ZAHN (Physical Rev., 1926, [ii], **27**, 329—340).—Measurements were made, in the case of water vapour, of the variation of the dielectric constant with change of pressure (3—20 mm.) and of temperature (23·3—165°). At the ordinary temperature, the curve connecting ϵ—1 with the pressure consists of two straight portions connected by a transition curve; the change of slope disappears at about 47°. The anomalous upper portion is not ascribed to the effect of association, but to adsorption of water on the condenser plates. A. A. ELDRIDGE.

Electric moment of the benzene molecule. R. SÄNGER (Physikal. Z., 1926, **27**, 165—174).—Debye's theory, with the Lorentz–Lorenz value $\nu=4\pi/3$ for the inner field factor, gives an imaginary moment when applied to benzene in the liquid state. Gans' extension of the theory as interpreted by Graffunder gives zero moment, but according to Smyth gives a moment $\mu=0{\cdot}2\times10^{-18}$. A critical examination of the methods of calculating the electric moment from the dielectric constant shows that no definite value can be deduced from the available experimental results. Any inferences as to the electric moment of a liquid based on the variation of the dielectric constant with temperature are untrustworthy. For benzene, the experimental results are in accord with a zero moment. A. B. MANNING.

Diffusion of light in liquids. Y. ROCARD (Compt. rend., 1926, **182**, 690—691).—The depolarisation of carbon tetrachloride was found to be 0·106, and that of benzene to be 0·438, both measured for red light, fluorescence being eliminated. The diffusion of white light in benzene is 2·85 times that in carbon tetrachloride. Both liquids had been purified by slow filtration. Several errors in ordinary measurements are discussed and avoided. The results are used to test a molecular theory of the diffusion of light and formulæ are deduced. W. THOMAS.

Refractometry. K. VON AUWERS (Rec. trav. chim., 1926, **45**, 307—313).—Critical in reply to van Woerden (this vol., 293). The difference between the "theoretical" and the "comparative" views of refractometry is regarded as immaterial. The empirical basis of spectrochemistry is stressed. R. BRIGHTMAN.

Changes in the refractive index of helium produced in a glow discharge. W. H. MCCURDY and A. BRAMLEY (Physical Rev., 1926, [ii], **27**, 314—

317).—An account of preliminary attempts to measure the refractivity of helium in the spectral region close to emission or absorption lines. The requirements of Lorentz's and of Kramers' theories are considered.
A. A. ELDRIDGE.

Dependence of optical rotatory power on chemical constitution. VI. Rotatory powers of phenyl, *o*-, *m*-, *p*-tolyl, and β-naphthyl derivatives of *d*-camphorimide and *d*-camphoramic acid. B. K. SINGH and A. N. PURI (J.C.S., 1926, 504—508).—The optical rotatory powers of a number of aryl derivatives of *d*-camphorimide and *d*-camphoramic acid have been examined in methyl alcohol, ethyl alcohol, and acetone solutions at different concentrations. The substitution of the imido-hydrogen atom by an aryl group increases the rotatory power. The magnitude of the increase is greater than that obtained by Singh and Biswas (A., 1924, i, 1211) for the benzyl derivatives. The influence of the solvent is considerable in the case of *d*-camphoramic acid derivatives, but is small in those of *d*-camphorimide. The effect of the solvent appears to be a function of its dielectric constant, but is not directly proportional to it. Frankland and Cohen's rules do not apply to any of these derivatives. Contrary to the usually accepted rule, the rotatory powers of the open-chain derivatives are greater than those of the corresponding cyclic compounds. A. E. MITCHELL.

Mutarotation of mixtures of molybdates and ethyl malate. Probable constitution of the molybdomalate derivatives. E. DARMOIS (Compt. rend., 1926, **182**, 455—457; cf. A., 1923, i, 299, 535, 751).—The mutarotation of mixtures of molybdates and ethyl malate has been studied at 80°. The rate of mutarotation becomes marked only in the presence of molybdates more basic than $NaH_3(MoO_4)_2$. It depends also on the ratio ester : MoO_3, and on the total concentration. Two series of mixtures were investigated in which the ester : MoO_3 ratios were, respectively, 1 : 2 and 2 : 1, the molybdates used being $NaH_3(MoO_4)_2$, $Na_2H_2(MoO_4)_2$, Na_2MoO_4, and Na_2MoO_4,NaOH. The rotation, always negative, passes through a maximum, and then returns towards zero. In both series, the malate is saponified. It is suggested that this occurs in two stages, the first leading to the formation of ethyl hydrogen malate, which reacts with molybdic acid to give a lævorotatory compound, $MoO_3,2C_4H_4O_5NaEt$, whilst the second is characterised by complete saponification giving the dextrorotatory compound,

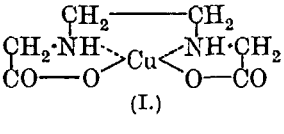
$$4MoO_3,2C_4H_4O_5Na_2.$$

F. G. TRYHORN.

Optical activity and the polarity of substituent groups. III. Menthyl acetophenone-*o*-carboxylate. H. G. RULE and J. SMITH (J.C.S., 1926, 553—556).—The rotatory dispersion of menthyl acetophenone-*o*-carboxylate is found to be normal and apparently simple in character. The optical rotatory power of the substance, $[M]_D^{24}$ −261°, lies above that of the unsubstituted benzoate, but below that of menthyl phthalate. Thus, as in the case of the other positive substituents examined previously (A., 1924, ii, 645; 1925, ii, 1120), the substitution of the acetyl group raises the rotatory power of menthyl benzoate. The relative influence of the acetyl group on the rotatory power is in agreement with its relative influence on the nitration of benzene shown by Rule and Paterson (A., 1925, i, 29). A. E. MITCHELL.

Experimental proof of the existence of semi-polar double linkings. T. M. LOWRY (Bull. Soc. chim., 1926, [iv], **39**, 203—206; cf. J.C.S., 1923, **123**, 822).—The values obtained by Sugden (A., 1925, ii, 936) for the parachor show a constant increment for each double linking present in the molecule. Exceptions are found in the case of the groups :S:O and :P:O in substances such as phosphoryl chloride. This agrees with the author's contention that such linkings are of a semi-polar nature, $:\overset{+}{S}\cdot\overset{-}{O}$, and this is further supported by the observation by Phillips (this vol., 159) of optical activity among sulphinates of the type $Mc\cdot C_6H_4\cdot SO\cdot OEt$, which cannot be accounted for by a simple double linking :S:O. The position of the ultra-violet absorption bands of camphor and similar ketones indicates that the valency electrons, and not the inner kernels, are activated, and this activation is regarded as the transformation of the inactive co-valent double linking into the active semi-polar linking $:\overset{+}{C}\cdot\overset{-}{O}$. Substances such as ethylene exist chiefly in the non-polar form, but the reactive form of the molecule is probably semi-polar; this agrees with the retardation of the velocity of bromination when vessels lined with paraffin are used (Norrish, J.C.S., 1923, **123**, 3006).
W. HUME-ROTHERY.

***Cis–trans* isomerism of co-ordinatively quadrivalent complex salts.** H. REIHLEN (Z. anorg. Chem., 1926, **151**, 71—76).—Compounds of bivalent platinum of the type PtA_2B_2 exist in two isomeric forms, which is explained by Werner as *cis–trans* isomerism with the four groups in one plane. Similar compounds of other metals exist only in one form. In liquid ammonia, platinum *cis*-dichlorodiammine has the normal mol. wt., whereas the *trans*-compound has double this value. It is therefore possible that such compounds are polymerides. Schlesinger (A., 1925, i, 1249) ascribes *cis–trans* isomerism to compounds of copper with polymethylene-bis-α-imino acids of the type (I), but this is unnecessary. If the four valencies of the nitrogen atoms are arranged tetrahedrally, it is found that the two similar rings in such compounds do not lie in the same plane, but at right angles to each other. Each nitrogen atom and the copper atom are then asymmetric, and three pairs of optical isomerides are possible. The number to be expected in a particular compound depends on the number of methylene groups in the chain; some of the theoretically possible isomerides would involve too great a strain in chains of less than seven carbon atoms. In some cases, further isomerism is possible, due to more than one strain-free position of the polymethylene chain. Isomeric ethylene compounds can be explained only by this tetrahedral arrangement


(I.)

round the copper atom, unless the ethylene chain is assumed to be greatly strained. The absence of isomeric copper glycine, sarcosine, and picoline compounds is not accounted for by a plane formula. Copper compounds of acids of the type

$CO_2H{\cdot}CRR^1{\cdot}NH{\cdot}[CH_2]_n{\cdot}NH{\cdot}CRR^1{\cdot}CO_2H$,

containing two similar asymmetric carbon atoms, have twenty possible isomeric forms. Many of these may be unobtainable, since the configuration of the two carbon atoms may control the arrangement of the remainder of the molecule in complex compound formation. A. GEAKE.

Comparison of some of the physical properties of alkali cyanates and azides. J. A. CRANSTON and A. Y. LIVINGSTONE (J.C.S., 1926, 501—503).—Examination of some physical properties of sodium and potassium azide and cyanate has shown a great resemblance between sodium azide and sodium cyanate on the one hand and potassium azide and potassium cyanate on the other. The properties examined were the densities and refractive indices of solutions in alcohol–water mixtures, the densities of the crystalline salts, the solubilities of the salts in alcohol and alcohol–water mixtures, and the electrical conductivities of methyl-alcoholic solutions at 25°. The result, taken in conjunction with the similarity of crystal structure noted by Langmuir (A., 1919, ii, 506), is evidence that the arrangement of the electrons and atoms in the cyanate and azide ions is the same. A. E. MITCHELL.

Residual valency of organic compounds. G. WEISSENBERGER, F. SCHUSTER, and L. PIATTI (Z. anorg. Chem., 1926, **151**, 77—80).—The tendency of an organic substance to form molecular compounds may be measured by determining its partition between various pairs of liquids, one of the pair being always the same. Thus, when acetic acid is shaken with water and *cyclo*hexanol, the ratio of the concentrations in the two liquids is 1·14. When *cyclo*hexanol is replaced by cresol, the ratio is only 1·02, indicating complex formation between acetic acid and cresol. A. GEAKE.

Prediction of the relative stabilities of isosteric isomeric ions and molecules. L. PAULING and S. B. HENDRICKS (J. Amer. Chem. Soc., 1926, **48**, 641—651).—The qualitative prediction of the stabilities of certain aggregations of atoms with small kernels, and containing only *K*-level electrons, is described, it being postulated that the differences in the free energies of isosteric isomeric molecules or ions arise principally in the terms involving the mutual potential energy of the positive kernels, the energy terms due to the outer electrons being too small to cancel the effect due to the kernels. It is also assumed that the interkernel distances are unchanged by rearrangement. Carbon dioxide and nitrous oxide, it is shown, are probably OCO and NNO, and the greater stability of the NCO′ ion as compared with the CNO′ ion is explained. Carbimides, R·NCO, should, theoretically, be more stable than the cyanates, R·OCN; fulminates are probably M·CNO and not M·ONC. Nitrile oxides are considered to be fulminic esters, R·CNO. The instability of carbylamines, R·NC, in comparison with the stability of nitriles, R·CN, is explained, and the structures HCN for hydrocyanic acid, M′(CN)′ for alkali cyanides, and MCN for heavy metal cyanides, are shown to be in agreement with chemical properties. The formula NCCN for cyanogen is confirmed, and the formula NCX is predicted for its halides. S. K. TWEEDY.

Relationships between molecular diameter and density of a fluid. J. H. SHAXBY (Compt. rend., 1926, **182**, 847—849).—On the assumption that the density, d, of a fluid is determined by the equilibrium between the molecular attraction and the thermal molecular motion, the following relationships are deduced: (i) $d^{\frac{1}{3}}-d_1^{\frac{1}{3}}=\alpha T(\log_e d^{\frac{1}{3}}-\log_e d_0^{\frac{1}{3}})$, where (ii) $\alpha T_c=d_c^{\frac{1}{3}}$, (iii) $2d_1^{\frac{1}{3}}=3d_c^{\frac{1}{3}}$, and (iv) $d_0^{\frac{1}{3}}=e^{\frac{1}{3}}d_c^{\frac{1}{3}}$; also (v) $\sigma=e^{-\frac{1}{3}}(M/Nd_c)^{\frac{1}{3}}$. d_c is the critical density, T_c the critical temperature, and σ the molecular diameter, of the fluid; α, d_1, and d_0 (the density for zero molecular potential energy, V) are characteristic quantities defined by (ii), (iii), and (iv), respectively. (i) is confirmed for liquid heptane; it holds less satisfactorily for saturated heptane vapour. Mills' expression for the latent heat of evaporation of a fluid (A., 1902, ii, 596) is deduced from (i), which is based directly on the kinetic theory. (v) is confirmed for several gases, but not for hydrogen and helium. The characteristic molecular energy of a fluid, E ($V=E-Bd^{\frac{1}{3}}$, where $d/d_0=e^{-V/RT}$, B being a characteristic constant), is three times the kinetic energy at the critical temperature.

S. K. TWEEDY.

Crystal angles measured under a microscope. E. A. HILL (J. Amer. Chem. Soc., 1926, **48**, 651—654).—The parallel edges of a small crystal suitably mounted on an object slide are successively focussed through a microscope. The apparent distance between each edge is measured on a micrometer scale in the eyepiece and the successive positions of the objective, which should be of high power and small depth of focus, are determined by counting the divisions on the fine-adjustment screw. From these measurements the angles between the crystal faces are readily calculated trigonometrically. S. K. TWEEDY.

Evidence from crystal structures in regard to atomic structures. M. L. HUGGINS (Physical Rev., 1926, [ii], **27**, 286—297).—From the cubical symmetry, the equivalent scattering power of all the atoms, and the absence of pyro- and piezo-electric effects, it is concluded that the atoms in the diamond are not held together as a result of the transfer of electrons from one atom to another; further, no cubical arrangement of electrons or electron orbits around each atom, with two electrons or orbits shared between each two adjacent atoms, is possible. Since the atoms in beryllium oxide, zinc sulphide, silver iodide, and other compounds are held together in a manner similar to that in diamond, any arrangement of four electrons rotating about each atomic kernel is regarded as being very improbable. Comparison with the sodium chloride type of crystal also indicates the improbability of the valency electrons rotating about two atomic centres. It is

therefore concluded that in the diamond and crystals of similar structure the valency electrons are in pairs at tetrahedron corners around each atomic kernel, each electron pair being held jointly by two atoms. In general, the valency shells of electronegative atoms are tetrahedra of electron pairs, and not cubes of single electrons. A. A. ELDRIDGE.

Discussion of fine structure and *X*-ray methods with regard to optical anomalies [of crystals]. F. RINNE (Zentr. Min. Geol., 1925, **A**, 225—241; from Chem. Zentr., 1925, II, 2310).—Laue exposures on crystals with anomalous optical properties and double refraction yield the same diagrams as for normal crystals. Optical anomalies in crystals are due to progressive alterations in the electron orbits which are a result of slight rearrangements in the nucleus. This view is extended to optically anomalous mixed crystals. J. S. CARTER.

Relative intensities of reflexion of *X*-rays from the principal atomic planes of fluorite. D. A. MACINNES and T. SHEDLOVSKY (Physical Rev., 1926, [ii], **27**, 130—137).—The values of the relative intensities of the palladium α- and β-lines when reflected from three principal planes of fluorite fall into three groups for each line, decreasing according as calcium and fluorine atoms act together, calcium atoms act alone, or calcium and fluorine atoms are out of phase. Smooth curves are obtained when the square root of the relative intensities is plotted against the cosecant of the angles of reflexion.

A. A. ELDRIDGE.

Crystal structure. I. Symmetrical grouping of discontinuous point distribution. II. Atom groups in crystals and their physical significance. K. WEISSENBERG (Z. Krist., 1925, **62**, 13—51, 52—102; from Chem. Zentr., 1925, II, 2306).—A detailed consideration of the subject, including a description of homogeneous discontinuity as defined by Schönfliesz and the interpretation of structures as given by Röntgenograms.

J. S. CARTER.

Distribution of two atom-types in mixed crystals. G. TAMMANN (Ann. Physik, 1926, [iv], **79**, 81—84).—A defence of the author's views regarding the "normal" distribution of atoms in mixed crystals and the applicability of *X*-ray interference measurements (A., 1925, ii, 20) against the criticisms of von Laue (this vol., 12). J. S. CARTER.

Determination of the orientation of the crystallites in metallic conglomerates. G. TAMMANN and A. MÜLLER (Z. Metallk., 1926, **18**, 69—74).—Three methods of determining the orientation of a crystallite in a metallic conglomerate are described, viz., determination of the angle of reflexion of light from a polished and etched surface, production of deformation figures, and development of surface colorations. When etched with 10% ammonium persulphate, the cube planes of a copper crystal show square, and the octahedron planes triangular etching pits, the sides of which are parallel to the edges of the cube and octahedron, respectively. The rhombic dodecahedron faces develop wavy lines parallel to the short diagonal of the face. The direction of maximum reflexion in the case of cubic or octahedral crystals is perpendicular to the sides, and, in the case of the rhombic dodecahedral crystals, perpendicular to the short diagonal. Deformation figures are produced by pressing small plungers of circular, square, or triangular cross-section into the crystal; that produced by a square plunger, pressed into the side of a cubic crystal of copper so that its sides are parallel to the diagonals, consists of a series of lines also parallel to the diagonals of the cube face, and similar lines parallel to the sides of the octahedron are produced by impressing a triangular plunger into an octahedral crystal. Characteristic deformation figures are obtained by pressing a steel needle into the centre of the face of a copper crystal; the slip planes are always parallel to the sides of the octahedron and the figures consist of three or four pincer-like markings enclosing parallel slip lines (in the case of the cubic face, parallel to its diagonals). When copper is heated in the air at 260°, the rate of thickening of the oxide film varies according to the crystal face, increasing in the order: cube, octahedron, rhombic dodecahedron, and, by observing the colour changes of neighbouring crystallites, it is possible to determine their orientation; thus the (001) faces are coloured violet-indigo when the (111) faces are yellowish-green and the (011) faces yellow. A square plunger produces on the cube faces of α-iron a series of squares the sides of which are parallel to the diagonals of the face, whilst a circular plunger produces a pattern in the form of a cross, the arms of which are parallel to the diagonals, showing that slip takes place on octahedral planes and not on those of the icositetrahedron (Neumann lines). The deformation figures on γ-iron are similar to those on α-iron in general shape, but may be differentiated from them by the fact that the different series of parallel lines meet each other in sharp angles in γ-iron, whereas in α-iron these angles are rounded off. The impression produced on the hexagonal basal plane of zinc by a gramophone needle is in the form of a six-pointed star superimposed on concentric hexagonal markings, the sides of the hexagons being parallel to the sides of the crystal and the arms of the star bisecting these sides.

A. R. POWELL.

***X*-Ray investigations of the structure of some alloys.** S. HOLGERSSON (Ann. Physik, 1926, [iv], **79**, 35—54).—The variation of the lattice parameter with atomic concentration in the binary alloys silver–gold and copper–nickel has been investigated. The values of a for the pure components are: silver, 4·076; gold, 4·080; copper, 3·620; nickel, 3·519 Å. These numbers are in good agreement with existing data. Measurements on the silver–gold alloys lead to values differing from those of McKeehan (A., 1923, ii, 428). The lattice parameter–atomic concentration curves are convex to the concentration axis, indicative of a contraction of the lattice, due to an increase in the field of force within the alloy. The significance of this increased field is briefly discussed with reference to the physical properties (conductivity etc.) of binary alloys. J. S. CARTER.

Crystal structure of Heusler alloys. L. HARANG (Physikal. Z., 1926, **27**, 204—205).—The structure of Heusler ferromagnetic aluminium–manganese bronzes has been determined. The magnetic properties are due to a complex $(AlM_3)_x$, in which M_{3x} is an isomorphous mixture of manganese and copper. Three lattices are found: two cubic space-centred with constant distances 2·975 and 2·903 Å., and one cubic face-centred lattice with a variable distance (3·709—3·552 Å.). The first consists of copper and manganese atoms in a 1 : 1 ratio. Two copper atoms enter into the second lattice for each manganese atom. The third lattice presumably arises from mixed crystals, since the length of the side increases with decreasing aluminium content. There is no simple relationship between the magnetic properties and the appearance of the different lattices. R. A. MORTON.

Crystal structure of magnesium fluoride and other compounds of this crystal-type. A. E. VAN ARKEL (Physica, 1925, **5**, 162—171; from Chem. Zentr., 1925, II, 2306).—Magnesium fluoride forms ditetragonal-bipyramidal crystals having a rutile structure. The elementary parallelepiped contains two molecules and possesses the space-group D_{4h}^{14}; a=4·69, c=3·08 Å.; $d_{cal.}$ 3·05. Co-ordinates: magnesium (0, 0, 0), $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, fluorine $(u, u, 0)$, $(\bar{u}, \bar{u}, 0)$, $(u+\frac{1}{2}, u-\frac{1}{2}, \frac{1}{2})$, $(u-\frac{1}{2}, u+\frac{1}{2}, \frac{1}{2})$. The structure of prepared magnesium fluoride agrees with that of the mineral sellaite. From the structure factor the value of u is approximately 0·304. Potassium magnesium fluoride forms cubic crystals, the elementary parallelepiped containing one molecule; a=4·00 Å.; $d_{cal.}$ 3·18. Co-ordinates: potassium (0, 0, 0), magnesium $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, fluorine $(\frac{1}{2}, 0, \frac{1}{2})$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, 0)$. Lead dioxide probably possesses a rutile structure. Since the scattering power of the oxygen atom is very small compared with that of the lead atom, only the arrangement of lead atoms can be determined. These form a space-centred tetragonal elementary parallelepiped, a=4·97, c=3·40 Å. Of the elements of group IV, titanium, tin, and lead form dioxides having a rutile structure; thorium and zirconium do not. J. S. CARTER.

Structure of nickelin and pyrrhotin. W. F. DE JONG (Physica, 1925, **5**, 194—198; from Chem. Zentr., 1925, II, 2306).—An examination of the crystal structure of the dihexagonal-bipyramidal nickel arsenide, NiAs, leads to a structure differing from that given by Aminoff (Z. Krist., 1923, **58**, 212) in that to the elementary parallelepiped, which contains two molecules, the space-group D_{6h}^4 is assigned. The atom co-ordinates are: nickel (0, 0, 0), $(0, 0, \frac{1}{2})$; arsenic $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$, $(\frac{2}{3}, \frac{1}{3}, \frac{1}{4})$; a=3·57, c=5·10; nickel–arsenic distance =2·42 Å. Pyrrhotin, FeS, has probably the same structure: a=3·43, c=5·71 Å. J. S. CARTER.

Structure of breithauptite. W. F. DE JONG (Physica, 1925, **5**, 241—243; from Chem. Zentr., 1925, II, 2306—2307).—Breithauptite, NiSb, has the same structure as the corresponding arsenide (cf. preceding abstract). a=3·938, c=5·138; nickel–antimony distance =2·61 Å. J. S. CARTER.

Crystal structure [of carbon compounds]. A. NOLD (Z. Krist., 1925, **62**, 127—137; from Chem. Zentr., 1925, II, 2310).—A space model for carbon compounds is described. J. S. CARTER.

Crystal structure of iodoform. I. NITTA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 49—58).—Laue diagrams and spectrometric results indicate two molecules to the cell, with a=6·87 and c=7·61 Å. The former make it certain that whilst c is a hexad axis of symmetry, there are no planes of symmetry parallel to c; hence the crystal is of lower symmetry than dihexagonal-dipyramidal. All six atoms of iodine are in equivalent positions in the lattice. From a study of the disymmetry of intensities between Laue spots corresponding with $\{hkl\}$ and $\{khl\}$ planes, the parameters of the iodine atoms are arrived at, with the result that the shortest distance between any two is 3·60 Å. Of the two possible space-groups C_6^6 and C_{6h}^2, the former, although appearing incompatible with the plane of symmetry parallel to a, is regarded as the more probable, because otherwise the tetrahedral arrangement of hydrogen and iodine atoms about the carbon atom meets with difficulties. For the intrinsic symmetry of the molecule, C_3 (trigonal-pyramidal) is proposed. An illustration of the suggested spatial configuration is given. W. A. CASPARI.

***X*-Ray investigations of highly polymerised organic substances to determine the limiting values of their molecular weights.** E. OTT (Physikal. Z., 1926, **27**, 174—177).—The Debye–Scherrer method of *X*-ray analysis has been applied to a number of complex carbohydrates, such as amylose, starch, cellulose, etc., of the general formula $(C_6H_{10}O_5)_n$. The diagrams obtained consist of a series of concentric rings of varying intensity. A limiting value for the length of the side of the elementary cell has been calculated from the diameter of the innermost ring. The cube of this gives an upper limit for the volume of the elementary cell. The volume occupied by the group $C_6H_{10}O_5$ has been calculated from Bragg's values for the atomic radii and, since the elementary cell must contain at least one molecule, the ratio of these volumes gives an upper limit for n in the general formula. In no case do the values of n thus obtained conflict with the values deduced from purely chemical evidence. Triamylose and hexa-amylose give identical diagrams, and n=6. Inulin gives the same value for n, but a different diagram. Cellulose and starch give n equal to 3 and 2, respectively, agreeing with recent views of their structure based on chemical evidence. A. B. MANNING.

Crystal structure of pyrocatechol. W. A. CASPARI (J.C.S., 1926, 573—577).—*X*-Ray examination of crystals of pyrocatechol shows that it belongs to the space-group C_{2h}^3. The unit cell contains eight asymmetric pyrocatechol molecules. The crystal-molecule is thus devoid of intrinsic symmetry, each primary molecule having three differently oriented molecules near it. The dimensions of the unit cell are a=17·46, b=10·74, and c=5·48 Å. The axial ratio should thus be written 1·6086 : 1 : 0·5114, and not

1·6086 : 1 : 1·0229, as given by Beckenkamp (Z. Krist., 1900, **33**, 599). A. E. MITCHELL.

Electrical conductivity of salts as single crystals and as crystal conglomerates. G. TAMMANN and G. VESZI (Z. anorg. Chem., 1926, **150**, 355—380).—The electrical conductivities of single crystals and of compressed pastilles of sodium nitrate, chloride, and bromide, and potassium chloride and bromide, and of mixed crystals of potassium chloride and bromide, have been determined over a range of temperatures. In order to obtain good contact between the electrodes and the salt, the latter was placed between platinum electrodes at a pressure of 5 kg. per cm.^{2} and heated at 30° below the m. p.; the electrodes then adhered strongly to the salt. The maximum variations from the mean conductivities were 25% for sodium nitrate, which has a very high temperature coefficient, and less for the other salts. The absolute values show considerable differences from older measurements, but in general the temperature coefficients agree well. The relation between log κ and T is linear over a considerable temperature range. In all cases, the conductivity of the pastilles is greater than that of single crystals. The difference is greatest for sodium nitrate, for which it varies from 230% at 310° to 660% at 270°, calculated on the conductivities of the single crystals, and is least for sodium chloride and bromide, for which differences greater than 35% were not found. This is due neither to the direction of measurement in relation to the crystal axes, nor to a different distribution of impurities. It is ascribed to the ions near the surface of crystals being capable of moving more freely than those in the interior (cf. Hevesy, A., 1922, ii, 623). It is calculated that if this surface loosening extends to a depth of 20 lattice planes, the conductivity of this surface layer is 300—15,000 times greater than that of the body of the crystal. A. GEAKE.

Temperature coefficient of magnetic permeability of sheet steel. T. SPOONER (Physical Rev., 1926, [ii], **27**, 183—188).—Between −20° and +46° the coefficient decreases (+0·12 to −0·021% per 1° for 0·9% Si, +0·08 to −0·08% for 2·2% Si, −0·03% to −0·18% for 4% Si) as the induction is increased from 2 to 10 kilogauss, and thereafter increases. The temperature coefficient is more directly related to the induction than to the permeability. A. A. ELDRIDGE.

Crystallography and optical properties of schafarzikite. L. TOKODY (Z. Krist., 1925, **62**, 123—126; from Chem. Zentr., 1925, II, 2310—2311).—The mineral schafarzikite exists as opaque, reddish-brown, ditetragonal, bipyramidal crystals having a metallic lustre, $n>1·74$, strong pleochroism, and weak double refraction, $D=4·3$, and hardness 3·5. J. S. CARTER.

Flow of natural salts. F. RINNE (Ber. Sächs. Ges. Wiss. Math.-phys., 1925, **77**, 25—35; from Chem. Zentr., 1925, II, 2124).—The conclusions of Mügge and Geller (Z. Krist., 1924, **60**, 414) on the flow of crystals are based on experiments which do not reproduce conditions obtaining in nature. The flow of single crystals is influenced by that of aggregates, and also by the effect of the height of the test-piece on the flow pressure. There is also a time effect. The values obtained by the method are about 100 times too high and do not agree with the results obtained by Joffé (A., 1924, ii, 384). G. W. ROBINSON.

Temperature variation of the molecular weights of elements. A. JOUNIAUX (Bull. Soc. chim., 1926, [iv], **39**, 150—158).—With mercury, iodine, and tin as solvents, the mol. wt. of a number of metals at various temperatures have been deduced from cryoscopic and ebullioscopic data, on the assumption that the change in f. p. or b. p. is produced by molecules of the solute element, without chemical combination between solvent and solute. Below a certain temperature t, the mol. wt. of a metal is constant and indicates polymerisation. Between temperatures t and τ, the mol. wt. diminishes with rise in temperature, and then between τ and θ it is constant and usually indicates a monatomic molecule. Above the temperature θ, however, the mol. wt. increases with rise of temperature to a maximum, beyond which dissociation into free atoms begins. The temperatures t, τ, and θ are different for different metals and in some cases exceptions are shown, especially as regards the behaviour at high temperatures. Existing data on vapour densities at high temperatures confirm the general rule. W. HUME-ROTHERY.

Total radiation and specific resistance of tungsten at high temperatures. W. GEISS (Ann. Physik, 1926, [iv], **79**, 85—88).—The data of Forsythe and Worthing (Astrophys. J., 1925, **61**, 146) and of Zwikker (A., 1925, ii, 1041) differ in that for a given total radiation η the latter author's values for the specific resistance ρ are about 5% lower. The present investigation leads to values of the specific resistance which are only slightly lower than those of Zwikker. The variation of specific resistance (microhms/cm.) with total radiation (watts/cm.^{2}) is represented in a satisfactory manner over the temperature range 1700—2700° Abs. by the equation $\eta=1·425\times10^{-6}\times\rho^{4·14}$. J. S. CARTER.

Crystallography and optical properties of monobromotyrosine. W. R. ZARTNER (Z. Krist., 1925, **62**, 144—145; from Chem. Zentr., 1925, II, 2315—2316).—Monobromotyrosine exists as rhombic bipyramidal crystals, very similar to those of monochlorotyrosine, exhibiting pronounced negative double refraction, $\gamma=1·632$ (for monochlorotyrosine $\gamma=1·628$). J. S. CARTER.

Sublimation and crystallisation of metals. T. PECSALSKI (Compt. rend., 1926, **182**, 516—517).—When nickel chloride was heated at 800° in an iron tube, particles of iron and small cubic iron–nickel crystals were found to have separated, the former in concentric layers. When a copper rod having its lower half surrounded by chromium chloride replaced the nickel chloride, cementation was produced throughout its length, especially on the portion in contact with the salt. Metallic chromium was deposited on the rest of the rod,

whilst rhombohedric copper crystals were found in the salt. If the rod was contained in exhausted "pyrex" tubes, surrounded by chlorides of copper, nickel, or chromium, deposits of copper were found to have penetrated the glass after 5—10 hrs. at 600—800°. J. GRANT.

Thermal conductivity of air and hydrogen. E. SCHNEIDER (Ann. Physik, 1926, [iv], **79**, 177—203; cf. Weber, A., 1918, ii, 185, 216).—Schleiermacher's method has been refined so that the gaseous pressure, the temperature differences between wire and surroundings, and the surrounding temperature were the only variables. For air free from carbon dioxide the thermal conductivity was found to be $2{\cdot}477\times10^{-4}$ and the temperature coefficient $3{\cdot}90\times10^{-3}$; for hydrogen these values were, respectively, $1{\cdot}752\times10^{-3}$ and $2{\cdot}67\times10^{-3}$. Weber's values are $2{\cdot}379\times10^{-4}$, $3{\cdot}65\times10^{-3}$, $1{\cdot}744\times10^{-3}$, and $2{\cdot}8\times10^{-3}$, respectively. The thickness of the wire was found to exert little effect. R. A. MORTON.

Coefficient of interior thermal conductivity of mercury. M. I. ISTRATI (Ann. sci. Univ. Jassy, 1926, **14**, 23—27).—A simple apparatus is described whereby the difference in temperature between two points in a column of mercury is measured thermoelectrically. Procopiu's method (A., 1918, ii, 156) is then used to arrive at a preliminary value of 0·020 for the coefficient of interior thermal conductivity. R. A. MORTON.

Theory of the specific heats of electrolytes. F. ZWICKY (Proc. Nat. Acad. Sci., 1926, **12**, 86—92).—The specific heats of aqueous solutions of non-electrolytes are shown to be nearly the sums of the specific heats of the pure solvent and solute and therefore the interaction between molecules of the solute and solvent does not affect the specific heat appreciably. This principle is applied to aqueous solutions of electrolytes, considering at the same time the degrees of freedom of the solute molecules, the change of specific heat of water due to electric polarisation in the field of the ions, the variation of the specific heat of water under the high pressure produced by its attraction in the inhomogeneous field of an ion, the hydration of the ions, and the ion atmosphere. It is shown that the pressure effect may be of considerable magnitude. The deductions are in qualitative agreement with some measurements of the specific heats of aqueous solutions of sodium, potassium, rubidium, cæsium, and lithium chlorides. A. E. MITCHELL.

Accurate measurement of heats of vaporisation of liquids. J. H. MATHEWS (J. Amer. Chem. Soc., 1926, **48**, 562—576).—A direct electrical method of measuring latent heats of evaporation of liquids, based on that of Brown (J.C.S., 1903, **83**, 987), is described, the order of accuracy being 0·1 cal. or less. The limit of accuracy is considered to be merely a question of reproducibility of the materials. The latent heats of evaporation of many hydrocarbons and their halogen derivatives, alcohols, esters, etc. are recorded. The results are considered to be more trustworthy than those calculated from the most accurate vapour-pressure data obtainable. S. K. TWEEDY.

Absolute critical temperatures. II. M. PRUDHOMME (Bull. Soc. chim., 1926, [iv], **39**, 145—150; cf. this vol., 16).—By means of additive relations similar to those previously described (*loc. cit.*), the hypothetical critical temperature of formaldehyde is calculated as 410° Abs., but actually transformations occur on heating to this temperature. Taking the absolute critical temperature (T_c) of hydrogen as 31 or 32, the T_c value of benzene (561) is nearly 18 times that of hydrogen; using the Kekulé structural formula, each CH group has three valencies, making eighteen valencies, each producing the same effect on the T_c value as one hydrogen atom. In toluene (593) and *p*-xylene (621), each methyl group increases the T_c value by approximately 31, *i.e.*, the value for hydrogen. In diphenyl (768) the T_c value is 24 times that of hydrogen (32); in this case eight CH groups each share three valencies with neighbouring carbon atoms. In naphthalene (T_c= 741=approx. 24×31) there are again eight such CH groups. The difference between the T_c values of chlorobenzene (635) and benzene (561) is approximately equal to one-fifth of the T_c value of chlorine; similar relations hold for bromo- and iodo-benzene. If the dynamic valency is taken as representing the change of energy when atomic linkings are formed, the sum of such valencies in a given compound is regarded as measured by the critical temperature. On this assumption, values are given for the dynamic valencies. W. HUME-ROTHERY.

Connexion between the properties of normal liquids. W. HERZ (Z. anorg. Chem., 1926, **150**, 335—338).—If Mv is the mol. volume at the b. p. T, the ratio $T:\sqrt[3]{Mv}$ is nearly constant for normal liquids with not very low b. p. For 27 liquids, it lies between 71·36 and 82·33. Chlorine, pentane, hexane, octane, and ethyl ether have lower values, and organic nitrogen and halogen compounds have higher values. The product $p_c(M/d_c)^{\frac{1}{3}}$, where M is the mol. wt., is also fairly constant, lying between 1482 and 2104 for 42 liquids, and $T_c(d_c/M)^{\frac{1}{3}}$ is equally constant. A. GEAKE.

Elasticity and melting point. J. P. ANDREWS (Physikal. Z., 1926, **27**, 210—211).—Widder's linear relation in the elasticity–temperature curve of metals (A., 1925, ii, 1043) requires the line when produced to the zero elasticity to cut the temperature axis at the m. p. The expression leads to erroneous m. p. values. The curve consists of two portions: (*a*) $E_T=E_0e^{-b_1T}$, valid up to about half the m. p. in degrees Abs. and in which b_1 is small, (*b*) $E'_T=E_0'e^{-b_2T}$ for the remainder of the curve, b_2 not being small, and the elasticity decreasing quite rapidly. A better relation is now advanced: $E_T=E/V^x.e^{-bT/T_0}$, in which V is the atomic volume, x is a constant [1·6 for (*a*) and 2·3 for (*b*)], and b is also a constant. R. A. MORTON.

Polymorphism of iron. H. BREDEMEIER (Z. anorg. Chem., 1926, **151**, 109—112).—The identity of the α-form of iron (stable below 900°) and the δ-form (stable above 1400°) is thermodynamically

possible if the curvature of the thermodynamic potential–temperature curve for the γ-form (stable from 900° to 1400°) is different from that of the other form so that the curves can intersect in two places. The heats of transformation of the α- to the γ- and from the γ- to the δ-form must both be positive, so that at some temperature between 900° and 1400° transformation from the α-form (unstable) to the δ-form could take place with no heat effect. Since $\delta^2\mu/\delta T^2 = -C_p/T$, where μ is the thermodynamic potential, and the curvature of the line for the γ-form is greater (has a smaller negative value) than that of the α-δ-form, the latter must have the higher specific heat. This is in accordance with the observations of Wüst, Meuthen, and Durrer and of Dinkler, from which the heats of transformation from the α- to the γ-form and from the γ- to the δ-form are calculated to be 6·67 and 1·94 cal. per g., respectively. A. GEAKE.

Free energy and heat of formation of iron carbide between 650° and 700°. H. L. MAXWELL and A. HAYES (J. Amer. Chem. Soc., 1926, **48**, 584—593).—The system α-iron, iron carbide, carbon monoxide and dioxide was studied at 650° and 700°. From the observed equilibrium constants the free energy change of the reaction $3Fe(\alpha)+C(graphite)=Fe_3C(solid)$ was calculated to be 3138 cal. at 650° and 2281 cal. at 700°, from which the heat of the reaction is found to be 19,163 and 19,161 cal. at the respective temperatures (cf. Ruff and Gersten, A., 1912, ii, 260). S. K. TWEEDY.

Iodine and bromine tensions of metallic iodides and bromides. K. JELLINEK and R. ULOTH (Z. anorg. Chem., 1926, **151**, 157—184).—The tensions have been obtained from measurements of the equilibria between the halides and hydrogen at 300—750° and under atmospheric pressure by means of existing data for the dissociation of the hydrogen halides. The values are in satisfactory agreement with those deduced from the *E.M.F.* measurements with fused salts by Czepinski (A., 1899, ii, 267) and Weber (*ibid.*, ii, 724). Nickel and cobalt halides give exceptionally high values, possibly due to passivity. In general, the graph of the tension against the reciprocal of the temperature (Abs.) is rectilinear throughout, and includes values derived from *E.M.F.* measurements with aqueous solutions. With all the bromides examined, the measured tension is mainly due to monatomic bromine molecules; the iodides behave variously. From available *E.M.F.* data for aqueous solutions of iodides the chemical constant of iodine at the ordinary temperature is calculated to be 3·57.

R. CUTHILL.

Coefficients of expansion at equal reduced densities. W. HERZ (Z. anorg. Chem., 1926, **150**, 326—328).—Values are given of the coefficients of expansion of liquids at 2·0 and 2·75 times the critical densities, and of saturated vapours at 0·10 and 0·02 times the critical densities. The values are nearly the same for 32 organic and inorganic substances, but carbon monoxide, nitrogen, oxygen, and argon have much higher coefficients. The ratios of the coefficients at different reduced densities are nearly the same in all cases, especially when the comparison is between two liquid coefficients or two vapour coefficients. Thus $\alpha_{0\cdot02}:\alpha_{0\cdot1}$ varies from 1·26 to 1·59, $\alpha_2:\alpha_{0\cdot1}$ from 0·159 to 0·202, and $\alpha_2:\alpha_{2\cdot75}$ from 2·25 to 2·89. A. GEAKE.

Isotherms of diatomic substances and their binary mixtures. XXXIII. Isotherms of oxygen between −40° and −152·5° and pressures from 3 to 9 atm. G. P. NIJHOFF and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 963—970).—With the view of determining the virial coefficient B, previous measurements of the isotherms of oxygen between 20 and 60 atm. and at temperatures from 20° to −117° (cf. Onnes and Kuypers, A., 1923, ii, 735) were extended to pressures between 3 and 9 atm. and down to a temperature of −152·5°. M. S. BURR.

"Degeneration" of gases and the properties of fluids at low temperatures. A. SCHIDLOF (Arch. Sci. phys. nat., 1926, [v], **8**, 5—22).—The theory of gases (A., 1925, ii, 843) based on the quantum hypothesis and the statistical method due to Bose, has been modified by the introduction of a term involving the internal energy of the molecules, and has been further developed. The modification does not affect the results previously obtained. Expressions are deduced for the energy and entropy of a perfect gas with monatomic molecules as functions of a variable α, itself a transcendental function of $VT^{3/2}$, such that for small values of α, and neglecting α^2 and higher powers, the expressions lead to the equations of the classical gas theory. A second approximation, involving α^2 but neglecting higher powers, leads to the following equations for the pressure and energy of a slightly "degenerate" gas: $p=RT/V-a/V^2\sqrt{T}$, $U=3/2(RT-a/V\sqrt{T})$. For helium, the constant a has the value $5\cdot76\times10^{-3}$ litres^2 atm. degrees$^{\frac{1}{2}}$. A means of verifying the theory is therefore possibly offered by a study of the isothermals of helium at low temperatures, or of the specific heat of the compressed gas. Equations applicable to a more highly "degenerate" fluid are developed, and lead, in the case of helium, to a minimum value for the product $VT^{3/2}$ which should be attained at 2·9° Abs. Kamerlingh Onnes found a maximum density for liquid helium at 2·4° Abs. Further applications of the theory to the thermodynamic properties of helium are briefly discussed.

A. B. MANNING.

Einstein's gas theory. E. SCHRÖDINGER (Physikal. Z., 1926, **27**, 95—101; cf. A., 1925, ii, 495, 624).—The statistical methods employed by Einstein are investigated mathematically and their implications contrasted with those of older methods.

R. A. MORTON.

Entropy of perfect gases at the absolute zero. J. E. VERSCHAFFELT (J. Chim. phys., 1926, **23**, 238—241; cf. Arch. Néerland., 1924, **8**, 109).—Polemical against Kolossovski (A., 1925, ii, 496).

L. S. THEOBALD.

Compressibilities of gases. S. F. PICKERING (U.S. Bur. Standards, Misc. Papers, No. 71, 1—14).—Large-scale curves for use in the calculation of the compressibilities of air, argon, helium, hydrogen, methane, neon, nitrogen, and oxygen at various temperatures between 0° and 200° and at pressures ranging up to 200 atm. are presented. Nearly all the published data have been used in their construction, and the curves have been drawn in accordance with what appear to be most probable values. Curves are also given for use in the calculation of the volumes delivered from cylinders containing argon, helium, hydrogen, nitrogen, and oxygen at various temperatures and various high pressures.

J. S. CARTER.

Relation between the surface tension and viscosity of liquids. R. K. SHARMA (J. Indian Chem. Soc., 1925, **2**, 310—311).—The absolute temperatures at which two liquids, *e.g.*, ethyl ether and chlorobenzene, have the same surface tension bear a constant ratio to one another. The logarithm of the surface tension of certain liquids is a linear function of the logarithm of the viscosity over a wide range of temperature. R. W. WEST.

Viscosity of fluids as a function of density. Equation of state. J. DUBIEF (Compt. rend., 1926, **182**, 688—689).—The values for the co-volume in the equations previously given (A., 1925, ii, 498) are not in agreement at very high densities. The values of the co-volume calculated from the densities agree well with those given by the equation of Nadeschdin and Kannonikof ("Recherches Physiques," Kiev, 1887, 111) in the case of carbon dioxide, benzene, chloroform, ether, acetic anhydride, and sulphur dioxide. The following equation of state has been deduced: $(p+a/v^2+\beta/v)(v-b_0+d^2/v^2+c)=(1-\gamma/v)RT$, and is found to be in good agreement with the compression of carbon dioxide according to Amagat.

W. THOMAS.

Diffusion of salt vapours in a Bunsen flame. F. J. SYMON (Proc. Roy. Soc. Edin., 1926, **46**, 15—19; cf. Wilson, A., 1912, ii, 744).—From observations on the conductivity of flames containing sodium and potassium phosphates the diffusion coefficients of the vapours of sodium and potassium in the Bunsen flame are found to be 13 and 5·8, respectively.

R. CUTHILL.

Theory of concentrated solutions. III. Physical constants of mixtures of *m*-nitrotoluene and *m*-toluidine with some hydrocarbons. A. DESSART (Bull. Soc. chim. Belg., 1926, **35**, 9—28; cf. this vol., 475).—Determinations are recorded of the f. p. and of the density, viscosity, and refractive index at two temperatures of series of mixtures of *m*-nitrotoluene and of *m*-toluidine with each of the hydrocarbons hexane, *cyclo*hexane, methyl*cyclo*hexane, benzene, and toluene, values for a number of different concentrations being given in each case. The systems *m*-toluidine–hexane and *m*-toluidine–methyl*cyclo*hexane form two liquid phases, the critical solution temperatures being +21·3° and −8·3°, respectively, whilst the remaining mixtures involving a saturated hydrocarbon are near their critical solution temperatures without actually separating into two liquid phases. The critical solution temperatures for the systems *m*-toluidine–*cyclo*hexane and *m*-nitrotoluene–hexane are below the f. p., but are calculated to be at −18° and −30°, respectively. *cyclo*Hexane forms a eutectic with *m*-toluidine at −42° (12 mol. % of hydrocarbon) and with *m*-nitrotoluene at −6° (82·7 mol. % of hydrocarbon), whilst the corresponding systems with benzene as hydrocarbon show eutectics at −54° (21·2 mol. %) and −22° (59·2 mol. %).

The results are discussed from the point of view of deviation of the observed values from those calculated for ideal solutions, and in particular with reference to Mortimer's theory (A., 1922, ii, 621). The systems involving benzene and toluene follow the law of Mortimer, the values of internal pressure for *m*-nitrotoluene and *m*-toluidine being 1·07 and 1·35, respectively, and the coefficient f 1·13—1·14 and 1·41—1·42. For the systems with saturated hydrocarbons the values of f are of the order 1·82—1·86 and 2·10—2·14 for the nitrotoluene and toluidine, respectively, but for these systems near the critical solution temperature Mortimer's relation is not accurately obeyed. The values of each of the other properties considered show deviations from the ideal calculated figures. Values of fluidity show better agreement than those of viscosity, but they are markedly below the calculated values for the mixtures near the critical solution temperature. The magnitude of the Mortimer coefficient f is a qualitative indication of the degree of departure from ideality of a series of solutions, but the parallelism is not absolute.

The preparation of pure *m*-nitrotoluene and *m*-toluidine is described in detail and the following constants are recorded: for *m*-nitrotoluene, b. p. 231·0°/760 mm. and dt/dp 0·46°/10 mm., m. p. 16·0°, d_4^{15} 1·1630, d_4^{30} 1·1483, η^{15} 256×10^{-4}, η^{20} 224×10^{-4}, η^{30} 189×10^{-4}, n_α^{15} 1·54266, n_D^{15} 1·54919, n_β^{15} 1·56685, n_α^{30} 1·53627, n_D^{30} 1·54262, n_β^{30} 1·56024; for *m*-toluidine, b. p. 203·15°/760 mm., m. p. −31·5°, d_4^0 1·0092, d_4^{15} 0·9970, d_4^{22} 0·9913, d_4^{30} 0·9848, d_4^{32} 0·9832, η^{15} 438×10^{-4}, η^{30} 269×10^{-4}, n_α^{15} 1·56448, n_D^{15} 1·57068, n_β^{15} 1·58725, n_α^{30} 1·55762, n_D^{30} 1·56381, n_β^{30} 1·57991.

G. M. BENNETT.

System ethyl alcohol–benzene–water. Densities and refractive indices of mixtures at 25°. J. BARBAUDY (Bull. Soc. chim., 1926, [iv], **39**, 371—382).—The densities and refractive indices of mixtures of alcohol and benzene are slightly less than the mixture rule requires; in general, this is true for the specific volumes of mixtures of alcohol, benzene, and water. Mixtures of alcohol and water have a maximum refractive index at a concentration of 80% of alcohol. The specific refractive powers (Lorentz and Lorenz) of mixtures of alcohol, benzene, and water can be calculated from those of the pure components by the mixture rule. From the data recorded such a mixture can be analysed by a determination of its density and refractive index.

R. CUTHILL.

Organic molecular compounds. X. Vapour-pressure curves. G. WEISSENBERGER and F. SCHUSTER (Monatsh., 1926, **46**, 157—165; cf. A., 1925, ii, 766; this vol., 282, 283).—Expressions for the partial pressures of the components of the binary mixtures are deduced in terms of d and r, where $d=(b_2\sqrt{a_1}-b_1\sqrt{a_2})^2/b_1{}^3$ and $r=(b_2-b_1)/b_1$, a_1 and a_2, b_1 and b_2 being the usual constants of van der Waals' equation for each component. The dependence of a and b on temperature is shown in a table in which the values from 0° to 40° are collected. Both a and b increase with rise of temperature, but over ranges of 10° this increase is negligible. From the data for 29 alcohols, ethers, esters, and hydrocarbons, over the range 0—20° it is shown that isomeric substances have almost equal values of a and b, but in homologous series of alcohols of the "water" type the values increase regularly. From the above data, the values of d and r are determined for the binary systems formed by m-cresol and each of the 29 compounds investigated. From these the maximum deviation of the vapour-pressure curves derived from the Raoult–van 't Hoff and the van Laar formulæ are calculated; in all cases this deviation is about 0·34 when the molecular proportions are 2 : 1. For particular values of d and r, tables are also given for the binary systems formed by m-cresol with acetone, ethyl ether, and benzene, showing the actual difference between the values obtained from the two formulæ. In no case is this difference large, but the Raoult–van 't Hoff value is always the smaller, and the maximum difference always corresponds with the molecular proportions 2 : 1. In the case of benzene, the differences are least, and it is assumed that dissociation of previously associated components has taken place. J. GRANT.

Organic molecular compounds. XI. Dolezalek's theory. G. WEISSENBERGER and F. SCHUSTER (Monatsh., 1926, **46**, 167—169; cf. preceding abstract).—The partial pressures of the components of a binary mixture are eliminated between the Dolezalek and Raoult–van 't Hoff vapour-pressure formulæ, and the point of intersection of the corresponding curves is thus determined. The position of this point with respect to its dependence on the pressure has been examined, and it is shown from the signs of the two isotherms that the Dolezalek theory breaks down if the compound formed is not equimolecular. J. GRANT.

Organic molecular compounds. XII. Chloroacetic acids and pentachloroethane. G. WEISSENBERGER, F. SCHUSTER, and H. PAMER (Monatsh., 1926, **46**, 281—289; cf. preceding abstracts).—The vapour pressures of mixtures of the three chloroacetic acids with acetone, methyl acetate, ethyl acetate, and ethyl ether have been measured. All show negative deviations, but whilst the molecular compounds formed between the mono- and di-chloro-derivatives and the above substances contain 1 mol. of the acid to 1 mol. of the other component, those formed by trichloroacetic acid contain twice this molecular proportion of the second component (cf. Kendall, A., 1914, i, 858; Stobbe and Haertl, *ibid.*, 1910, i, 43). This result indicates that the residual valency of the carboxyl group of the mono- and di-chloro-derivatives is simply increased by the neighbouring halogenated group, but that in the case of trichloroacetic acid the trichloromethyl group, as well as the carboxyl group, is exerting a residual valency. This view is supported by the vapour pressures of mixtures of benzene with dichloroacetic acid (positive deviations) on the one hand, and by those of mixtures of benzene with pentachloroethane (negative deviations) on the other, which again bring out the residual valency of the trichloromethyl group. The attraction of this group for various oxygenated compounds and for aromatic hydrocarbons is only shown when the fourth valency of the group is attached to a carbon atom, since carbon tetrachloride, for instance, does not form similar molecular compounds. This indicates that the residual valency of the group is centred in the carbon atom. Investigation of the vapour pressures of mixtures of pentachloroethane with acetone, methyl and ethyl acetates, and ethyl ether indicates the formation of molecular compounds containing 1 mol. of each component in each case, whilst the molecular compounds of pentachloroethane with aromatic hydrocarbons contain the components in the molecular ratio of 2 : 1. Measurements of heats of formation of the above mixtures support generally the conclusions deduced, individual cases showing deviations ascribed to heats of dissociation etc. F. G. WILLSON.

Organic molecular compounds. XIII. Calculation of vapour-pressure curves. G. WEISSENBERGER, F. SCHUSTER, and H. PAMER (Monatsh., 1926, **46**, 291—294; cf. preceding abstracts).—The observed vapour pressures of eighteen binary liquid mixtures have been compared with those calculated from the equations of Margules (Sitzungsber. Akad. Wiss. Wien, 1895, [2], **104**, 1243). Satisfactory agreement was found only in six cases. In the remainder, the index α of Margules' equation $p_2=P_2x^\alpha$ shows a drift and passes through a maximum at which the molecular proportions of the components are in a simple ratio. As the pure component is reached, α tends to attain a limiting value, which can be arrived at by graphic extrapolation, and the value of α at any point can be written $\alpha=a+b(1-x)^mx^n$, where a is the limiting value, b a constant, and m and n are the molecular proportions at which the maximum is shown. Substituting the new expression for α in Margules' formula, the new formula was found to give satisfactory agreement between calculated and observed values in the cases of ten other of the systems examined. The two systems dichloroacetic acid–ether and trichloroacetic acid–ether remain anomalous. F. G. WILLSON.

Organic molecular compounds. XIV. Chlorophenols and bromoform. XV. Aromatic amines. G. WEISSENBERGER, F. SCHUSTER, and J. LIELACHER (Monatsh., 1926, **46**, 295—300, 301—307; cf. preceding abstracts).—XIV. The vapour pressures of mixtures of p-chlorophenol with acetone, methyl acetate, and methyl alcohol show negative deviations from those calculated, whilst the system p-chlorophenol–benzene shows positive deviations. The compounds between p-chlorophenol and alcohols,

esters, and ketones contain the two components in the molecular proportion 1 : 1 (cf. Bramley, J.C.S., 1916, **109**, 469), and the residual valency of the phenol does not appear to have been reduced by the introduction of the halogen atom. Vapour-pressure measurements on mixtures of bromoform with acetone, methyl acetate, and ethyl ether indicate that the molecular compounds of bromoform are analogous to those of chloroform, containing the two components in equimolecular proportions, but the residual valency of bromoform is markedly less than that of chloroform.

XV. Vapour-pressure measurements of mixtures of aniline with acetone, methyl acetate, and methyl alcohol indicate the formation of equimolecular compounds. The vapour-pressure curve of the system aniline–chloroform shows no deviations from the normal, whilst the system aniline–benzene shows positive deviations. Similar measurements with mixtures containing dimethylaniline in place of aniline indicate the formation of a molecular compound (1 : 1) only in the case of dimethylaniline–chloroform. The residual valency relationships of the aromatic amines are thus similar to those of the phenols, whilst the dialkylarylamines resemble the phenol ethers. The residual valency of the amines is appreciably less than that of the phenols; this is also true for the derivatives of the two classes of compounds. F. G. WILLSON.

Organic molecular compounds. XVI. Dihydric phenols and their ethers. G. WEISSENBERGER, R. HENKE, and L. BREGMANN (Monatsh., 1926, **46**, 471—482; cf. preceding abstracts).—Determinations of the vapour pressures of binary mixtures, within the limits of miscibility, of pyrocatechol, resorcinol, guaiacol, veratrole, and salicylaldehyde with ethyl alcohol, ethyl ether, and acetone, respectively, and of guaiacol, veratrole, and salicylaldehyde with benzene, have been made in order to compare the behaviour of dihydric phenols and their derivatives with that previously observed in the case of mono- and tri-hydric phenols. Negative deviations of the vapour pressure have been found for all the mixtures containing pyrocatechol, resorcinol, or guaiacol, except for guaiacol and benzene, where the deviation is positive. The composition of the mixtures showing maximum negative deviation indicates that pyrocatechol and resorcinol form equimolecular compounds with ether and acetone, but 1 mol. of each combines with 2 mols. of alcohol, whilst guaiacol, having only half the active groups of pyrocatechol, forms an equimolecular compound with alcohol and compounds containing 2 mols. of guaiacol and 1 mol. of ether or acetone. The behaviour of all three with acetone and ether is intermediate between that of mono- and tri-hydric phenols. Of the remaining pairs studied, salicylaldehyde with acetone shows a slight negative deviation, indicating a very feeble tendency to compound formation, and the remainder show positive deviations which are almost negligible for veratrole with acetone and with benzene. The steric effect of different negative groups or atoms on the degree of affinity between the members of the various molecular compounds, as measured by the relative vapour-pressure deviations, is discussed. Viscosity and surface-tension measurements for the same systems have also been recorded. M. S. BURR.

Relation of ferrous metals. I, II. J. E. FLETCHER (Foundry, 1925, **53**, 878—881, 890, 929—933).—A description of the effects of remelting pig iron, and the structural relation between the cast, wrought, or malleable iron or the steel and the original pig iron. CHEMICAL ABSTRACTS.

Influence of very slight traces of water on solubility equilibria. II. E. COHEN and S. MIYAKE (Z. physikal. Chem., 1926, **119**, 247—253; cf. this vol., 18).—Small amounts of water (less than 0·1%) have a marked influence on the solubility equilibria, at 30·5°, in the systems salicylic acid–benzene, salicylic acid–chloroform, *o*-nitrobenzoic acid–benzene, *o*-nitrobenzoic acid–chloroform, but not in the systems salicylic acid–carbon tetrachloride and anthracene–benzene. L. F. GILBERT.

Influence of minute traces of water on solution equilibria. II. E. COHEN and S. MIYAKE (Proc. K. Akad. Wetensch. Amsterdam, 1925, **27**, 936—941).—See preceding abstract.

Solubility of calcium carbonate. R. STUMPER (Bull. Soc. chim. Belg., 1926, **34**, 422—427).—The discrepancies between the solubility of calcium carbonate in water charged with carbon dioxide, as calculated by Bodländer (A., 1900, ii, 715), and the experimental values obtained by Schlœsing (Compt. rend., 1872, 1552) are due to the use by Bodländer of an inaccurate constant for the dissociation of carbonic acid. Using the value $K_2=6{\cdot}0\times10^{-11}$ obtained by Auerbach and Pick, in place of $K_2=1{\cdot}3\times10^{-11}$, Bodländer's equation gives results in close agreement with the experimental figures of Schlœsing. For the solubility of precipitated calcium carbonate in pure water at 17° the author gives the value 14·5 mg. per litre. R. BRIGHTMAN.

Dithionic acid and its salts. (MLLE.) W. C. DE BAAT (Rec. trav. chim., 1926, **45**, 237—244).—The following data are given for the solubility of dithionates in water at 20°: sodium ($+2H_2O$), 13·39%; potassium, 6·23%; ammonium ($+0{\cdot}5H_2O$), 62·43%; magnesium ($+6H_2O$), 33·91%; calcium ($+4H_2O$), 20·25%; strontium ($+4H_2O$), 10·80%; barium ($+2H_2O$), 15·75%; cupric ($+4H_2O$), 44·91%. Equilibrium conditions have been studied for the following ternary systems: water–alcohol–RS_2O_6 (where R = Ca, Sr, or Ba); water–BaS_2O_6–MgS_2O_6; water–BaS_2O_6–$K_2S_2O_6$; water–$Ba_2S_2O_6$–$Na_2S_2O_6$; water–SrS_2O_6–$Na_2S_2O_6$; water–SrS_2O_6–$(NH_4)_2S_2O_6$; and water–CuS_2O_6–$(NH_4)_2S_2O_6$. Only in the last case was double salt formation indicated, although in the further system water–BaS_2O_6–$(NH_4)_2S_2O_6$, the study of which is incomplete, it is possible that double salts or mixed crystals appear. In the systems water–alcohol–alkaline-earth dithionate, the hydrate is the only stable form at 30°. Dithionic acid is decomposed into sulphuric and sulphurous acids in dilute solutions (3—4%) to the extent of 3% in 945 hrs. at 25°, and 20% in 245 hrs. at 47°.
R. BRIGHTMAN.

Solubility of salts. R. MACHELEIDT (Z. Elektrochem., 1926, **32**, 129—136).—Simple formulæ for reproducing the solubility of potassium and magnesium sulphates are derived. C. H. D. CLARK.

Detection and measurement of the diffusion of adsorbed molecules on the surfaces of solid substances. M. VOLMER and G. ADHIKARI (Z. physikal. Chem., 1926, **119**, 46—52).—The rate of spread of solid benzophenone over a glass surface was determined from the loss in weight occasioned by continuous treatment of part of the surface of the glass with drops of mercury beyond the original nucleus of benzophenone. This removed the adsorbed film of benzophenone formed by spreading. A method by which the vapour pressure of the saturated adsorbed film was determined is described. From these data, the calculated frictional resistance to diffusion of adsorbed benzophenone is about $1{\cdot}5\times10^{13}$ dynes/mol., which is about one hundred times as great as that for molecules of similar dimensions in aqueous solutions. L. F. GILBERT.

Theories of adsorption and the technique of its measurement. J. W. MCBAIN (Nature, 1926, **117**, 550—551).—Existing data on the sorption of gases and vapours are largely invalid quantitatively in that they refer to insufficiently cleaned surfaces. The behaviour of a surface when cleaned assumes a different and highly significant form. The amount of various substances adsorbed by charcoal can be considerably increased by previously heating the material in a vacuum after adsorption has once taken place in the usual way. With cleaned surfaces, the sorption is practically complete at comparatively low pressures, and attains a normal and characteristic saturation value; the adsorption is nearly instantaneous and is perfectly reversible. The theories of adsorption due to Langmuir and Henry, to Pólányi and Williams, to Lamb and Coolidge, and to Gurwitsch and Patrick are considered; the fact that in the new experiments adsorption is practically complete at relatively low pressure is offered as almost conclusive support for the hypothesis of a unimolecular film (Langmuir, Henry, etc.). A. A. ELDRIDGE.

Adsorption of ethylene and hydrogen by zinc oxide, iron oxide, nickel, and copper. W. A. LAZIER and H. ADKINS (J. Physical Chem., 1926, **30**, 353—358; cf. Adkins and Lazier, A., 1924, i, 1278).—The adsorption of ethylene and hydrogen at the ordinary temperature and pressure by various catalysts has been measured. The catalysts were (1) cupric oxide prepared by heating the dehydrated nitrate at 450° for 4 hrs., and Merck's granules containing 1·1% of Ni_2O_3, 0·21% of Fe_2O_3, and 0·47% of SiO_2; (2) ferric oxide precipitated from the chloride by ammonia and dried at 110°; (3) nickel oxide on pumice, prepared by heating the nitrate at 350—400° for 5—6 hrs.; (4) zinc oxide, from the hydroxide heated for 24 hrs. at 110°, and zinc oxide prepared from the *iso*propoxide; and (5) copper and nickel obtained by reduction of their oxides by hydrogen at 200° and 400°, respectively. Nickel oxide was also reduced by alcohol. In most cases, the adsorbents were pressed into the form of pellets. The following numbers (c.c. per 100 g. of adsorbent) are recorded for the adsorption of ethylene and hydrogen, respectively: copper (Merck) 7·2 and 24·0, copper (nitrate) 2·0 and 0·55, nickel (by hydrogen) 70·0 and 84·0, nickel (by alcohol) 205·0 and 61·0, zinc oxide (from hydroxide) 57·0 and 1·8, zinc oxide (from *iso*propoxide) 160·0 and 23·4, iron oxide 588·0 and 0·0. The effect of 1% of nickel in increasing the adsorption by copper and of promoting its catalytic activity is indicated by the behaviour of the material prepared from Merck's copper oxide compared with that derived from the nitrate.

Observations on the hydrogenation of ethylene in presence of the above catalysts were also made. With nickel and copper (Merck's) the reaction was practically complete in 5 min. when equimolecular quantities of hydrogen and ethylene were admitted to nickel, and there was no evidence of an induction period, such as has been noted when the catalyst is first treated with hydrogen.

There is a qualitative, but no quantitative agreement between total adsorption and catalytic activity (cf. Russell and Taylor, J. Physical Chem., 1925, **29**, 1325). L. S. THEOBALD.

Adsorption and cataphoresis. K. VAN DER GRINTEN (J. Chim. phys., 1926, **23**, 209—237).—The adsorption of crystal-violet on glass, colloidal selenium, and colloidal gold has been investigated. The colloidal selenium was prepared by the reduction of selenium dioxide with hydrazine and purified by dialysis in collodion sacs for 3 weeks until the specific conductivity at 19° equalled $6{\cdot}6\times10^{-6}$ mho. The specific conductivity of the colloidal gold after purification was $7{\cdot}6\times10^{-6}$ mho. at 19°. The size of particle for the selenium ranged from 0·1 to 0·05 μ, and for the gold, 0·01 μ or less. Glass laminæ and powder were used. The amounts of crystal-violet adsorbed by the former in solutions of concentrations varying from N/100,000 to N/2000 were measured by comparison of the intensities of absorption spectra of the original solution and of the solution after adsorption. The curve showing the number of molecules of crystal-violet adsorbed/concentration approaches a limit which corresponds with the formation of a unimolecular layer on the surface concerned at a concentration N/10,000, when the number of molecules adsorbed per cm.^{2} is $1{\cdot}5\times10^{14}$, a value in good agreement with those found for organic acids by other workers. The crystal-violet apparently is attached to the glass by the active quaternary ammonium group. With finely-powdered glass, the adsorption was measured ultramicroscopically by following the variations in the rate of cataphoresis. With N/20,000-solutions of crystal-violet, a change of sign occurs, the particles becoming positively charged; with colloidal gold and selenium, a similar change takes place in N/10,000-solutions. In all three cases, the curves obtained by plotting the rate of cataphoresis against concentration of crystal-violet are similar, and show a change in direction, leading to a limiting value, between the same concentrations, viz., N/10,000 and N/20,000, of crystal-violet. This curve for powdered glass also follows

closely that obtained by plotting the number of molecules adsorbed against concentration of crystal-violet, up to a concentration $N/5000$, after which a divergence, so far unexplained, occurs; similarly, the curves for colloidal selenium and gold follow their derived adsorption-concentration curves up to the same concentration and then diverge.

With $N/2000$-solutions of crystal-violet, the number of molecules of dye adsorbed per cm.^{2} is, for colloidal gold and for glass, $1{\cdot}6\times10^{14}$, and for colloidal selenium $1{\cdot}58\times10^{14}$, these numbers corresponding, in each case, with the formation of a unimolecular layer.

The behaviour of suspensions of glass under a *P.D.* show, in agreement with Hückel, that von Smoluchowski's extension of the Helmholtz law to cataphoresis and electrical osmose is incorrect. A *résumé* of previous work on adsorption is given.

L. S. THEOBALD.

Adsorption of sulphides by colloidal chromium hydroxide. H. N. HOLMES and M. A. DIETRICH (J. Amer. Chem. Soc., 1926, **48**, 678—682).—Mercuric sulphide is not precipitated by hydrogen sulphide from a $0{\cdot}5N$-hydrochloric acid solution containing green chromic chloride and mercuric chloride in excess of the ratio 2 : 1, but is adsorbed by the colloidal chromic hydroxide produced by the hydrolysis of the chloride. The hydrolysis increases on keeping, and after 48 hrs. precipitation does not occur when the above ratio is 1 : 3·5, but this ratio may be depressed by a sufficient concentration of hydrogen or sulphate ions. Thus, chromic sulphate has no influence on the precipitation. The formation of colloidal chromic hydroxide is probably preceded by the conversion of the green chromic chloride into the violet form. The order of the adsorption is reversed by using a large excess of mercuric chloride and precipitating from a hot $0{\cdot}5N$-acid solution.

S. K. TWEEDY.

Hydroxides of yttrium and lanthanum as adsorbents. J. KLEEBERG (Kolloid-Z., 1926, **38**, 226—229).—Lanthanum hydroxide is useless as an adsorbent. Yttrium hydroxide, however, is an outstanding adsorbent, both when fresh and when 3 months old. It adsorbs both acid and basic dyes, whether they are colloidal or of molecular dispersion, in part according to the general adsorption isotherm. The adsorption can be observed with filter-paper impregnated with yttrium hydroxide, although it is much weaker in this case. The attainment of equilibrium is independent of the concentration. It is complete after 1½ hrs.' shaking. Yttrium hydroxide carries a positive charge. It can be regenerated quantitatively. N. H. HARTSHORNE.

Influence of sodium hydroxide on the adsorption of arsenious acid by "saccharated" iron. L. HERBOTH (Arch. Pharm., 1926, **264**, 181—186; cf. Mannich and Rojahn, *ibid.*, 1924, **262**, 239; A., 1922, i, 718).—Colloidal "saccharated" iron is used as an antidote in arsenic poisoning, but its adsorptive capacity depends on the alkalinity of the medium. A commercial preparation, containing 0·75% of sodium hydroxide, takes up 12·57% of arsenious oxide (reckoned on the iron present). When sodium hydroxide is added, more arsenious oxide is adsorbed, until the additional sodium hydroxide amounts to 0·53%. The arsenious oxide taken up is then 27%, and that figure is the maximum. Conversely, when carbon dioxide is passed into the "saccharated" iron, or when hydrochloric acid is added, the adsorptive capacity is diminished. This property also depends on the age of the preparation. The adsorptive capacity is greatest when the sodium hydroxide present suffices to form disodium hydrogen arsenite. W. A. SILVESTER.

Formation of an alkali-cellulose compound in an aqueous-alcoholic medium. J. R. KATZ (Z. Elektrochem., 1926, **32**, 125—128).—The curve representing the adsorption of sodium hydroxide from aqueous solution by cellulose shows a flat portion which Vieweg has attributed to the formation of a compound (A., 1907, i, 893; 1908, i, 857). Using aqueous-alcoholic solutions, the flat portion is absent, and a linear relationship was found, which was thought to indicate the formation of solid solutions of sodium hydroxide in cellulose (cf. A., 1925, i, 12). These results are discussed in relation to the *X*-ray investigations of cellulose, swollen by sodium hydroxide, carried out by the author. It is found that this evidence favours the view that an alkali-cellulose compound is formed also in aqueous-alcoholic solutions, since the observed bands are similar to those obtained using aqueous solutions. The presence of alcohol exerts little influence on the limiting concentration at which the cellulose spectrum vanishes (see Katz, A., 1925, i, 639), but it slightly hinders the formation of the compound. This is extremely difficult to reconcile with the observation that alcohol greatly assists the absorption of sodium hydroxide by the cellulose. The author also lays some emphasis on the fact that the points on the aqueous-alcohol curves obtained by Vieweg do not lie quite accurately on a straight line, the departure being possibly not accidental. C. H. D. CLARK.

Structure of films of water on salt solutions. II. Surface tension of calcium chloride solutions at 25°. W. D. HARKINS and E. C. GILBERT (J. Amer. Chem. Soc., 1926, **48**, 604—607; cf. Harkins and McLaughlin, A., 1925, ii, 959).—Accurate measurements of the surface tension and density at 25° of calcium chloride solutions for concentrations up to 7 moles of salt per 1000 g. of water are recorded; from the results, the thickness of the water film on a $1{\cdot}25M$-solution is calculated to be 3·1 Å. This is the cube root of the volume of a water molecule. The film is thicker at lower and thinner at higher concentrations, but is essentially unimolecular up to concentrations of 3 or $4M$ at least.

S. K. TWEEDY.

"Gas laws" in surface solutions. N. K. ADAM and G. JESSOP (Nature, 1926, **117**, 484—485).—Marcelin's experiments (A., 1925, ii, 772; this vol., 120), leading to a relation between the surface pressure, F, and the area, A, of certain films, of $FA=kT$, where k is much smaller than the universal gas constant, are criticised. Films of oleic acid on distilled water, and

of benzyl benzoate have been examined; the latter gives very unstable films. Oleic acid gives an "expanded" film above about 0·2 dyne/cm., when it has an area of 49·7 Å.²/mol., with an abrupt transition from this state to one at which the pressure is constant at about 0·08 dyne/cm., the "vapour-pressure" region (cf. Adam and Jessop, this vol., 348).

A. A. ELDRIDGE.

Molecular association of phenol in benzene and water. K. ENDO (Bull. Chem. Soc. Japan, 1926, **1**, 25—29; cf. Philip and Clark, J.C.S., 1925, **127**, 1274).—Measurements of the partition coefficient of phenol between benzene and water at 25° are quantitatively accounted for on the assumption that no association of phenol molecules occurs in the aqueous phase, but polymerisation to $(C_6H_6O)_3$ in the benzene solution. On the other hand, the conclusion is reached from f.-p. determinations of aqueous solutions of phenol that for concentrations above 0·2*N* the observed slight deviation from Raoult's law is to be attributed to a similar polymerisation to $(C_6H_6O)_3$ in the aqueous solution at 0°. G. M. BENNETT.

Colloidal solutions of alkaline-earth carbonates. A. BURZÁGH (Kolloid-Z., 1926, **38**, 222—226).—Alkaline-earth oxides when suspended in absolute methyl alcohol and subjected to a stream of carbon dioxide for some hours by Neuberg's method (cf. A., 1906, ii, 753; 1908, ii, 39, 495) gave colloidal solutions of the alkaline-earth methyl carbonates. By using barium hydroxide in place of oxide and keeping the methyl alcohol at boiling temperature, a colloidal solution of barium carbonate was obtained which was miscible with alcohol, benzene, chloroform, acetone, or water without coagulation. It contained 1·2% of barium carbonate and could be concentrated to 4—5% by evaporation in a vacuum. By dialysing against water, the methyl alcohol could be replaced by water, but the process was very slow and incomplete. With strontium hydroxide, solutions containing only 0·1—0·2% of strontium carbonate can be obtained, but with calcium hydroxide the result is completely negative. By decomposing solid calcium methyl carbonate with a small quantity of water and subsequently dialysing against water, a colloidal solution of calcium carbonate was obtained free from methyl alcohol and containing a maximum of 3·9%. Barium and strontium carbonate solutions were similarly obtained with maximum concentrations of 5·6 and 4·4%, respectively. These concentrations can be increased by careful evaporation in a vacuum. The solutions are quite stable. They may also be prepared from the ethyl carbonates. N. H. HARTSHORNE.

Complex-formation as an intermediate stage in the synthesis of colloid particles. A. DUMANSKI, A. P. BUNTIN, S. J. DIJATSCHKOVSKI, and A. G. KNIGA (Kolloid-Z., 1926, **38**, 208—218).—The view that ionic complexes are formed as intermediate products when sols or gels are produced by chemical reactions, and that there is a gradual change from ions to ionic complexes and so to micelles, has been tested in the following manner. A range of synthetic mixtures of solutions of the reactants was made and their electrical conductivity (X_1) and f.-p. depressions (Δ_1) were compared with those (X_2 and Δ_2) calculated on the assumption that no intermediate reactions occurred and that those of the colloid were negligible. In the preparation of molybdic and tungstic acid sols by the action of hydrochloric acid on sodium molybdate and tungstate, respectively, it was found that with increasing quantities of hydrochloric acid (X_1-X_2) and ($\Delta_1-\Delta_2$) were at first negative, passing through a minimum and then rising to zero at the neutralisation point, and then became positive and rose to a maximum when a quantity of acid equivalent to the tungstate or molybdate had been added. These results are explained by assuming that at first the MoO_4'' or $NaMoO_4'$ ions combine with the H_2MoO_4 formed or with MoO_3 to give complexes of the type $[MoO_4 \cdot nMoO_3]''$ or $[NaMoO_4 \cdot nMoO_3]'$. This results in a diminution in the number of ions in the solution, and hence $X_1 < X_2$ and $\Delta_1 < \Delta_2$. As more acid is added, the relative number of sodium ions bound in these complexes decreases and more sodium chloride is formed, whilst after the neutrality point is reached, the hydrogen ions increase rapidly; X_1 and Δ_1 therefore increase. The positive values of (X_1-X_2) and ($\Delta_1-\Delta_2$) finally reached are due to the fact that molybdic acid is a semi-colloid having a marked conductivity and f.-p. depression. Similar considerations apply to the tungstic acid solutions. Analogous results were shown by ferric ferrocyanide prepared from potassium ferrocyanide and ferric chloride, by copper ferrocyanide from potassium ferrocyanide and copper sulphate, and by silicic acid from sodium silicate and hydrochloric acid. With true hydrosols which readily form hydrogels on addition of an excess of the reagent, viz., ferric hydroxide from ferric chloride and sodium carbonate, stannic acid from potassium stannate and hydrochloric acid, and zirconium hydroxide from zirconium nitrate and sodium carbonate, however, the values of (X_1-X_2) and ($\Delta_1-\Delta_2$) were negative throughout except to a very small extent with stannic acid. This is due to the adsorption of ions by the precipitated hydrogels.

A comparison of the (X_1-X_2) curves for the tungstic and molybdic acid solutions shows that the former (with the higher atomic weight) has the larger negative portion, *i.e.*, more pronounced colloidal properties. The effect of dilution is to increase the positive portion of the curve. Some applications of the research to the preparation of colloidal solutions are described. N. H. HARTSHORNE.

Sulphur solutions of all colours of the spectrum. P. P. VON WEIMARN (Koll. Chem. Beihefte, 1926, **22**, 38—62).—The paper deals chiefly with blue sulphur solutions. When sulphur is dissolved in glycerol or ethylene glycol, a colourless solution is obtained which, on heating to 160° and above, becomes a clear blue. The depth of colour increases with rise of temperature and with increase of the sulphur concentration. On cooling, the colour disappears again and on further cooling sulphur separates. At no stage is the slightest trace of opalescence observed. The colour is not due to an oxidation product arising from oxygen dissolved in the glycerol etc., since it is not altered when the oxygen

is expelled by hydrogen or carbon dioxide. Acids (even boric) completely inhibit the colour, but the smallest addition of alkali suffices to intensify it to an indigo-blue. Methyl, ethyl, propyl, butyl, and amyl alcohols give either colourless or yellowish-green solutions of sulphur, but if a little alkali or alkaline-earth oxide be added, a blue or greenish-blue solution is obtained. Similar results are given with acetone and even with water. Ammonium polysulphide solution at certain dilutions, and sulphur dissolved in fused potassium thiocyanate or potassium chloride show the same colour. From the widely differing nature of the solvents cited, and the necessity of their being neutral or alkaline, it is concluded that the colour is due to the formation of polysulphides in which the sulphur is held by a specially weak linking. The presence of single sulphur atoms or of combinations of sulphur atoms not stable under ordinary conditions is regarded as possible. The blue colour of sulphur sesquioxide (solutions of sulphur in sulphur trioxide) and of compounds of nitrogen and sulphur (solutions of sulphur in liquid ammonia) is held to be due to the same condition of the sulphur atoms. All such compounds are embraced by the term "sulphurates" and they give true solutions. A classification of blue sulphur solutions is made in which, in addition to the sulphurate group described, three other groups are defined as follows: (i) in which the colour is observed only by reflected light, *i.e.*, due to opalescence; (ii) in which the colour is observed by transmitted light, but is due to the scattering of light from comparatively coarse colloid particles; (iii) in which the colour depends on the relation between the refraction coefficients of the dispersing and dispersed phases. N. H. HARTSHORNE.

Hydrodynamic behaviour of ammonium oleate solutions. E. N. DA C. ANDRADE and J. W. LEWIS (Kolloid-Z., 1926, **38**, 260—261; cf. this vol., ii, 240).—An apparatus described by the authors, in which the movements of a liquid are observed between two cylinders which move coaxially relatively to each other at known speeds, has been employed to investigate the anomalies described by Hatschek and Jane using ammonium oleate solutions. Small index particles of metallic aluminium are suspended in the solution, and their movements are observed through a microscope, the inner cylinder only being rotated. At a certain critical angular velocity, the circular stream-line motion ceases and vibratory movements commence, followed by the appearance of turbulence, which is indicated by the formation of circular vortices in the liquid. The velocity at which turbulence commences is about two-thirds of that calculated for homogeneous liquids by means of Taylor's formula. It is thus reduced in the required ratio 80 : 120 (see following abstract). The critical velocity is susceptible to previous mechanical treatment of the solution, and Hatschek and Jane's anomalous observations are thus confirmed and explained as due to turbulence. C. H. D. CLARK.

Apparent increase of viscosity of ammonium oleate solutions at higher velocities. E. HATSCHEK (Kolloid-Z., 1926, **38**, 259).—With reference to the observations of Hatschek and Jane on the increased viscosity of vigorously sheared ammonium oleate solutions (this vol., ii, 240) at angular velocities from 70° to 90° per second, attention is directed to the work of Andrade and Lewis (see preceding abstract). Turbulence does not set in with water until an angular velocity of 120° per second is reached, but Andrade and Lewis have detected turbulence in these solutions at lower shear gradients than is the case for water, so that the phenomena observed may be explained on this ground.
C. H. D. CLARK.

Viscosity of colloidal solutions in presence of electrolytes. K. C. SEN (Kolloid-Z., 1926, **38**, 253—257).—The available data relative to the influence of electrolytes on the viscosity of colloidal solutions appear to show that the viscosity of the solution increases with the thickness of the layer of water covering the colloidal particle, an oil emulsion representing a limiting case. The addition of an electrolyte in small quantities increases the potential of the electrical double layer at the surface of the particle, whilst, in excess, it diminishes the charge by coagulation. Since the former effect increases the viscosity and the latter diminishes it, a minimum on the viscosity–electrolyte concentration curve is anticipated. For soap solutions and alkali salts, this has been observed by Farrow (J.C.S., 1912, **101**, 347), who suggested that the lowering of viscosity for small additions of electrolytes is due to loss of water (due to osmosis) by the colloidal particle and consequent shrinkage. The author, however, believes the cause to lie not in shrinkage, but in loss of water due to increase of charge brought about by the preferential absorption of either positive or negative ions from the solution. At higher concentrations, coagulation occurs accompanied by water absorption, and the viscosity increases. If no absorption of water occurs, the viscosity does not increase with coagulation, and viscosity is therefore closely connected with the homogeneity of the coagulum. Colloidal proteins have high viscosities, and contain solid particles which occlude large volumes of water, which can no longer function as solvent. In the case of inorganic colloids, it is very difficult to find a theory which covers the facts, but it is suggested that the addition of an electrolyte may cause an increase of cataphoretic potential, with corresponding diminution in viscosity.
C. H. D. CLARK.

Viscosity of colloidal solutions in the structural, laminar, and turbulence regions. V. Velocity function of viscosity of disperse systems. W. OSTWALD and R. AUERBACH (Kolloid-Z., 1926, **3**, 261—280; cf. A., 1925, 291, 392, 589, 663).—The sigmoid curve which is obtained when the viscosity, v, of a colloidal solution is plotted against the pressure, p (cf. Part III, *loc. cit.*), shows three portions, named the structural, laminar, and turbulence regions. In the structural region, the law $v=kp^n$ is obeyed, where n is a constant greater than 1, which may be as great as 7. The law of Hagen and Poiseuille is obeyed in the laminar region, the viscosity being independent of the pressure. By observations conducted in this region, values of the absolute viscosity of water in

agreement with those given in the Landolt–Börnstein tables are obtained. In the turbulent region, the relation $v=k_1 p^{1/n}$ holds, the value $n=1{\cdot}75$ suggested by Blasius being found to fit the results fairly well. The appearance of turbulence is marked by a constant "Reynold number" $R_K=v_K\rho r/\eta$, where v_K is the critical velocity of turbulence, ρ and r are the density and radius of the viscosity tube, respectively, and η is the absolute viscosity of the solution, R_K being independent of the dimensions of the tube and the viscosity of the liquid. Examples of the S-curves obtained are shown for colloidal solutions of gelatin, mercury sulphosalicylate, gum arabic, glycerol, and starch. The anomalies found by Hatschek and Jane using ammonium oleate (this vol., 240) are attributed by the authors to "structural turbulence," which is different from the normal turbulence effect. The observation that previous mechanical treatment of the sol lowers the viscosity and also the critical velocity of the turbulence effect is confirmed.

C. H. D. Clark.

Viscosity and elasticity of soap solutions. H. Freundlich and H. Jores (Koll. Chem. Beihefte, 1926, **22**, 16—37).—The viscosity and elasticity of solutions of sodium oleate, sodium stearate, and mixtures of the two have been measured by means of the Couette apparatus. Some measurements have also been carried out with mixtures in which one or other of the above was replaced by sodium palmitate, laurate, stearolate, erucate, or ricinoleate. Some of the solutions contained coagels. Pure dilute solutions of sodium oleate (up to 2·0%) and of sodium stearate (up to 0·1%) show no elasticity. Concentrated solutions of sodium stearate are markedly elastic, and still more striking is the elasticity of solutions containing both sodium oleate and sodium stearate which show this property at concentrations at which they would be non-elastic if alone. Elasticity was not observed above 20°. The appearance under the ultramicroscope of fine, elongated fibres is always accompanied by elasticity. This is observed both in concentrated sodium stearate solutions and in the mixtures. The fibres are probably a mesomorphic unstable form of sodium stearate. Supersaturation in the case of pure solutions and the presence of sodium oleate in the case of the mixtures are apparently favourable to the formation of the fibres. With age the viscosity of the solutions decreases, whilst the elasticity shows first a maximum and then decreases. The elasticity increases regularly with increasing sodium stearate content, but the influence of different concentrations of sodium oleate on this property was not clearly established. The one-dimensional Brownian movement of coagel submicrons along the coagel fibres, found by McBain and Salmon (A., 1921, ii, 398), was observed. Pure oleate solutions show a very slight negative-flow double refraction or none at all. The stearate solutions are positively birefractive in proportion to the concentration of stearate. The same holds for the mixtures. By the action of carbon dioxide from the air, the positive double refraction changes its sign. It disappears on heating, but returns on cooling. The negative double refraction produced by carbon dioxide does not disappear on heating, since it is probably due to the formation of small quantities of the free insoluble acids. N. H. Hartshorne.

Time change of electric double refraction in sols with non-spherical particles. I. Behaviour of vanadium pentoxide sol. II. Behaviour of benzopurpurin sol. H. Freundlich and H. Dannenberg (Z. physikal. Chem., 1926, **119**, 87—95; 96—103).—I. The rate of change of the electric double refraction of vanadium pentoxide sols has been studied; it is due to ageing. Small concentrations of arsenic acid strongly retard the change, whereas phosphoric acid has no effect, and sodium chloride has only a slight effect. As arsenic acid in presence of sodium chloride has no influence on the coagulation of vanadium pentoxide sols, it is considered that the ageing of these sols is not a coagulation, but a crystallisation process, consisting in the precipitation of the smallest on the largest particles in suspension. This view is corroborated by the previously observed facts that the ageing is a reaction of the second order and has a large temperature coefficient. The influence of arsenic acid is due to its adsorption on the surface of crystals.

II. The influence of temperature and of the addition of sodium chloride on the rate of change of the electrical double refraction of benzopurpurin sols has been studied. Sodium chloride markedly accelerates the change. At the b. p., no double refraction is exhibited, but it returns on cooling. The increase in double refraction with time is explained as due to coagulation. L. F. Gilbert.

Influence of ions carrying the same charge as the dispersed particles in the inversion of emulsions. S. Ghosh and N. R. Dhar (J. Physical Chem., 1926, **30**, 294—305; cf. Powis, A., 1915, ii, 138; Clowes, *ibid.*, 1916, i, 589; Bhatnagar, *ibid.*, 1922, ii, 204, 268).—Theoretical, in which it is shown that an oil emulsion closely resembles a colloidal suspension, and that the generalisations advanced for a sol apply to an emulsion. The stability of sols and emulsions on dilution when coagulated by certain electrolytes, the antagonistic effect observed on coagulation towards a mixture of electrolytes, and the acclimatisation shown are all due to the adsorption of an ion carrying the same charge as the suspended particles. The separation of oil-in-water emulsions into two layers can be regarded as the coagulation of the dispersed oil globules, whilst the reversal of phase of oil-in-water to water-in-oil is probably the dispersion of water particles carrying a positive charge in the oil. From the results of various workers, it is concluded that sodium and potassium chlorides, sodium citrate, sodium hydroxide, etc. favour the formation of oil-in-water emulsions, showing that the respective anions are adsorbed by the globules of oil. The adsorption of anions is also mainly responsible for the antagonism observed between electrolytes of univalent cations and of bi- and ter-valent cations on the inversion of an oil emulsion. It is further shown that this antagonistic effect and the abnormal dilution effect are essentially connected and go hand in hand. Finally, it is emphasised that the stability of an oil

emulsion in the presence of soaps mainly depends on the electric charge on highly adsorbed micelles.

L. S. THEOBALD.

Influence of protective colloids on the size of coagulated particles. A. S. MENON, D. L. SHRIVASTAVA, and S. PRASAD (Kolloid-Z., 1926, **38**, 242—248; cf. A., 1924, ii, 395).—The relative sizes of the particles in the coagula obtained from various protected and unprotected sols by the addition of electrolytes have been investigated by the elutriation method. In all cases the particles formed from protected sols are larger than those from unprotected sols. This is not to be attributed to the fact that a greater amount of electrolyte is necessary for coagulation of the protected sols, since unprotected sols coagulated with the same amount of electrolyte which is just sufficient for protected sols give smaller particles than the unprotected sols. At a certain concentration of protective colloid, the size of the particles obtained is a maximum. The theory of protection is discussed, and it is suggested that chemical compounds between the protective substance and the colloid particle play a part. The sols used were arsenic sulphide, antimony sulphide, or manganese dioxide, and as protective agents gum arabic, sodium oleate, and sucrose.

C. H. D. CLARK.

Precipitation of ferric hydroxide sol by different electrolytes. T. TAKAMATSU (Kolloid-Z., 1926, **38**, 229—231).—The precipitation of ferric hydroxide sol by ions which form insoluble or sparingly soluble salts with ferric ion, *e.g.*, ferrocyanide, sulphate, dichromate, carbonate, phosphate, and hydroxyl ions, requires quantities of these ions which are proportional to the concentration of the sol. With ions which react with ferric ion giving a colour change but without forming an insoluble salt, *e.g.*, acetate and iodide ions, the quantities required depend on the concentration, but are not proportional to it, whilst with ions which do not appear to react with ferric ion under these conditions, *e.g.*, nitrate and chloride ions, the quantities are independent of the concentration. The explanation given is that ions of the nitrate type have no affinity either for ferric ion or for the colloid. They are therefore not markedly adsorbed by the latter. Their action is almost wholly confined to influencing the electrical double layer of the micelles, and this influence depends only on the concentration of the ions, and not on that of the colloid. On the other hand, ions of the ferrocyanide type are strongly adsorbed by the colloid particles, leaving a negligible amount in solution. The adsorbed ions effect the precipitation and the quantities required are thus proportional to the concentration of the colloid. Ions of the acetate type are intermediate in their action.

N. H. HARTSHORNE.

Precipitation of sols by multivalent ions. I. W. W. TAYLOR (Proc. Roy. Soc. Edin., 1925, **45**, 323—333).—The coagulation of a ferric hydroxide sol by potassium methanetrisulphonate, sodium naphthalenetrisulphonate, sodium chloride, sodium sulphate, and disodium hydrogen phosphate has been studied. In the case of the phosphate, the range of concentrations causing coagulation is succeeded by a range over which no precipitation occurs, and finally at very high concentrations coagulation is again caused. With the trisulphonates, complete precipitation persists over the whole range of concentrations beyond that at which it begins. It is therefore probable that the anomalous behaviour of the phosphate is due to the presence of hydroxyl ions formed by hydrolysis. With increasing salt concentrations, the rates of precipitation do not increase continuously, but appear to pass through successive maxima and minima. The rule connecting the precipitating power of an ion and its valency does not hold for the trisulphonates.

R. CUTHILL.

Coagulation of proteins by means of different organic acids in relation to their structure. N. ISGARISCHEV and M. BOGOMOLOVA (Kolloid-Z., 1926, **38**, 238—242).—The coagulation of casein and edestin by different organic acids has been studied under comparable conditions. The results with edestin proved unsatisfactory, but the experiments with casein show that there is no connexion between the affinity constants of the different acids and their protein-coagulating activities, and that the action depends on the chemical nature of the acids rather than on the charge or the surface densities of the charge on the respective anions. Fumaric is more active than maleic acid, and monochloroacetic more active than acetic acid. A second carboxyl group in the molecule has no marked influence, but a hydroxyl group generally increases the activity of fatty acids, whilst in the aromatic series the converse is usually true. The process is considered to be due to the formation of compounds of varying solubility between the caseinate in solution and the sodium salts of the organic acids, formed during neutralisation, coagulation occurring when the solubility products of the individual compounds are reached.

C. H. D. CLARK.

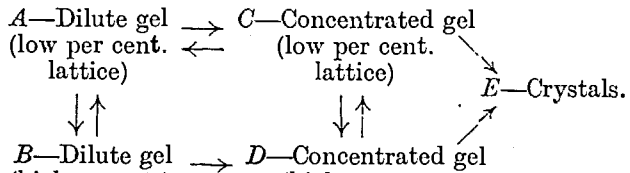
Swelling in presence of organic acids in connexion with their structure. N. ISGARISCHEV and A. POMERANZEVA (Kolloid-Z., 1926, **38**, 235—238).—The swelling of casein under the influence of twenty-five organic acids has been studied by Fischer's method, the end volume after 2 days being taken as a measure of swelling. No direct connexion exists between the degree of swelling and the affinity constant of the acid. The presence of a hydroxyl group or of a second carboxyl group in the acid molecule increases the degree of swelling, but, when both of these are present, they retard each other's influence. Maleic has a somewhat stronger influence than fumaric acid, whilst aminoacetic acid has a smaller, and monochloroacetic acid a greater influence than acetic acid. It appears that the molecule of acid as a whole is concerned in swelling, and the results point to adsorption phenomena. The results depend on the degree of division of the casein, the extent to which the acid is adsorbed, and the structure of the acid–casein complex. The effects produced by different acids are in general similar to those observed in coagulation processes (cf. preceding abstract).

C. H. D. CLARK.

Gel structure. W. C. ARSEM (J. Physical Chem., 1926, **30**, 306—311).—Theoretical, in which a new view of gel structure is outlined and discussed. A normal gel consists of (*a*) the associated phase and (*b*) the free phase. The former is a single large molecule of the same shape and volume as the entire mass of gel, and is composed of molecular units held in combination by residual valency. It differs from a normal crystal lattice in the irregular orientation of the molecular units, only a fraction of the residual valencies being employed to hold the structure together. In consequence, the lattice is much expanded and contains many voids of approximately molecular dimensions. The free phase fills these voids and, in special cases, molecules of it may take part in forming the lattice structure of the associated phase. Two types of gel are distinguished, *viz.*, normal gels, having a uniform space distribution of the molecular units of (*a*), with voids approximately of molecular dimensions, and segregated gels, with a non-uniform distribution of molecular units and a resultant coarse structural framework in which the voids are much larger.

Changes in the phases, both reversible and irreversible, are discussed on this theory. The structural arrangement of units in a gel is unstable, and further condensation of the associated phase becomes possible through re-orientation of units, the release of loosely combined molecules of the free phase, and the union of previously non-functioning residual valencies. Syneresis results from shrinkage of the solid phase through re-orientation of molecular units. Changes in rigidity of the solid phase accompany changes in the proportion of free residual valencies. In a gel, some of the residual valencies function permanently as lattice linkings, whilst others are available for the molecules of the free phase. Swelling then becomes the result of the union of the latter with the free valencies of the gel lattice.

The relations of gel states as indicated by the lattice theory can be illustrated as follows:



The changes $A \rightleftharpoons C$ and $B \rightleftharpoons D$ are usually reversible, and involve both phases as in drying or swelling processes. Probably there is no change in the number of lattice-forming linkings in this case. The changes $A \rightleftharpoons B$ and $C \rightleftharpoons D$ occur in the associated phase involving the number of lattice-forming linkings. They may or may not be reversible.

L. S. THEOBALD.

Hydrogels and hydrates. R. ZSIGMONDY (Ber., 1926, **59**, [*B*], 467—470).—Doubts are expressed concerning the general validity of the hypothesis of Willstätter and Kraut (A., 1924, ii, 767, and following abstracts) that the existence of chemical hydrates is established by the constancy of composition of gel residues over a considerable range of temperature. Many hydroxides have a tendency to lose water even under water (*e.g.*, carbon dioxide, silica), and products of this type (after removal of adherent water by acetone) give analytical results which may readily lead to false conclusions as to their constitution. The possibility of complete removal of adsorbed water by acetone is not established, since at low temperatures the water becomes extremely viscous if not frozen, and, further, the capillaries may be so fine as to act as semi-permeable membranes towards acetone.

H. WREN.

Capillary theory of the swelling and shrinkage [of gels]. K. SCHULTZE (Kolloid-Z., 1926, **38**, 232—234).—To understand the behaviour of gels on drying and rewetting, it is necessary to bear in mind that their capillary channels are in all probability not circular in section except in cases where the channels are formed by gases. The influence of the nature of the cross-section is considered in the light of earlier observations (cf. *ibid.*, 1924, **35**, 76; A., 1925, ii, 287, 856). The values of the radius of the capillaries derived by Zsigmondy and Anderson from measurements of the vapour pressure are held to be incorrect through neglect of this consideration.

N. H. HARTSHORNE.

Freezing of inorganic hydrogels. J. R. I. HEPBURN (Rec. trav. chim., 1926, **45**, 323—327).—The effects of prolonged freezing on some typical inorganic hydrogels, such as the hydroxides of iron, copper, aluminium, and silicon, the ferrocyanides of copper and iron, and the sulphides of manganese and zinc, have been studied. Curves showing the rate of desiccation of frozen ferric and aluminium hydroxides, with and without preliminary supercooling, indicated that in the former case practically no dehydration occurs. The absence of the mother-liquor during freezing does not affect the dehydration curve or the composition after desiccation. In general, the products of freezing are colloidal in nature, but present many physical properties characteristic of the crystalline state. Optical activity, which was detected in some cases, may be due to strains set up by pressure.

J. GRANT.

Rhythmic formation of precipitates. Liesegang's rings. C. K. JABŁCZYŃSKI and S. KOBRYNER (Bull. Soc. chim., 1926, [iv], **39**, 383—388).—In continuance of previous experiments (A., 1924, ii, 157) the formation of rings of silver chromate in discs of gelatin containing potassium dichromate by diffusion of silver nitrate from the periphery inwards has been investigated. The results agree with the equation, deduced as previously described, $\{3r_0^2(r_1-r_2)-(r_1^3-r_2^3)\}/(t_2-t_1)=$constant, where r_0 is the radius of the disc, and t_1 and t_2 are the times of formation of rings of radius r_1 and r_2, respectively. The formation of successive layers of silver chromate in gelatin spheroids has also been examined. For a particular set of rings the ratio of the widths of two successive spaces is constant, whether they are formed in a disc, spheroid, or tube. This is not the case with the rings in agates.

R. CUTHILL.

Electrostatic virial of strong electrolytes. E. Q. Adams (J. Amer. Chem. Soc., 1926, **48**, 621—626).—A virial term for the energy of strong electrolytes in aqueous solution is really a free energy term, ΔF (thermodynamic potential), and not an intrinsic energy term, ΔU, as assumed by Debye and Hückel. These two energies only become equal when the dielectric constant, κ, of the medium is independent of temperature. The expressions for ΔU must therefore be multiplied by $1+(d\log_e\kappa/d\log_e T)$, which, for water, is approximately $-0{\cdot}5$ between 10° and 100°. Milner's method of calculating the virial gives neither ΔF nor ΔU, but a work term ΔA, which, for an inverse square force, is equal to $\frac{2}{3}\Delta F$. This explains why Milner's electrostatic virial is approximately two-thirds of that of Debye and Hückel (cf. Noyes, A., 1924, ii, 658, 659). The osmotic pressure can be calculated from ΔA (or ΔF) without any knowledge of the variation of κ with temperature. S. K. Tweedy.

Activity coefficients of electrolytes calculated from freezing-point data. W. H. Rodebush (J. Amer. Chem. Soc., 1926, **48**, 709).—The activity coefficients of salts of various types in 0·01, 0·005, and 0·001M-solutions are calculated graphically from the f.-p. data obtained by Hovorka and Rodebush (A., 1925, ii, 772). S. K. Tweedy.

Inter-ionic attraction theory of ionised solutes. V. Testing of the theory by solubility experiments at higher temperatures. W. P. Baxter (J. Amer. Chem. Soc., 1926, **48**, 615—621).—The validity of the factor $(\kappa T)^{\frac{3}{2}}$ in the denominator of the Debye–Hückel equation for the activity of an ion, κ being the dielectric constant of the solvent, is tested by measurements at 75° of the solubility of silver iodate in solutions up to 0·1M of other salts (magnesium sulphate, potassium nitrate, etc.). The limiting equation of Debye and Hückel is confirmed completely up to an ionic strength of 0·01M (cf. Brönsted and La Mer, A., 1924, ii, 306); at higher concentrations, the mean activation values are larger than theory requires. S. K. Tweedy.

Activity coefficients of hydrochloric acid in glycerol–water mixtures. W. W. Lucasse (J. Amer. Chem. Soc., 1926, **48**, 626—631).—The $E.M.F.$ of cells of the type $H_2|HCl(M)|AgCl|Ag$ have been measured at 25°, the acid solution containing 1 and 5 mols. % of glycerol and varying from 0·001 to 4M. The activity coefficients of the electrolyte agree with those calculated from Hückel's equation (A., 1925, ii, 513) when M is less than unity. The discrepancies at higher concentrations may be due to approximations in determining the concentrations or to uncertainties with regard to the value of the dielectric constant. S. K. Tweedy.

Law of neutral salt action in concentrated solutions. I. Influence of neutral salts on the acid hydrolysis of cyanamide. G. Grube and G. Schmid (Z. physikal. Chem., 1926, **119**, 19—45).—The influence of ammonium, lithium, sodium, potassium, magnesium, and calcium nitrates on the rate of hydrolysis of cyanamide to carbamide, in presence of nitric acid as catalyst, has been investigated. At constant acid concentration, the velocity coefficient increases with the salt concentration in accordance with the equation $k=k_0.e^{rc}$, where k_0 and k are the velocity coefficients in solutions of the same acidity in absence and in presence of neutral salt, respectively, c is the concentration of neutral salt in the latter case, and r is a constant, specific for each salt. In the absence of neutral salt, the velocity of reaction is not proportional to the nitric acid concentration, the nitric acid apparently exerting, in addition to its ordinary catalytic influence, a neutral salt action, which can be quantitatively expressed by an equation analogous to the above. This type of equation is applied to data regarding other catalyses and appears to hold generally so long as the neutral salt concentration is not greater than normal. A similar formula, subject to the same limitation, governs the effect of neutral salts on the electrometrically measured activities of hydrogen and of copper ions. L. F. Gilbert.

Temperature of vapour given off by a solution. B. Block (Z. angew. Chem., 1926, **39**, 376—377).—Reissmann's results (A., 1925, ii, 105) are criticised, on the ground that blank experiments carried out with the apparatus used in the investigations gave unsatisfactory and untrustworthy results. B. W. Clarke.

Thermal dissociation of sodium cyanide. E. W. Guernsey and M. S. Sherman (J. Amer. Chem. Soc., 1926, **48**, 695—704).—Attempts to determine the equilibrium constants of the reactions $2Na+2C=Na_2C_2$ and $Na_2C_2+N_2=2NaCN$ by vapour-pressure measurements are described. Pure sodium cyanide, prepared by adding a slight excess of liquid hydrogen cyanide to a solution of pure sodium hydroxide in absolute alcohol at 0° and allowing to crystallise for some hours in a stoppered vessel, was heated at 600—1255° in a current of helium or (at higher temperatures) nitrogen, both in the presence and absence of iron powder (cf. A., 1925, ii, 889). The results were more reproducible with a graphite-lined furnace than with one of Monel metal. The vapour over sodium cyanide consists mainly of dissociation products (including sodium carbide); the dissociation in nitrogen is greater than that in helium would lead one to expect. Sodium carbide is largely dissociated into sodium and carbon over the above temperature range; the approximate results obtained indicate that its stability increases with rising temperature. The non-reproducibility of the results is attributed to the changing composition of both liquid and gas phases during the experiments. S. K. Tweedy.

Amalgams of gold and mercury. G. T. Britton and J. W. McBain (J. Amer. Chem. Soc., 1926, **48**, 593—598).—The solubility of gold in mercury rises slowly with temperature to about 300°, where the rise becomes more rapid and passes through a maximum at 342° (14·6 atoms % of gold), probably indicating the formation of the compound $AuHg_6$. A minimum occurs at 320° (22 atoms % of gold); this is probably a eutectic point at which $AuHg_6$ is one of the solid phases, but the composition of the second is unknown. On the other side of

this eutectic point, the proportion of gold in the liquid phase increases very rapidly up to 410°. The results differ slightly from those of Parravano (A., 1919, ii, 69) and disagree entirely with those of Braley and Schneider (*ibid.*, 1921, ii, 406).

S. K. TWEEDY.

System iron–tin. F. WEVER and W. REINECKEN (Z. anorg. Chem., 1926, **151**, 349—372; cf. Isaac and Tammann, A., 1907, ii, 469).—Thermal analysis of the system has been effected by means of time–temperature and temperature-difference curves. The saturated mixed crystal contains 18% of tin. This combines with the liquid phase at 1132° to form the compound Fe_3Sn if the alloy contains between 18% and 48% of tin. Below 890°, this compound decomposes into $FeSn_2$ and mixed crystals, or, if the alloy contains more than 41·3% of tin, combines with tin to form the same compound. The compound $FeSn_2$ undergoes polymorphic transformations at 780°, 755°, and 490°. Tin does not affect the temperature of the magnetic (α–β) transformation of iron. The α–γ transition point, however, is raised 40° by 1% of tin, and the γ–δ transition point depressed 140°. With a concentration greater than about 1·9% of tin, iron does not pass through the γ-phase at all in cooling. Contrary to the statement of Isaac and Tammann (*loc. cit.*), there is no gap in the miscibility of the liquid phase. R. CUTHILL.

System water–aluminium oxide. M. GUICHARD (Bull. Soc. chim., 1926, [iv], **39**, 190—194; cf. A., 1925, ii, 558).—The behaviour of aluminium oxide in the presence of water vapour at constant pressure has been investigated by placing the oxide and water in two limbs of an evacuated tube, kept at different but constant temperatures, prolonged exposure being necessary to obtain equilibrium. The hydrated oxide, precipitated from solutions of aluminium nitrate by ammonia, contains the unstable trihydrate, but on keeping in a vacuum the trihydrate is decomposed and the resulting product is a mixture of the dihydrate and adsorbed water. Under an aqueous vapour pressure of 26 mm., the dihydrate is stable below about 200°; it always contains adsorbed water, and gives reversible adsorption isobars. Above 200°, the dihydrate is decomposed, and a mixture of anhydrous oxide and adsorbed water exists between 200° and 500°. Exposure to temperatures above 200° makes the oxide chemically inert so that the dihydrate is not formed on cooling. Specimens once heated above 200° therefore show continuous isobars between 500° and 37°, but the numerical values depend on the exposure to the high temperature and are not reproducible. W. HUME-ROTHERY.

Thermal analysis of the system boron trifluoride–hydrogen sulphide. A. F. O. GERMANN and H. S. BOOTH (J. Physical Chem., 1926, **30**, 369—377).—The f.-p. diagram is characterised by two eutectics, one at −148° with 22% of hydrogen sulphide, the other at −140°, approximately, with 53% of hydrogen sulphide, a maximum at −137° corresponding with the compound BF_3,H_2S, and a transition point at −99° at which the compound $BF_3,7H_2S$ is decomposed. The flatness of the curve at the maximum indicates that the compound BF_3,H_2S is considerably dissociated at its m. p., so that there should be little difficulty in separating, by fractional distillation, hydrogen sulphide as an impurity from boron trifluoride. A comparison with the diagrams for other systems, *e.g.*, hydrogen halides and hydrogen sulphide, is shown. Methyl ether gives a diagram which is almost identical with that of the present system. A graphical representation of the structure of BF_3,H_2S is given.

L. S. THEOBALD.

Theory of concentrated solutions. J. LINARD (Bull. Soc. chim. Belg., 1925, **34**, 363—398).—The thermal diagrams of certain binary systems may be calculated from the formula of Mortimer (A., 1922, ii, 621; 1923, ii, 299) provided that the necessary data are available, that no additive compound is formed, and that separation into two liquid phases does not occur. Experiment is necessary to decide whether these conditions are fulfilled. The validity of Mortimer's formula having been established, the author uses his results to correct the values of latent heats of fusion previously recorded.

An equimolecular compound stable below −26° is formed in the system nitrobenzene–aniline (eutectic point at −30·9° and 37% nitrobenzene). The observations of Baud (A., 1913, ii, 475) on the system benzene–carbon tetrachloride are confirmed. Nitrobenzene and carbon tetrachloride form two complexes with 80 and 40 mols. % of the former (eutectic at −36° and 20% nitrobenzene). *cyclo*Hexane and aniline are only partly miscible, whilst the m.-p. curve for *cyclo*hexane and nitrobenzene (eutectic at −9° and 92% *cyclo*hexane) has a point of inflexion and is near the region of immiscibility in the liquid phase. In the supercooled state these two liquids are only partly miscible. The relative internal pressure for *cyclo*hexane is found to be 0·57 (as compared with 0·56 for hexane) from a study of the system naphthalene–*cyclo*hexane (eutectic at −3·6° and 5·6% naphthalene).

The data for the system nitrobenzene–benzene (eutectic at −24°, 51% nitrobenzene) are in good agreement with those of Dahms (Wied. Ann., 1895, **54**, 486) and are accurately reproduced by Mortimer's formula, using the values 2760 and 2370 cal. for the latent heats of nitrobenzene and benzene, respectively. For the system aniline–benzene (eutectic at −28·2°, 35·2% benzene) the data of Kremann and Borjanovics (A., 1916, ii, 472) are shown to be inaccurate. For this and also for the systems aniline–*m*-toluidine (eutectic at −60°, 42·6% aniline) and aniline–chloroform (Tsakalotos and Guye, J. Chim. phys., 1910, 8, 340), good agreement is obtained by taking 1580 cal. for the latent heat of aniline in place of the mean published value of 2240.

From the data for the systems ethylene dibromide–carbon tetrachloride (eutectic at −48°, 18% dibromide; transition point of ethylene dibromide −24°, of carbon tetrachloride −46·2°), ethylene dibromide–chlorobenzene (eutectic at −55°, 17% dibromide), and ethylene dibromide with benzene and nitrobenzene (Dahms, *loc. cit.*) the latent heat

of fusion of ethylene dibromide is revised to the value 2950 cal., which also gives satisfactory agreement for the curves of Paternò and his co-workers (Paternò and Ampola, A., 1897, ii, 476; Paternò and Montemartini, A., 1895, ii, 6, 205). These and the system chlorobenzene–*o*-chlorotoluene (eutectic at −70·7°, 39·4% *o*-chlorotoluene) also require the value 1785 cal. for the latent heat of chlorobenzene and 2550 for that of *o*-chlorotoluene. The f.-p. curves are also recorded for the systems: *p*-nitrotoluene–*cyclo*hexane (eutectic at −7·5° and 10% nitrotoluene), *p*-toluidine–*cyclo*hexane (eutectic at −6·2°, 10% toluidine), *p*-toluidine–benzene (eutectic at −5·1°, 20·2% toluidine), and *p*-nitrotoluene–benzene (eutectic at −8·5°, 23·4% nitrotoluene). G. M. BENNETT.

Binary systems. II. Thermal diagram for partly miscible pairs. H. RHEINBOLDT and M. KIRCHEISEN (J. pr. Chem., 1926, [ii], **112**, 187—195; cf. this vol., 25).—The pairs of substances considered are only partly miscible in the liquid state, and, as in the earlier investigation, do not form solid solutions. In the system picric acid–triphenylmethane the temperature at which solid picric acid connects with the two liquid layers is 114°, the critical solution temperature 144·5°, and the eutectic 86° (91·5% triphenylmethane. For the system 2 : 4-dinitrotoluene–carbamide, the two molten components are only very slightly miscible, and the curves which correspond with the beginning of melting at 68·5° and the completion at 130·5° are both horizontal from 1% to 90—99% of carbamide. No compounds are formed in either of these systems.

The system *m*-phenylenediamine–triphenylmethane affords an example of compound formation (1 : 1) in which the compound melts to form two liquid layers. The system shows two eutectics at 80° and 58·5° with 10% and 97% of *m*-phenylenediamine, respectively; the temperature at which the two liquid layers coexist with solid *m*-phenylenediamine is 83°, and the critical solution temperature is 98°. These figures are in fair agreement with those obtained in a different way by Kremann and Zawodski (A., 1921, i, 601) and by Kremann, Mauermann, Müller, and Rösler (*ibid.*, 1923, i, 332). C. HOLLINS.

Heat of dilution of a solution of ions in the theory of Debye and Hückel. Theory of heat effects in a dielectric. N. BJERRUM (Z. physikal. Chem., 1926, **119**, 145—160).—On the basis of the Debye–Hückel theory, the author has independently arrived at the same formula for the heat of dilution as was obtained by Gross and Halpern (A., 1925, ii, 866). Qualitative considerations concerning the ionising influence of the thermal movement of molecules are in agreement with this formula. Debye's two methods of deriving a formula for ionic activity coefficients lead to identical expressions if the correct value for the heat of dilution is used. Available data relating to heats of dilution are not in agreement with the values given by these formulæ, which are applicable only to dilute solutions, *i.e.*, of the order of 0·01*M* or less. The energy changes occasioned in a dielectric by an applied electric field are calculated both thermodynamically and from the principles of electrostatics. L. F. GILBERT.

Thermochemistry of beryllium. C. MATIGNON and (MLLE.) G. MAROHAL (Bull. Soc. chim., 1926, [iv], **39**, 167—190; cf. this vol., 28).—Measurements have been made of the heats of solution of various beryllium compounds in water, and in solutions of hydrochloric and hydrofluoric acids and sodium hydroxide, and also of the heat evolved in the double decomposition of solutions of beryllium sulphate and barium chloride. In addition to those mentioned in the previous abstract, the following heats of formation are deduced: (1) $Be+F_2+aq=BeF_2(aq.)+191·7$ Cal.; (2) $Be+Cl_2=BeCl_2$ (solid)$+112·6$ Cal.; (3) $Be+S+O_4=BeSO_4$ (solid)$+276·9$ Cal.; (4) $N_2+3O_2+Be+aq=Be(NO_3)_2(aq.)+182·7$ Cal. The following values are obtained for the heats of solution in water: $BeCl_2$, 51·1 Cal.; $BeSO_4$, 18·5 Cal.; $BeSO_4,2H_2O$, 8·0 Cal.; $BeSO_4,4H_2O$, 1·5 Cal. For the heats of formation of the solid hydrates from the anhydrous substances and liquid water, the values are: BeO,H_2O, 2·9 Cal.; $BeSO_4,2H_2O$, 10·45 Cal.; $BeSO_4,4H_2O$, 17·0 Cal. The heat of formation of beryllium oxide (137·4 Cal.) is of the same order as that of barium and much greater than that of sodium oxide. Aluminium and beryllium are among the very few metals the chlorides of which have a smaller heat of formation than the corresponding oxides. W. HUME-ROTHERY.

Thermochemistry of fluorine. I. H. VON WARTENBERG and O. FITZNER (Z. anorg. Chem., 1926, **151**, 313—325).—The heat of formation of gaseous hydrogen fluoride has been found by direct synthesis to be 63·0 Cal. per mol. (indirectly, 65·0) and the molar heat of solution in 400 mols. of water is 11·56±0·01 Cal. (cf. Guntz, A., 1884, 544). R. CUTHILL.

Thermochemistry of fluorine. II. H. VON WARTENBERG (Z. anorg. Chem., 1926, **151**, 326—330; cf. preceding abstract).—The following revised molar heats of formation (Cal.) have been calculated: antimony trifluoride, 210·6; boron trifluoride (from amorphous boron), 258·1; fluoboric acid (from amorphous boron) 359·2; silicon tetrafluoride (from amorphous silicon), 360·2; fluosilicic acid (+aq.), 545·4; fluorides of lithium, 144·7; sodium, 136·6; potassium, 134·5; rubidium, 132·8; cæsium, 131·5; barium, 278·9; thallium (-ous) (+aq.), 80·5; calcium, 289·4; strontium, 289·3; magnesium, 264·3; zinc, 193; cadmium (+aq.), 173·7; ferrous iron (+aq.), 177·2; manganese (+aq.), 206·1; cobalt (+aq.), 172·8; nickel (+aq.), 171·4; ammonium, 36·9; aluminium, 331·5; chromium, 171·3 (heat of hydration unknown); ferric iron (+aq.), 253·1; copper (+aq.), 129·8; silver, 50·1; lead, 156. R. CUTHILL.

Action of thallium on dissolved alcohols and acids, and on excess water and ethyl alcohol. R. DE FORCRAND (Compt. rend., 1926, **182**, 609—612; cf. A., 1923, i, 84; ii, 420).—The heats of reaction of thallium and of sodium with various alcohols, acids, and water according to the equation RH+M=RM+H, have been studied. The heats of reaction of thallium and sodium, respectively, are

as follow (in Cal.): *cyclo*hexanol, −14·35 and +44·05; water, −14·65 and +44·10; phenol, −6·14 and +52·10; acetic acid, −0·67 and +57·40; hydrofluoric acid, +1·79 and 60·4; hydrochloric acid, −0·95 and +57·82; sulphuric acid, +0·98 and +59·79; ethyl alcohol, −10·37 and +48·15; the difference between the heats of reaction of the two metals is nearly identical in every case, the mean difference being 58·522 Cal. Thallium dissolves in excess of alcohols, acids, or water at a negligible rate unless oxygen is present, when the reaction $2R{\cdot}OH+Tl_2+O=2R{\cdot}OTl+H_2O$ proceeds. In this case, the reactions are exothermic, the heats of reaction of thallium with water and ethyl alcohol being +19·85 and +24·13 Cal., respectively. L. F. HEWITT.

Correction of thermochemical data. W. A. ROTH (Rec. trav. chim., 1926, **45**, 248—256).—The author considers that the data given by Lemoult (A., 1911, ii, 583) are inaccurate in consequence of systematic errors which are not eliminated by the corrections of Swientoslawski and Popov (A., 1925, ii, 1139); it is probable that Lemoult did not work with homogeneous substances. Values previously published for the heats of combustion of styrene and methylstyrene (A., 1911, ii, 1065) are supported by the more recent determinations of von Stohmann, Kleber, and Langbein, and of Moureu and André. The increment for substitution by the phenyl group is given as 718·0 (±0·6) cal. for conjugated and 722·2 (±0·5) cal. for unconjugated compounds; the correction factor previously suggested (*loc. cit.*) brings Lemoult's results into approximate agreement with these values. The following values (in cal.) are given for the heats of combustion of the compounds named: phenacetin, 7170; azobenzene, 8464; diphenylacetic acid, 1651·4; diphenylacetic anhydride, 3311·9. R. BRIGHTMAN.

Heat of combustion of benzoic acid. W. JAEGER and H. VON STEINWEHR (Z. physikal. Chem., 1926, **119**, 214—218; cf. this vol., 28, 127).—A critical discussion of published values.
L. F. GILBERT.

Calculation of some characteristic constants of free ammonium. A. BALANDIN (Z. physikal. Chem., 1926, **119**, 144).—Corrigenda to a previous paper (this vol., 29). L. F. GILBERT.

Equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion. H. R. RAIKES, A. F. YORKE, and F. K. EWART (J.C.S., 1926, 630—637).—The equivalent conductivities of solutions of sodium hydroxide have been measured at 18° and 10°, using special precautions to exclude carbon dioxide. The water used was obtained from a still of the Bourdillon type, and had a conductivity of approximately 0·085 gemmho. The sodium hydroxide was prepared by the electrolysis of a solution of sodium chloride, and showed no trace of carbonate or chloride when tested nephelometrically. The equivalent conductivity at infinite dilution is 217·0 at 18° and 180·2 at 10°. Using Washburn's value for the sodium ion, the corresponding mobilities of the hydroxyl ion are 173·8 and 144·3. A. B. MANNING.

Conductivity measurements in mixtures of methyl and ethyl alcohols. H. GOLDSCHMIDT and H. AARFLOT (Z. physikal. Chem., 1926, **119**, 1—7).—The electrical conductivities of solutions of hydrogen chloride and sodium bromide in mixtures of methyl and ethyl alcohols have been determined at 25°. Addition of methyl alcohol to ethyl alcohol solutions raises the conductivity, and *vice versa*, with the exception that addition of methyl alcohol to solutions of hydrogen chloride in ethyl alcohol has little effect until the methyl alcohol concentration is 0·5*N*, after which a steady rise in conductivity occurs. The changes in conductivity of the hydrochloric acid solutions on dilution with the second alcohol are proportional to the corresponding changes of the sodium bromide solutions; this is contrary to what has been found previously for the influence of water on the conductivities of the ethyl-alcoholic solutions (cf. A., 1925, ii, 128). L. F. GILBERT.

Conductivity and surface tension of univalent salts of higher fatty acids in the molten state. I. S. S. BHATNAGAR, M. PRASAD, and B. SINGH (Kolloid-Z., 1926, **38**, 218—222).—The electrical conductivity and surface tension of molten sodium oleate, sodium linoleate, and potassium linoleate have been measured. The conductivity is electrolytic in nature. It was measured with both alternating and direct current, and the difference between the two values can be accounted for by polarisation. The conductivity increases with rise of temperature up to a constant value, which is reached at 275° with sodium oleate, 224° with sodium linoleate, and 225° with potassium linoleate. This limiting value is considered to indicate complete dissociation. The surface tension was measured by a drop method and gave: for sodium oleate at 260°, 17·62; for sodium linoleate at 225°, 36·38; and for potassium linoleate at 210°, 27·92 dynes/cm.
N. H. HARTSHORNE.

Electrolytic conductivity in fused metal alloys. X. Prevention of diffusion of metals in mercury by a direct electric current. R. KREMANN and A. HRASOVEC (Monatsh., 1925, **46**, 409—451).—A comparison has been made of the rates of diffusion of the metals zinc, cadmium, lead, tin, and bismuth through mercury, both alone and under the influence of an electric current. The diffusion experiments were carried out in a vertical capillary tube, the bottom portion of which was filled with the metal to be studied, whilst the rest of the tube contained mercury. The progress of diffusion was followed by cutting the tube into lengths of 3 cm. and measuring the *E.M.F.* of the contents in a suitable electrolyte solution against a normal calomel electrode. The results indicate that, for a certain distance from the metal, there is a practically saturated amalgam present, followed by a diffusion layer, of a width varying with the metal under consideration, in which the potential changes rapidly from the potential of the amalgam to that of almost pure mercury. Beyond the diffusion layer is mercury alone. The rate of movement of the diffusion layer increases rapidly with temperature. It appears to bear no relation

to the at. wt. or at. vol. of the metal. Whilst the curves obtained by plotting distance of the diffusion layer from the origin against the logarithm of the time are of similar form for cadmium, zinc, tin, and bismuth, simply showing a diminishing rate of diffusion in the order given, the curve for lead is somewhat different, indicating that, whereas at the beginning of the diffusion process lead moves more rapidly than bismuth, afterwards it travels more slowly. Diffusion experiments under the influence of an electric current were carried out in ice, because the heat produced by the current caused a large increase in the rate of diffusion. The current was passed in such a direction that the solid metal formed the electrode to which the same constituent of the amalgam should travel (cf. Kremann, Müller, and Ortner, A., 1925, ii, 132; Kremann and Kapaun, *ibid.*, 313). When the current density is very small and the current is passed for only a short time, there is a reduction in the rate of diffusion, as is to be expected, and this is more evident in the case of the more rapidly diffusing metals. At higher current densities there is an increase in diffusion velocity, probably due to the heating effect.

M. S. BURR.

Electrical conductivity of solid salt mixtures. P. FISCHER (Z. Elektrochem., 1926, **32**, 136—143).—The electrical conductivity of various salt mixtures, in the form of compressed powders and solidified masses, has been studied by the use of both direct and alternating current at varying voltages. For compressed mixtures of cupric sulphide and sulphur, the conduction is metallic in nature, and a mixture containing 10% of sulphur shows maximum conductivity at 1 volt. The conductivity is always different, according as direct or alternating current is used. Other mixtures studied were: silver iodide with silver bromide or with potassium iodide, silver bromide with potassium bromide or with lead bromide, and cuprous chloride with lead chloride. In these cases, Ohm's law is not obeyed, and the compressed and melted mixtures show different conductivities under similar conditions. In general, more than one maximum of conductivity is shown. No direct connexion appears to exist between the variations of conductivity of mixtures and the corresponding f.-p. curves. It is suggested that the results depend on deformations of one or both of the crystal lattices present, but it appears impossible to predict the form of the conductivity curve.

C. H. D. CLARK.

Transference numbers of sodium and hydrogen in mixed chloride solution. (MISS) M. TAYLOR (J. Amer. Chem. Soc., 1926, **48**, 599—603).—The transport numbers of the ions in a solution 0·15*N* with respect to hydrochloric acid and 0·05*N* with respect to sodium chloride are: $Na^{\cdot}$ 0·0333, Cl' 0·197, $H^{\cdot}$ 0·770. These are in agreement with the values calculated from conductivity measurements and show that the complex anions containing sodium and chlorine suggested by Schneider and Braley do not exist (cf. A., 1923, ii, 456; Dewey, *ibid.*, 1925, ii, 873).

S. K. TWEEDY.

Aqueous solutions of sodium silicates. II. Transport numbers. R. W. HARMAN (J. Physical Chem., 1926, **30**, 359—368; cf. A., 1925, ii, 1065).—Transport numbers of sodium silicates of ratios $Na_2O : SiO_2$, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 at concentrations ranging from 0·1 to 2·0N_{Na} have been measured at 25° by the Hittorf method, both electrode portions being analysed for sodium and silica. No large variation in the transport number occurs over the range of concentrations investigated. For the ratio 1 : 1, sodium metasilicate, the mean of six values of n_{Na} is 0·31, of n_{SiO_3} 0·16, and of n_{OH} (found by difference) 0·53. This is to be expected, since *E.M.F.* measurements show that 10—30% of the silicate is hydrolysed according to concentration. The concentration of the hydroxyl ions is not nearly equivalent to that of the sodium ions. In the ratios 1 : 2, 1 : 3, and 1 : 4, the transport number of the silicate ion is high, it is approximately twice that of the sodium ion in the ratio 1 : 2, three times in the ratio 1 : 3, and four times in the ratio 1 : 4. The silicate anion thus contains more than one SiO_2 for two units of charge, the average number of mols. of SiO_2 being equal to the ratio. The mobility of the SiO_3 ion in the metasilicate is about 70, whilst in the ratios 1 : 2, 1 : 3, and 1 : 4, it becomes approximately equal to that of the sodium ion, thus agreeing with the mobilities calculated from conductivity experiments (*loc. cit.*). In these same ratios, the silicate anion is not the simple SiO_3H ion, but is either an aggregation of simple silicate ions with or without colloidal silica, or a definite complex silicate ion. In the case of sodium metasilicate, the transport number shows no evidence of complex silicate ions or of micelle formation.

L. S. THEOBALD.

Theory of *E.M.F.* in condensed systems. J. J. VAN LAAR and R. LORENZ (Z. anorg. Chem., 1926, **151**, 331—337).—By means of the expression previously derived (A., 1925, ii, 866) for the thermodynamic potential of a component of a condensed system and van Laar's relation between thermodynamic potential and electrode potential in such a system ("Lehrbuch der theoretischen Elektrochemie," 1907, pp. 119, 129), the *E.M.F.* of concentration cells consisting of fused salts and fused metals has been calculated.

R. CUTHILL.

Determination of the potential of fluorine from decomposition voltages of molten fluorides. R. LORENZ (Z. Elektrochem., 1926, **32**, 172—173; cf. Neumann and Richter, A., 1925, ii, 1164).—The author supports the view of Ruff and Busch (this vol., 129) that their electrodeposition series for the metals should not be identified with the corresponding potential series. On the other hand, these authors are held to be wrong in identifying the deposition series with that of thermal equilibrium, and also in supposing that the Neumann–Kopp law is applicable only to completely condensed systems and inapplicable in cases where gases take part in the reactions concerned.

C. H. D. CLARK.

Anomalies of electrocapillary curves. E. LIEBREICH (Z. Elektrochem., 1926, **32**, 162—172).—The electrocapillary and current-potential curves of

mercury in 0·1% sulphuric acid, *N*-potassium nitrate, and *N*-sodium hydroxide have been investigated, with a view to explain certain anomalies. According to the electrical double layer theory, the electrocapillary curve should be parabolic, but this theory fails to account for all observations, in that it makes no distinction between the behaviour of different electrolytes and assumes the capacity of the electrical double layer to be constant. The theories of Warburg, Krüger, and Stern are also discussed critically. On the basis of recent observations (Liebreich and Wiederholt, A., 1925, ii, 44), it is suggested that the maximum of the electrocapillary curve (connecting surface tension and applied current) corresponds with the formation of hydroxide or basic salt on the surface of the mercury by cathodic polarisation. After passing the maximum, hydrogen is evolved, and the surface film begins to be reduced to metal, this process becoming ultimately complete. In some cases, especially when using sodium hydroxide, the changes are rendered visible by turbidity of the solution near the surface and the evolution of bubbles of hydrogen. The theory advanced is supported by photomicrographic evidence. The formation of compounds, their solubility in mercury, and the adsorption of anions may cause the observed lowering of surface tension at higher current strengths.

C. H. D. Clark.

Theory of overvoltage. M. Knobel (J. Math. Phys. Mass. Inst. Tech., 1926, **5**, 65—74).—Postulating (1) that the electromotively active gas is monatomic and (2) that overvoltage is due to an excess surface concentration of the adsorbed atomic gas, the relation between surface concentration and pressure being given by the equation $P=\text{const.}\ H_a^m$, where P and H_a represent the pressure and surface concentration of (say) monatomic hydrogen, respectively, and m is a constant greater than unity, a mechanism of the action at polarised electrodes is suggested. The general equation for overvoltage, $E=RT/nF \times \log_e P/P'$, P and P' being the pressures under overvoltage conditions and at equilibrium, respectively, becomes $E=mRT/nF \times \log_e H_a/H_a'$, H_a and H_a' being the excess and equilibrium surface concentrations. Actual measurements yield values corresponding with a 0·01-molecular layer for low polarisations, increasing to an almost unimolecular layer at higher current densities. The calculated maximum hydrogen overvoltage is 1·4 volts, a value which is in agreement with experiment. The variation of overvoltage with different electrode metals and different surface conditions is due to the changes in the adsorbing power of the material, the more adsorbent the surface the smaller the value of m and the lower the overvoltage. The influence of varying current density is considered and an equation derived. The change in overvoltage with pressure is represented by the equation $E=E_0-RT/2nF \times \log_e P$, where E is the value at a gas pressure P and E_0 at atmospheric pressure. Other factors influencing overvoltage are surface tension, the presence of colloids, temperature, and the agitation of the medium.

J. S. Carter.

Penetration of electrolytic hydrogen through iron. M. Knobel and R. B. Norton (J. Math. Phys. Mass. Inst. Tech., 1926, **5**, 75—83).—The equation of Bodenstein (Z. Elektrochem., 1922, **28**, 517) expressing the rate of penetration D of hydrogen through iron as a function of the hydrogen overvoltage E is in error in that proportionality is assumed between the concentration of adsorbed hydrogen and the pressure. From a consideration of the theory of overvoltage (preceding abstract), the equation has been modified by the introduction of the quantity m, the resulting expression being: $E=0{\cdot}059m \log D+$ const. From a plot of the log D–E curves, the value of m is 5·8. The values obtained from the overvoltage–current density and overvoltage–time (A., 1925, ii, 211) equations are 6·4 and 5·1, respectively. The approximate agreement of these values is held to be important evidence in favour of the authors' overvoltage theory. J. S. Carter.

Electrolysis of acid solutions of copper sulphate. II. Constant currents. J. T. Burt-Gerrans (J. Physical Chem., 1926, **30**, 396—413).—An extension of the work of Redman (*ibid.*, 1925, **29**, 1548) to test the theory of the changes of concentration at the electrode (Rosebrugh and Miller, A., 1911, ii, 181) according to which the diffusion constant of copper is independent of its concentration in the electrolyte employed. Apparatus and circuits for recording the *P.D.* over an electrolytic cell during the first few seconds of electrolysis and for calibrating the oscillograph record with respect to time and voltage are described. The electrolyses were carried out at 18·0° with solutions of copper sulphate in maximum conducting sulphuric acid. Uniform fluid friction over the whole surface of the revolving cathode was obtained by mounting the latter on a vertical shaft between two auxiliary electrodes of the same dimensions. In order to secure a uniform electrolytic field, the three electrodes were supplied with currents of the same intensity; only the central cathode was connected to the oscillograph. The rate of revolution of the cathode shaft was recorded on the oscillogram. The empirical relation established between the limiting current, the rate of revolution, and the concentration of electrolyte is (limiting current) × (sec. per revolution)$^{0{\cdot}77}$ = 0·0790 × (g. copper per litre), between the concentrations 0·46 and 4·0 g. copper per litre. Further, it is shown that a diffusion film of uniform thickness over the surface of a rotating electrode must not be assumed unless the latter is well removed from the stationary ends of the electrolytic cell. Experimental data for 42 time–voltage curves are given and the value of the diffusion constant, k, computed from these is $4{\cdot}0 \times 10^{-6}$ in 7·6*N*-sulphuric acid at 18° for concentrations between 0·5 and 4·0 g. copper per litre. From the empirical relation found and the mathematical theory mentioned above, the time which must elapse before hydrogen will be liberated by a known current passing through a solution of known concentration into a cathode revolving at a given rate can be predicted. With the above value of k, these predictions agree with the time intervals recorded by the oscillograph. Results of electrolyses

between flat copper electrodes are also in agreement with the predictions.

The effects of variation in thickness of the diffusion film and of an unsymmetrical electrolytic field are discussed. L. S. THEOBALD.

Nature of the "critical increment" of chemical action. T. C. SUTTON (Phil. Mag., 1926, [vii], **1**, 606—608; cf. A., 1915, ii, 14).—Considerations based on the kinetic theory favour Garner's view, as opposed to that of Hinshelwood (cf. A., 1925, ii, 552, 874, 1167), that the collision of "activated molecules," *i.e.*, molecules having specified energies, may result, not always in the formation of new compounds, but in the re-formation of the actual reactants. The criterion determining chemical reaction (in the ordinary sense) on collision will probably depend on some, as yet unknown, function of the translational, rotational, and internal energies of the molecule. A. B. MANNING.

Calculation of velocity constants. G. SCHMID (Z. physikal. Chem., 1926, **119**, 8—18).—A new method for the derivation of reaction velocity coefficients is described which entails less labour than the usual methods, and has the same order of accuracy as that of Moesveld (A., 1923, ii, 141).

L. F. GILBERT.

Comparison between explosion temperatures calculated from specific heats and from explosion pressures. H. MURAOUR (Bull. Soc. chim., 1926, [iv], **39**, 389—396).—Largely a review of work already published. Recalculation of the results of Burlot (A., 1925, ii, 558) shows that explosion temperatures calculated by means of the specific heats of Mallard and Le Chatelier are less than those calculated from pressure measurements with a free piston at temperatures above about 1600°, and are greater for lower temperatures. The specific heat data of Pier, Bjerrum, and Neumann give at lower temperatures values 8—10% greater than those calculated from the pressure. R. CUTHILL.

Combustion of well-dried carbon monoxide and oxygen mixtures. I. W. A. BONE and F. R. WESTON (Proc. Roy. Soc., 1926, **A, 110**, 615—633).—The intensity of the spark required to ignite a mixture of 2 vols. of carbon monoxide with 1 vol. of oxygen depends on the moisture content. Thus, when a mixture saturated at 17° and containing 2·0% of water vapour is sparked from a condenser charged to 110 volts, the minimum condenser capacity necessary to cause ignition is 0·76 microfarad, corresponding with an energy of discharge of $4{\cdot}6\times10^{-3}$ joule. When saturated at 0°, the mixture contains 0·60% by volume of water vapour, and the minimum energy required for ignition is $29{\cdot}0\times10^{-3}$ joule, and when dried over calcium chloride the water-vapour content is 0·03% and the minimum energy 126×10^{-3} joule. After drying over phosphorus pentoxide for 6 months with all necessary precautions, the mixture is ignited by the discharge from a condenser charged to 970 volts, the minimum energy required lying between 0·24 and 0·36 joule. The explosions thus obtained are softer than when moisture is present, and combustion is incomplete; when the energy of the spark is 0·36 joule, 74% of the gas is burnt, and this is increased to 88% when the energy is increased to 0·94 joule. It is concluded that there is some property of the electric spark, presumably its ionising power, which, if developed strongly enough, can overcome the resistance of a dry mixture to ignition.

A. GEAKE.

Combustion of well-dried carbon monoxide and oxygen mixtures. II. W. A. BONE, R. P. FRASER, and D. M. NEWITT (Proc. Roy. Soc., 1926, **A, 110**, 634—645).—The ignitibility of mixtures of carbon monoxide and oxygen, dried for 20 or 52 weeks over phosphorus pentoxide, increases with increasing pressure. At pressures below 2 atm., mixtures are not ignited by sparks from an induction coil or magneto across a 0·01-inch gap. When the pressure is 2·75—5·0 atm., ignition takes place, usually after several attempts, but 5—10% of the carbon monoxide remains unburnt. At pressures above 10 atm., ignition is instantaneous and complete. Spectrograms of explosion flames in dry mixtures at 25 atm., ignited in a tube with quartz windows, show a continuous and diffused band spectrum extending up to 2780 Å., but no steam lines; the spectrogram is the same whether the flame is travelling towards or away from the spectrograph. An ordinary carbon monoxide flame burning in air, when photographed through the filled explosion vessel, clearly shows the steam lines. It is concluded that water is not necessary for the combination of carbon monoxide and oxygen. When water is present, direct oxidation and indirect oxidation go on simultaneously and independently. High pressure favours direct oxidation; the presence of hydrogen favours indirect oxidation. A. GEAKE.

Gaseous combustion at high pressures. VI. Explosion of argon- and helium-diluted "knall-gases." W. A. BONE, D. M. NEWITT, and D. T. A. TOWNEND (Proc. Roy. Soc., 1926, **A, 110**, 645—659; cf. A., 1925, ii, 800).—Hydrogen and carbon monoxide "knall-gases" diluted with helium, argon, or nitrogen were exploded in a spherical nickel–chrome steel bomb of 239 c.c. capacity, and the initial and maximum pressures were corrected for deviations from Boyle's law. Hydrogen "knall-gas," mixed with twice its volume of diluent, was exploded at initial pressures of 64·3, 96·4, and 128·6 atm. There is little difference between argon and helium as diluents, but the former gives a slightly higher ratio of corrected maximum to corrected initial pressure, the maximum is reached slightly more slowly, and the calculated maximum temperature is about 0·5% higher; the rate of cooling is greater for helium than for argon, owing to its greater mobility. The maximum temperature is 2630—2970°, depending on the initial pressure. When the diluent is nitrogen, the maximum pressure is considerably lower and is attained more slowly; the maximum temperature is 1920—2300°. Mixtures of the composition $2CO+O_2+6R$, where R is helium or argon, were exploded at the same initial pressures, and mixtures $2CO+O_2+4R$ at pressures of 10—150 atm. The corrected pressure ratio is always 5—9% higher when the diluent is argon than when it is helium, whereas

for hydrogen "knall-gas" the difference is never more than 1%; it is concluded that helium has a specific influence on the carbon monoxide "knall-gas" explosion. When 4 vols. of diluent are used, explosions at initial pressures above 50 atm. are slower in the presence of helium than of argon, but with 6 vols. of diluent the reverse is the case. Maximum temperatures cannot be calculated on account of the unknown degree of dissociation of carbon dioxide. For both hydrogen and carbon monoxide "knall-gases," the corrected ratio of maximum to initial pressure increases with increasing initial pressure, and it is suggested that this may be due to an increasing opacity of the gaseous medium with pressure to the radiation emitted during the explosion. A. GEAKE.

Chemical action of α-particles on acetylene. W. MUND and W. KOCH (J. Physical Chem., 1926, **30**, 289—293; cf. A., 1925, i, 625; ii, 1173).—The influence of oxygen and of pressure and temperature on the rate of polymerisation of acetylene by radon has been studied. No variation outside the experimental error was detected at different pressures, or at 0°, 20°, and 100°, or in presence of small amounts of air. The mean of eleven measurements now obtained, in the absence of oxygen, with the two results previously published, gives the ratio of the number of molecules of acetylene polymerised per pair of ions produced as 20·2. L. S. THEOBALD.

Dynamic isomerism. XXI. Velocity of mutarotation of tetramethylglucose and of tetra-acetylglucose in aqueous acetone. G. G. JONES and T. M. LOWRY (J.C.S., 1926, 720—723).—Data are given for the velocity of mutarotation of tetramethylglucose and of tetra-acetylglucose in aqueous acetone. The acetone reduces the catalytic activity of the water more rapidly than its total concentration. There is no connexion between the velocity curves and the curve which shows the partial vapour pressure of water from the various mixtures. W. THOMAS.

Partial splitting [by saponification] of mixed-acid glycerides. J. P. TREUB (Rec. trav. chim., 1926, **45**, 328—336).—The mechanism of the saponification in stages of glycerides containing mixed fatty acid groupings is discussed mathematically. In the case of a triglyceride, the probabilities that one or more particular acid groupings will be saponified at a particular stage are calculated. Expressions are thus obtained for the relative concentrations of the free fatty acids, glycerol, and the mono-, di-, and tri-glycerides. The validity of Bauer's rule is discussed in relation to the velocities of saponification of the different groups. When these differ considerably, the course of the saponification can be followed step by step from the analysis of the separated acids; when they are equal, a simple mathematical treatment suffices (cf. A., 1917, ii, 528). J. GRANT.

Decomposition of substituted carbamyl chlorides by hydroxy-compounds. II. Influence of the hydroxy-compound. T. W. PRICE (J.C.S., 1926, 653—658; cf. A., 1924, i, 280).—The reaction between phenylmethylcarbamyl chloride and various hydroxy-compounds has been studied at 100° in sealed tubes, using a large excess of the hydroxy-compound. The following velocity coefficients for a unimolecular reaction were obtained: methyl alcohol, 0·222; ethyl alcohol, 0·0427; *n*-propyl alcohol, 0·0251; *iso*propyl alcohol, 0·0106; *n*-butyl alcohol, 0·0177; *iso*butyl alcohol, 0·0156; *iso*amyl alcohol, 0·0123; benzyl alcohol, 0·0185; allyl alcohol, 0·0420; cinnamyl alcohol, 0·00744; phenol, 0·308; *o*-cresol, 0·0541; *m*-cresol, 0·146; *p*-cresol, 0·175; ethylene glycol, too fast to measure. The whole reaction is made up of two consecutive reactions: (i) $NMePh\cdot COCl+R\cdot OH=NMePh\cdot CO_2R+HCl$, (ii) $HCl+R\cdot OH=RCl+H_2O$. The first was measured. The influence of the hydroxy-compound is probably due to its constitution and not to its solvent action. W. THOMAS.

Transformation of maleic acid into fumaric acid accelerated by colloidal sulphur. H. FREUNDLICH and G. SCHIKORR (Koll. Chem. Beihefte, 1926, **22**, 1—15).—Blood charcoal adsorbs fumaric acid from aqueous solution more strongly than it does maleic acid, corresponding with the smaller solubility in water of the former. The adsorption of both substances follows the ordinary adsorption isotherm. An accelerated transformation of maleic acid into fumaric acid on the blood charcoal was not observed. The adsorption of both acids by colloidal sulphur was found to be very small and was not measured. The acceleration of the transformation of maleic acid into fumaric acid by colloidal sulphur found by Skraup (Monatsh., 1891, **18**, 107) was, however, regularly observed and studied quantitatively between 60° and 100°. Equally good results were given by sulphur sol obtained from the interaction of sulphur dioxide and hydrogen sulphide, and from the decomposition of sodium thiosulphate with sulphuric acid. In all these cases the sulphur separated out after a time, but the accelerated transformation continued in the solution after this had occurred. The action is thus only indirectly due to the colloidal sulphur, and it is assumed that some substance is formed by the interaction of the sulphur and the maleic acid, and that this is responsible for the acceleration. The velocity of the reaction in its initial stages is proportional to the amount of maleic acid adsorbed; thus $-dc/dt=kc^{1/n}$, or by integration, $k=1/t(1-1/n)\{c_0^{1-1/n}-c^{1-1/n}\}$, the symbols having the usual significance. The velocity is for the same sol proportional to the concentration of the sulphur. The effect of temperature is represented by Arrhenius' equation $\log_e k=B-A/T$, in which A and B are somewhat greater than with most reactions. After a long time the reaction ceases before all the maleic acid has been transformed. This is not due to the establishment of an equilibrium, however, since the process is affected neither by the addition of fumaric acid nor by such substances as phenylurethane, but probably to the decomposition of the catalytic reaction product mentioned above. The dissociation constants of fumaric acid were determined at 20° by the electrometric titration method of Auerbach and Smolczyk (A., 1925, ii, 118), the results being $K_1=9\cdot2\times10^{-4}$; $K_2=7\cdot1\times10^{-5}$. N. H. HARTSHORNE.

Oxidisability of organic substances. G. LEJEUNE (Compt. rend., 1926, **182**, 694—696).—The mechanism of the oxidation of primary and secondary alcohols, aldehydes, and ketones by permanganate and dichromate in acid and alkaline solutions has been studied. The following reactions are assumed in solution: (i) Substance $\rightleftharpoons$ complex; (ii) complex $\rightleftharpoons$ activated form (directly oxidisable); (iii) activated form+oxidising agent $\longrightarrow$ product. In the oxidation of primary and secondary alcohols in alkaline solution, reactions (i) and (iii) are very rapid compared with the slow measurable unimolecular reaction (ii). Primary alcohols and ketones in acid solution show a very rapid reaction (iii), whereas the slow reactions (i) and (ii) are measured. The order is almost zero. In the oxidation of secondary alcohols and aldehydes in acid solution and of primary alcohols in the presence of acetic acid, the reaction measured is (iii). For all reactions between 25° and 35° the temperature coefficient was approximately 2. W. THOMAS.

Hydrolysis of substituted benzyl chlorides and the theory of steric hindrance. S. C. J. OLIVIER.—See this vol., 511.

Speed of dissolution of copper in aqueous solutions of ferric chloride. E. BEKIER and S. TRZECIAK (J. Chim. phys., 1926, **23**, 242—250; cf. van Name and Hill, A., 1916, ii, 608).—The action occurs according to the schemes $Cu+2FeCl_3 \longrightarrow CuCl_2+2FeCl_2$, followed by $Cu+CuCl_2 \longrightarrow 2CuCl$, and has been followed, in the presence of an excess of ammonium chloride and in an atmosphere of carbon dioxide, by titration with potassium permanganate. The velocity constant calculated from the formula $k=\{\log_e(a-x_1/2)-\log_e(a-x_2/2)\}v/O(t_2-t_1)$, where a is the initial concentration of ferric and cupric chlorides, $x_1/2$ and $x_2/2$ are the concentrations of cupric chlorides at the times t_1 and t_2, respectively, and O, the surface area of the metal plate, is 0·2044 at 25° where the rate of stirring is 1500 per min. It is independent of the composition of the solution starting with ferric chloride and ending with cupric chloride as the sole active constituents. It is also independent of variations in the concentration of ammonium chloride provided that a sufficient quantity of this salt is present. Initially, k increases with increasing concentration of ammonium chloride until a limiting value is reached. The value of k also increases with an increase in the rate of stirring. The temperature coefficient between 15° and 25° is 1·35, the value of k^{15} being 0·1508. These results support the original postulate that diffusion plays an essential rôle in this reaction.

An aqueous solution of ammonium chloride, completely freed from dissolved oxygen, had no action on copper over a period of several months.

L. S. THEOBALD.

Metals and nitric acid. Heterogeneous reactions. A. KLEMENC (Z. Elektrochem., 1926, **32**, 150—155).—The author's assumption as to the function of E-acid, $H_2N_3O_8$ (cf. A., 1925, ii, 212), in nitration and oxidation processes brought about by nitric acid has been applied quantitatively to the heterogeneous reactions occurring between nitric acid and metals. The observation of Rây (J.C.S., 1911, **99**, 1012) of the formation of mercurous nitrite by the action of nitric acid on mercury may be explained by the existence of the equilibrium $2HgNO_3+NO_2 \rightleftharpoons Hg_2N_3O_8$ in a diffusion layer near the surface of the metal, the mercury–E-acid compound diffusing away from the metal and becoming decomposed according to the equation: $2Hg_2N_3O_8+H_2O=HgNO_2+3HgNO_3+2HNO_3$. The diffusion process is studied quantitatively according to the theory of heterogeneous reaction developed by Noyes and Whitney and by Nernst and Brunner, a linear relation for change of concentration of equilibrium reactants with distance in the diffusion layer being assumed. A complicated expression is reached for the velocity of dissolution of a substance, which is applied to the rate of dissolution of iodine in dilute potassium iodide, with satisfactory results. Considering the dissolution of metals in nitric acid, the assumption of linear change of concentration leads to the conclusion that the concentration of E-acid in the diffusion layer reaches a maximum at a distance from the surface of the metal of five-sixths of the thickness of the layer. The observation of Drapier (A., 1914, ii, 206) that on rotating a copper cylinder in nitric acid the velocity of solution is very considerably lessened, may be explained on this basis as due to a loss of E-acid on the solution side of the diffusion layer caused by rotation.

C. H. D. CLARK.

Autocatalytic decomposition of thiosulphuric acid. C. K. JABŁCZYŃSKI and (MME.) Z. WARSZAWSKA-RYTEL (Bull. Soc. chim., 1926, [iv], **39**, 409—416).—The reaction between sodium thiosulphate and hydrochloric acid has been followed by measuring the opacity of the solution by the Koenig-Martens spectrophotometer. The curve connecting the relative degree of opacity (A., 1925, ii, 35) with the time is of the form typical of autocatalytic reactions. Hydrogen ions accelerate the reaction considerably, but sodium ions have little effect, so that mechanical coagulation appears to play little part in the process. Dilution of the solution or addition of sulphurous acid or protective colloids retards the reaction. It is suggested that the reaction consists of the decomposition of the thiosulphuric acid according to the unimolecular law, followed by the aggregation of the sulphur formed into nuclei which catalyse the decomposition of the acid and render the solution turbid. The experimental results agree fairly well with this view.

R. CUTHILL.

Production of catalysts for the synthesis of ammonia. I. W. CEDERBERG.—See B., 1926, 236.

Active hydrogen and catalytic hydrogenation at a distance. R. HOCART (Bull. Soc. chim., 1926, [iv], **39**, 398—401; cf. A., 1925, ii, 587).—Attempts to repeat Mitchell and Marshall's experiments (J.C.S., 1923, **123**, 2448) on the activation of hydrogen by passing over a catalyst have led to negative results.

R. CUTHILL.

Catalytic synthesis of water vapour in contact with metallic nickel. A. F. BENTON and P. H. EMMETT (J. Amer. Chem. Soc., 1926, **48**, 632—640).—The rate of formation of water when hydrogen

containing up to 5% of oxygen is passed over reduced nickel at 35° to about 100° was studied. Bone and Wheeler's results, it is shown, indicate that activated hydrogen plays an unimportant part in the mechanism (cf. A., 1906, ii, 434). At 100° and above, quantitative formation of water occurs. A relatively thick layer of nickel oxide is formed, the progressive formation of which prevents the attainment of steady states at efficiencies below 100%; at 35°, the catalyst loses nearly all its activity and large quantities of oxide are formed. The results show that although autocatalytic reduction of nickel oxide proceeds, even at 65°, at an appreciable rate so long as the nickel surface is incompletely covered with oxide, yet the maximum rates of reduction are always small compared with the rate of hydrogen and oxygen catalysis at the same temperature. The area of actual contact between nickel oxide and nickel (and, therefore, the rate of reduction) is considered to be much greater in the catalytic formation of water than in the reduction of a completely oxidised nickel surface by hydrogen alone. It is concluded that the catalytic formation of water at a nickel surface can be largely and perhaps entirely accounted for by the successive oxidation and reduction of catalyst.

S. K. TWEEDY.

Nature of the protective film of iron. T. FUJIHARA.—See B., 1926, 243.

Influence of alternating currents on the electrolytic corrosion of iron. A. J. ALLMAND and R. H. D. BARKLIE.—See B., 1926, 277.

Electrolytic separation of metals. D. J. BROWN (J. Amer. Chem. Soc., 1926, **48**, 582—583).—The auxiliary electrode described by Sand (J.C.S., 1907, **91**, 379) is replaced by a wire of the metal being deposited. While deposition is occurring, the cathode potential is kept at −0·1 to −0·2 volt with respect to the wire, except for metals tending to deposit in a powdery form, when the cathode potential is kept less negative. A platinum wire may also be used with certain precautions. S. K. TWEEDY.

Electrolysis of electrolytes containing cuprous chloride. G. HÄNSEL (Wiss. Veröff. Siemens-Konz., 1925, **4**, 111—157).—A detailed study has been made of the electrolysis of solutions of cuprous chloride in aqueous solutions of hydrochloric acid, or of alkali or alkaline-earth chlorides, with a view to test the possibility of copper refining using cuprous solutions. The variations in the nature of the deposit of copper on the cathode are described for various electrolytes under various conditions of temperature, current density, and manner of stirring. The addition of gelatin improves the smoothness of the deposit. The refining of copper is not possible by this method; a cathode deposit from crude copper contained 99·3—99·6% of copper with considerable amounts of arsenic, antimony, and silver. This is fully explained by the results of systematic *E.M.F.* measurements. The following equilibrium values in volts at 20° are recorded: Cu/0·33*N*-CuCl in 3*N*-NaCl, +0·09 (normal value Cu/Cu$^{\cdot\cdot}$, +0·52); Cu/0·33*N*-CuCl in 3*N*-HCl, +0·037; Bi/0·33*N*-$BiCl_3$ in 3*N*-NaCl, +0·078; Bi/0·33*N*-$BiCl_3$ in 3*N*-HCl, +0·039; Sb/0·33*N*-$SbCl_3$ in 3*N*-NaCl, +0·131; Sb/0·33*N*-$SbCl_3$ in 3*N*-HCl, +0·101; Ag/AgCl saturated in 3*N*-NaCl, +0·192; Ag/AgCl saturated in 3*N*-HCl, +0·139; As/0·33*N*-$AsCl_3$ in 3*N*-NaCl, +0·3; As/0·33*N*-$AsCl_3$ in 3*N*-HCl, +0·305. Of these values, only those for arsenic and antimony agree approximately with the known normal potentials: in the other cases, complex formation must be responsible for the difference. Measurements of these values of *E.M.F.* at 45° are also recorded and a large number of cathode potentials in each case at various current densities; the values at 20° and for 100 amps./m.^{2} for the solutions as above in 3*N*-NaCl are Cu + 0·069, Bi +0·061, Sb +0·054, and in 3*N*-HCl, Cu + 0·014, Bi +0·016, Sb +0·021.

Electrolysis of bismuth and antimony chlorides in chloride solutions is found to be satisfactory, but that of silver chloride solutions is not.

Solubility measurements show that the percentage of copper present in 3*N*-solutions of the following salts saturated with cuprous chloride at 20° with addition of 0·25*N*-hydrochloric acid is: ammonium chloride 7·22, sodium chloride 3·92, potassium chloride 7·85, magnesium chloride 3·095, calcium chloride 3·59, barium chloride 4·367, and for cuprous chloride in 3·465*N*-hydrochloric acid 4·096, in 5·9*N*-acid 11·04%. In the analysis of the mixtures cuprous copper is directly titrated by adding 15% hydrochloric acid (10 c.c.) to 2—3 c.c. (about 2·5% copper) and then 0·05*N*-potassium bromate solution, using methyl-orange as indicator, the latter being bleached by free bromine. G. M. BENNETT.

Conditions for satisfactory photographic spectrophotometry. H. M. KELLNER (Z. wiss. Phot., 1926, **24**, 79—84).—In photographic spectrophotometry, the absorbing substance brings about a decrease in light intensity. It is therefore necessary to vary in a known manner the intensity of the comparison beam, and not its time of exposure. The errors introduced by varying the exposure time, and by the use of rotating sectors in the comparison beam, are discussed with examples. The use of a time scale necessitates an accurate knowledge of the properties of each plate employed and involves considerable calculations. The most satisfactory method for varying intensity is the use of accurately photometered diaphragms, or of wire nets of different mesh numbers. W. CLARK.

Law and mechanism of unimolecular reaction. S. C. ROY (Proc. Roy. Soc., 1926, **A**, **110**, 543—560).—The part played by radiation in photochemical and thermochemical reactions and in the allied phenomena of photoelectric and thermionic emission of electrons is discussed. The rate of a thermochemical unimolecular reaction is considered from the point of view that all radiation above a certain limiting frequency can activate the molecule. The molecule passes through a number of stages of activation before reaching the final reactive state, and the reaction velocity is dependent only on the energy difference between this final reactive state and the normal state. On these assumptions, the following equation is derived for the specific rate of reaction:

$$k_1=(8\pi k^2 m_\Pi/h^3)\{AB/(A+B)\}(T\bar{\rho}_0/a)e^{-(Q_a{}^{AB}+Q_s)/1.T},$$

where A and B are the mol. wt. of the

products, Q_a^{AB} is the molecular heat of activation, Q_0 the heat of dissociation, $\bar{\beta}_0$ the cross-section of the reacting molecule, m_H the mass of a hydrogen atom, k the molecular gas constant, and a is a statistical weight factor determined by the number of the valency linkings between the components. The equation has been examined by reference to the data for the gaseous decomposition of nitrogen pentoxide, phosphine, and sulphuryl chloride and for the decomposition of derivatives of oxalacetic esters in solution. The agreement is satisfactory. F. G. SOPER.

Photochemical reaction between hydrogen and chlorine. A. L. MARSHALL (Trans. Amer. Electrochem. Soc., 1926, **49**, 97—132).—A comprehensive account of previous work on the effect of light on the halogens and the reaction between hydrogen and chlorine. W. HUME-ROTHERY.

Photochemical synthesis of hydrogen chloride. J. CATHALA (J. Chim. phys., 1926, **23**, 256).—A correction to certain calculations made from the experiments of Coehn and Jung (A., 1925, ii, 142). The diameter of collision of the molecules, S, should be 3×10^{-8} for H_2, and approximately 5×10^{-7} for Cl_3. The number of molecules of hydrogen, n_1, present at a pressure of 255 mm., instead of 205 mm. is 10×10^{19}. The total number of collisions will then be 8×10^{24}, and the proportion of these which are effective, 1 in 10^8.

The original hypothesis that the concentration of the molecules of "chlorozone" is equal to that of the chlorine atoms is erroneous. On the contrary, it is a small fraction, less than 1/1000th, of the concentration of chlorine atoms (cf. this vol., 252).

L. S. THEOBALD.

Influence of intensity of illumination on the velocity of photochemical changes. Determination of the mean life of a hypothetical catalyst. F. BRIERS, D. L. CHAPMAN, and E. WALTERS (J.C.S., 1926, 562—569).—The effect of varying the intensity of illumination on the velocity of the photo-combination of chlorine and hydrogen and of bromine and hydrogen is discussed. An experimental investigation of the photochemical reaction between iodine and potassium oxalate in aqueous solution is described. The rate of the reaction is proportional to the square root of the intensity of illumination, as found by Berthoud and Bellenot (A., 1924, ii, 327). On the assumption that the action is dependent on the formation of an unstable catalyst, the authors have shown how the "life" of the catalyst can be determined in light of varying intensity. The product of the life of the catalyst and the velocity of the change was found to be constant. The life of the catalyst in the dark is 6·31 seconds. W. THOMAS.

Magnitude of the energy quantum in comparison with the energy liberated in chemical reactions. H. MAYER (Z. angew. Chem., 1926, **39**, 306—308).—The value, for radiations of wave-length between 50 and 0·001 μ, of $Nh\nu$ (where N is Avogadro's number, h is Planck's constant, and ν is the frequency) has been calculated. From the results it appears that the energy quantum per mol. is approximately equal to the heat evolved in most chemical reactions for light in the visible spectrum, less than this for infra-red radiations, and greater for ultra-violet and X-radiations. The significance of these facts in relation to photochemical reactions is discussed with especial reference to the formation of hydrogen bromide from its elements (cf. Bodenstein and Lütkemeyer, A., 1925, ii, 218).

A. R. POWELL.

Budde effect in bromine. I. Photoactive constituent in wet bromine. II. Kinetics of the reaction and the light absorption of wet and dry bromine. B. LEWIS and E. K. RIDEAL (J.C.S., 1926, 583—596, 596—606).—I. Experimental data support the hypothesis that the Budde effect is due to a photo-sensitive bromine hydrate, Br_2,H_2O, and that the water does not function as a catalyst in the formation of a photo-sensitive polymeride of bromine. Light of wave-length longer than 5800 Å. produced no detectable Budde effect; light within a region 5600—5500 Å. was particularly effective. The Budde effect increases with the water-vapour pressure, attaining a maximum, which is shown to be due to a complete absorption of the active radiation. The effect is also dependent on the partial pressure of bromine, as is to be expected from the equilibrium $Br_2+H_2O \rightleftharpoons Br_2,H_2O$. The hydrate is strongly adsorbed by glass surfaces, and the relationship between the concentration in bulk and surface phases can be expressed in the form of an adsorption isotherm. The hydrate may be displaced from the glass surfaces by water.

II. The heat of formation of bromine hydrate (calculated by means of the van 't Hoff isochore from the Budde effect at various temperatures) is 1090 cal.; this is almost identical with the heat of dissolution of bromine in water. From the heat of formation, by means of the Nernst heat theorem, the equilibrium constant for the dissociation of bromine hydrate at 313° Abs. is of the order $3\cdot10\times10^9$. The absorption spectra of wet and of dry bromine were examined; the former commences to show a definite absorption at λ 6100 Å., whilst the latter shows no marked absorption before λ 5700 Å. This implies that the complex bromine–water requires an energy of excitation 3200 cal./g.-mol. less than that of dry bromine. When corrected for the absorption and probable fluorescence, it is found that the Stark–Einstein law of photoequivalence is obeyed. The absorption coefficient of bromine hydrate for the spectral region employed is $10\cdot5\times10^6$. A mechanism of excitation and decomposition of bromine hydrate molecules is advanced in explanation of the Budde effect.

W. THOMAS.

Decomposition of hydrogen iodide in light. M. BODENSTEIN and F. LIENEWEG (Z. physikal. Chem., 1926, **119**, 123—138).—The decomposition of gaseous and of liquid hydrogen iodide in light from a mercury-lamp source has been studied. The percentage decomposition of the gas is independent of the temperature (150—175°). Liquid hydrogen iodide requires one quantum for the complete decomposition of 1·84 mols., a figure which agrees within the limits of error with Warburg's value of one quantum per 2 mols. of the gas (A., 1918, ii, 49).

These results are in accordance with those obtained previously from theoretical considerations (A., 1913, ii, 819). Nitrogen has no effect on the reaction, which also is not sensitised by the presence of iodine. It is shown how the actual mechanism of the reaction could be established, although the present results are insufficient for this purpose.

The relatively small amounts of iodine liberated from liquid hydrogen iodide could not be determined accurately by titration with thiosulphate, but were satisfactorily determined by an absorption method, with the use of a spectrophotometer.

L. F. GILBERT.

Additive rule in mixed photochemical reactions. A. BERTHOUD (J. Chim. phys., 1926, **23**, 251—255).—A theoretical paper in which the validity of the additive rule for the light and the dark reactions in mixed photochemical changes is discussed. Experimental verifications are rare and are not completely satisfactory. Plotnikov's calculations (A., 1908, ii, 790) contain an error and, in consequence, his results indicate that the oxidation of hydrogen iodide by free oxygen probably does not follow the additive rule. The reverse is the case with the oxidation of potassium oxalate by chlorine and bromine, respectively, as examined by Berthoud and Bellenot (A., 1925, ii, 141). In the formation of hydrogen bromide (cf. Bodenstein and Lütkemeyer, *ibid.*, 218), the additive rule fails.

L. S. THEOBALD.

Formation of ozone by optically excited mercury vapour. R. G. DICKINSON and M. S. SHERRILL (Proc. Nat. Acad. Sci., 1926, **12**, 175—178).—The photochemical formation of ozone in oxygen at atmospheric pressure by the radiation from a cooled quartz mercury arc, filtered to remove the shortest wave-lengths, is sensitised by mercury vapour. Mercury atoms are excited from the normal to the $2p_2$ state by the absorption of radiation of wave-length 2537 Å. These collide with oxygen molecules, resulting in the reversion of mercury atoms to the normal state and the excitation or dissociation of oxygen. Ozone is then produced by reaction of excited or dissociated oxygen with normal oxygen.

J. S. CARTER.

Evidence for the existence of activated molecules in a chemical reaction. O. R. WULF (Proc. Nat. Acad. Sci., 1926, **12**, 129—131).—It is claimed that the radiation emitted when ozone decomposes into oxygen is explainable on the basis of the quantum theory, only if it be assumed that ozone under conditions favourable for its decomposition contains molecules in activated states of much higher energy content than that of the normal ozone molecule.

A. E. MITCHELL.

Photochemical inactivity of infra-red radiation with special reference to the decomposition of nitrogen pentoxide. F. DANIELS (J. Amer. Chem. Soc., 1926, **48**, 607—615).—The photochemical decomposition of nitrogen pentoxide is not brought about by infra-red radiation. The slight decomposition observed at 25° is due to a small elevation of temperature caused by the radiation; at 0°, where the thermal decomposition is negligible, no decomposition occurs. At least 99·5% of the absorbed radiation is chemically inactive. Infra-red radiation is inactive also in the decomposition of hydrogen chloride and carbon dioxide, and in the oxidation of alcohol vapour. A critical discussion is appended; the results suggest that absorption in the infra-red and in the ultra-violet have fundamentally different mechanisms and that the atoms in a molecule may be loosened only by displacement of the binding electrons.

S. K. TWEEDY.

Decomposition of nitrogen pentoxide and infra-red radiation. H. A. TAYLOR (J. Amer. Chem. Soc., 1926, **48**, 577—582).—The suggestion of Daniels and Johnston (A., 1921, ii, 249) and of Lewis (A., 1922, ii, 628) that nitrogen pentoxide may be decomposed by absorption of 3 or 5 quanta at 3·39 or 5·81 μ, at which wave-lengths this oxide possesses strong absorption bands, is shown to be probably incorrect. The accuracy of the experiments was insufficient to warrant a complete denial of the suggestion, but no marked acceleration of decomposition occurred at these wave-lengths, which is contrary to the predictions of the radiation theory. The application of radiation to unimolecular reactions is considered; it is pointed out that Tolman's explanation of such reactions (A., 1925, ii, 799) is also applicable without the assumption of radiation.

S. K. TWEEDY.

Effect of ultra-violet light on the oxidation of sodium sulphite by atmospheric oxygen [in presence of catalysts]. R. B. MASON and J. H. MATHEWS (J. Physical Chem., 1926, **30**, 414—420; cf. Bigelow, A., 1898, ii, 506; Titov, *ibid.*, 1904, ii, 113; Mathews and Weeks, *ibid.*, 1917, ii, 230; Bredig and Pemsel, Eder's Jahrb. Phot., 1900, 541).—The effect of ultra-violet light alone in the presence of certain catalysts has been investigated at 30° for 0·1*M*-aqueous solutions of purified sodium sulphite. The rate of oxidation depends on the rate at which air is bubbled through the solution. The shape and size of the bubble also greatly influence the rate. Pure oxygen and ozone increase it both in the light and in the dark, and the rate of the former reaction was more than doubled when the flow of air was increased from 30 to 60 litres per hr. To the light reaction, quinol and phenol (both 0·001*N*) act as positive catalysts, whilst sucrose, quinine sulphate, caoutchouc, and copper sulphate act in the negative sense. Quinol (0·001 or 0·002*N*) almost stopped the dark reaction, quinine sulphate and phenol had a similar, but less marked, effect, whilst copper sulphate had no effect (cf. Titov, *loc. cit.*; Milbauer and Pazourek, Bull. Soc. chim., 1922, [iv], **33**, 676). Pure carbon dioxide, when bubbled through the solutions, stopped both the light and dark reactions. Caoutchouc acted as a weak negative catalyst to both reactions, but became strongly negative to the dark reaction after exposure to ultra-violet light.

The rate of oxidation of the dark reaction is the same in diffused light as in absolute darkness, and at 0° is but little slower than at 30°. This is probably due to the greater solubility of oxygen at the lower temperature. A cadmium spark was the source of ultra-violet light used, it being found to give a reaction

which was more rapid than that obtained with a mercury-vapour lamp.

Absorption spectrograms of all reacting substances, products, and catalysts were taken, but no relationship between the light absorption of the catalysts and their action on the photochemical oxidation of sodium sulphite was apparent. L. S. THEOBALD.

Law of photochemical equivalents in photosynthesis by chlorophyll. R. WURMSER (J. Phys. Radium, 1926, [vi], **7**, 33—44).—Einstein's photochemical equivalent law has been tested in the case of the reduction of carbon dioxide by the sea-weed *Ulva lactuca*, according to the equation $CO_2+H_2O=O_2+\frac{1}{6}C_6H_{12}O_6$—120,000 cal. Langevin's theoretical expression for the proportions in which the radiation is used up by absorption and diffusion was first confirmed for layers of varying thickness by measurements with a thermopile of the incident and transmitted radiations. A measure of the photosynthesis is obtained by means of the ratio $R=(U+u)/Ea$, where U and u are the amounts of oxygen (expressed as cal.) liberated on exposure of the weed to light, and absorbed by it in the dark in the same time, respectively, E is the value in cal. of the total incident energy, and a the absorbing power calculated from Langevin's relation. Using red and green rays (mean λ=6600 and 5400 Å., respectively), a mean value of 1·146 for the ratio R_{green}/R_{red} is obtained. Comparison with the ratio of the wave-lengths of the rays used indicates that the simple form of Einstein's law does not apply in this case. J. GRANT.

Chemical effects produced by resonance radiation. E. K. RIDEAL and H. S. HIRST (Nature, 1926, **117**, 449—450).—An analysis of the views held by the authors (cf. this vol., 34) and by Taylor (*ibid.*, 252). Experiments with hydrogen and ethylene indicate that chemical removal may not be the only method by which mercury atoms lose their photosensitising powers. At high gas pressures practically all the chemical action is confined to a thin layer in close proximity to the liquid mercury.

A. A. ELDRIDGE.

Occurrence of sparks during the crystallisation of carbon disulphide. R. ANSCHÜTZ (Ber., 1926, **59**, [*B*], 455).—Small sparks are not infrequently observed during the solidification of carbon disulphide cooled by liquid air; the possibility of explosions being thus caused is not excluded. H. WREN.

Action of brass on cuprous chloride. G. MASING and K. MIETHING (Wiss. Veröff. Siemens-Konz., 1925, **4**, 225—229).—The deposition of copper from cuprous chloride solutions on brass in the laboratory is due, not to the spontaneous decomposition of the univalent copper ion, but to a reduction by the baser metal of the brass itself. The same process is probably responsible for the local loss of zinc by brass in marine and land engines. G. M. BENNETT.

Gold in mercury. W. VENATOR (Z. angew. Chem., 1926, **39**, 229).—It is extremely difficult to obtain mercury completely free from gold or to determine traces of gold in mercury. The gold, which is probably present as small particles of amalgam, is retained by the mercury even after repeated distillation, and the quantity retained is sufficient to account for the gold discovered by Miethe in his mercury, without having recourse to the explanation of transmutation. W. T. K. BRAUNHOLTZ.

Complex compounds of beryllium with sodium hydrogen carbonate. A. BALANDIN (Chem. News, 1926, **132**, 213—215).—A 1·08*N*-solution of sodium hydrogen carbonate dissolves 21·7 g. of beryllium hydroxide per litre at 21°, 23·9 g. at 52°, 16·3 g. at 80°, and none at all at 90°. From the saturated solution no carbon dioxide is evolved below 80°, and at 92° the beryllium is slowly but completely precipitated. Addition of half its volume of alcohol to a saturated solution of beryllium hydroxide in sodium hydrogen carbonate at 45° causes the separation of an oily layer which crystallises at 0°. The crystals melt at 3° and slowly lose alcohol at the ordinary temperature, leaving a white powder having the composition $2NaHCO_3,Be(OH)_2$. This compound is neutral to phenolphthalein and alkaline to methyl-orange, and its solutions have a salt taste instead of the usual sweet taste associated with beryllium salts. An explanation is given of the varying solubility of beryllium hydroxide in sodium hydrogen carbonate based on the formation and decomposition of four intermediate compounds. A. R. POWELL.

Action of carbonyl chloride on beryllia. C. MATIGNON and J. CATHALA (Compt. rend., 1926, **182**, 601).—Priority is accorded to Chauvenet (A., 1911, ii, 109) in the matter of the preparation of beryllium chloride by the action of carbonyl chloride on beryllia (cf. this vol., 260). Certain errors in the latter paper are corrected. L. F. HEWITT.

Bromination of zinc in the presence of different solvents. A. RAYNAUD (Bull. Soc. chim., 1926, [iv], **39**, 195—201).—Perfectly dry and pure bromine has no action on pure metallic zinc at temperatures up to 400°. No action occurs even on prolonged keeping at the ordinary temperature in the presence of petroleum, carbon tetrachloride, *n*-octane, or light petroleum. In the presence of benzene, the zinc is practically unaffected, but the benzene is brominated and hydrobromic acid produced. In the presence of small quantities of water an immediate reaction takes place, which ceases unless more water is added. The reaction probably takes place according to the scheme (i) $H_2O+2Br \rightarrow 2HBr+O$; (ii) $O+Zn \rightarrow ZnO$; and (iii) $ZnO+2HBr \rightarrow ZnBr_2+H_2O$. An immediate reaction also takes place in the presence of ethyl ether, a red liquid being formed which contains the *substance* $ZnBr_2,Et_2O$. This is better prepared by dissolving anhydrous zinc bromide in ether, distilling off the excess of ether, and allowing the solution to crystallise in a desiccator containing sulphuric acid, when white, deliquescent, leaf-like crystals are obtained which decompose when heated.

W. HUME-ROTHERY.

Mercury helides. J. J. MANLEY (Nature, 1926, **117**, 587—588).—The formation of the helide $HgHe_{10}$ previously reported (A., 1925, ii, 57, 314, 696) is confirmed; in addition, a second helide, HgHe, has now been obtained. This compound also is not

liquefied at the temperature of liquid air, and is not absorbed by charcoal. Experiments with argon were negative. A. A. ELDRIDGE.

Action of mercurous nitrate on chloroauric acid. W. B. POLLARD (J.C.S., 1926, 529—532).—In the presence of halides in sufficient amount to combine with the whole of the mercury the reaction is $HAuCl_4+3HgNO_3+2HCl=3HgCl_2+3HNO_3+Au$. In very dilute solutions the gold separates in the red, colloidal condition. In the absence of halides, the reaction is: $HAuCl_4+3HgNO_3=2HgCl_2+Hg(NO_3)_2+HNO_3+Au$. The mercuric nitrate formed reacts with more chloroauric acid, in presence of water, forming a brown basic gold compound and mercuric chloride. W. THOMAS.

Action of silica on metallic sulphates. (MLLE.) G. MARCHAL (Bull. Soc. chim., 1926, [iv], **39**, 401—408; cf. A., 1925, ii, 1162).—The reaction $MSO_4+SiO_2=MSiO_3+SO_2+0{\cdot}5O_2$, where M is Ca, Ba, or Mg, has been followed by measuring the equilibrium pressures at various temperatures. With calcium sulphate, the reaction commences at about 870°, and the pressure becomes 76 cm. at about 1270°. Barium sulphate commences to react at 1025°. The pressure–temperature curve for the reaction with magnesium sulphate runs nearly parallel to that for the thermal dissociation of the salt, but the reaction commences at 680° as compared with 880°. R. CUTHILL.

Influence of boric oxide on the properties of chemical and heat-resisting glasses. I. W. E. S. TURNER and F. WINKS.—See B., 1926, 238.

Optical glass. H. HEINRICHS and W. TEPOHL.—See B., 1926, 238.

Double decomposition between the halides of tin, arsenic, antimony, bismuth, silicon, and titanium. T. KARANTASSIS (Compt. rend., 1926, **182**, 699—701).—Preliminary experiments show that iodine combined with a metalloid is exchanged for bromine or chlorine in combination with a more metallic element. The reaction is complete only when the other halogen (bromine or chlorine) is in combination with a metal. W. THOMAS.

Hydronitric acid [azoimide] as desolvation product of "ammononitric," "hydrazonitrous," and "ammonohydrazonitrous" acids. Experimental formation of sodium azide by ammonolysis of sodium nitrate with sodamide. A. W. BROWNE and F. WILCOXON (J. Amer. Chem. Soc., 1926, **48**, 682—690).—By regarding azoimide as hydrazonitrous acid [obtained by the "hydrazinolysis" of nitrous acid and derivable by "dehydrazination" of normal hydrazonitrous acid, $N(N_2H_3)_3 \longrightarrow HN_3+2N_2H_4$], or as ammonohydrazonitrous acid, it is shown that all the known methods of its formation or preparation involve initial "solvolysis" and ultimate "desolvation" of an oxy-acid of nitrogen belonging to the ammonia or hydrazine series, or both. Sodium nitrate is "ammonolysed" in contact with fused sodamide, $NaNO_3+3NaNH_2=NaN_3+3NaOH+NH_3$; a 65·7% yield of sodium azide was obtained at 175°. The initial yield is probably theoretical, but temperature elevation favours the decomposition of the sodium azide. S. K. TWEEDY.

Oxidation of ammonia. J. R. PARTINGTON (Nature, 1926, **117**, 590).—Andrussov's suggestion (Ber., 1926, **59**, 458) that nitroxyl, NOH, is an intermediate product in the oxidation of ammonia is criticised in that the formation of nitrous oxide, which has not been detected, would be anticipated. As an alternative hypothesis, the following series of reactions is postulated: (i) $NH_3+O_2=NH_3O_2$; (ii) $2NH_3O_2=2NH_2(OH)_2$; (iii) $2NH_2(OH)_2=N_2H_2(OH)_2+2H_2O$; (iv) $N_2H_2(OH)_2+O_2=N_2H_2O_3+H_2O$; (v) $N_2H_2O_3=2NO+H_2O$. A. A. ELDRIDGE.

Action of hydrogen and water on phosphorus at high temperature under pressure. V. IPATIEV and W. NIKOLAJEV (Ber., 1926, **59**, [*B*], 595—597).—Red or yellow phosphorus is converted by water at 238—360° and 57—360 atm. into phosphine and orthophosphoric acid, $4P_2+12H_2O=3H_3PO_4+5PH_3$. If hydrogen is also present, the proportion of orthophosphoric acid diminishes and that of phosphine increases. In presence of hydrogen and absence of water at temperatures not exceeding 360°, phosphine is produced. Crystalline, *purple phosphorus*, *d* 1·93, temperature of ignition 210°, is produced when phosphorus is heated for a short time with water at 248° and 48 atm. and the reaction is rapidly interrupted. Crystalline, black phosphorus, *d* 3·06, temperature of ignition about 500°, is obtained from phosphorus and water at 360—380° and at least 89 atm.; it appears to be formed by decomposition of phosphine primarily produced. H. WREN.

Bismuth compounds. I. B. HEPNER and A. LIKIERNIK (Arch. Pharm., 1926, **264**, 46—55).—Chiefly a review of complex bismuth compounds in the light of Werner's theories. Bismuth nitrate, $Bi(NO_3)_3,5H_2O$, decomposes at 75·5° and has a vapour pressure of 8·3 mm. at 15° (cf. Rutten, A., 1902, ii, 386). In a dry atmosphere, it loses $1{\cdot}25H_2O$ in 1·5 months, and $1{\cdot}75H_2O$ in 3 months, together with a little nitric acid. On a basis of these and various titrimetric measurements it is formulated as $\left[Bi\begin{matrix}(H_2O)_3\\NO_3\end{matrix}\right]\begin{matrix}NO_3{\cdot}OH_2\\NO_3{\cdot}OH_2\end{matrix}$. With this formula those of the mannitol, sorbitol, and glycerol compounds, *e.g.*, $\left[Bi\begin{matrix}\frac{1}{2}C_6H_{14}O_6\\NO_3\end{matrix}\right](NO_3)_2$ (cf. Vanino and Hartl, J. pr. Chem., 1916, [ii], **74**, 144; Vanino and Hauser, A., 1902, i, 8) agree. Bismuth nitrate dissolves in aqueous solutions of neutral salts, *e.g.*, ammonium nitrate, and there crystallises thence the *compound*

$$\left[Bi\begin{matrix}(NH_4NO_3)_3\\NO_3\end{matrix}\right](NO_3)_2.$$

Basic bismuth nitrate combines with dulcitol and mannitol (Vanino and Hauser, *loc. cit.*) to give compounds in which the $\cdot NO_3$ radicals are not ionisable. Rosenheim and Vogelsang's compound (A., 1906, i, 231) of bismuth nitrate and tartrate,

$$\left[Bi\begin{matrix}(H_2O)_3\\NO_3\end{matrix}\right]\begin{matrix}O_2C{\cdot}CH{\cdot}OH\\O_2C{\cdot}CH{\cdot}OH\end{matrix}+2H_2O,$$

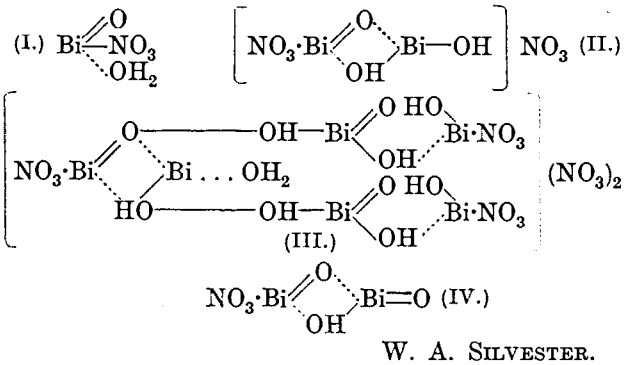
is converted by more tartaric acid into the compound

$\left[Bi\begin{matrix}(H_2O)_3\\C_4H_5O_6\end{matrix}\right]C_4H_4O_6$, and when this is dissolved in the appropriate amount of sodium hydroxide solution it yields a *sodium bismuth tartrate*,

$$\begin{matrix}CO_2Na\cdot CH\cdot OH \ldots . Bi\lessdot^{O}_{OH}\\ |\\ CO_2Na\cdot CH\cdot OH \ldots . Bi\lessdot^{O}_{OH}\end{matrix},$$

which readily crystallises, and is decomposed only in dilute aqueous solution. W. A. SILVESTER.

Bismuth compounds. II. B. HEPNER (Arch. Pharm., 1926, **264**, 55—65).—The constitution of the basic bismuth nitrates is discussed, with copious citation of the literature (cf. *e.g.*, Rutten, A., 1902, ii, 386). Four of the products obtained by treating bismuth nitrate with water have been again analysed, the nitrogen being determined by combustion, and the bismuth as oxide. The water was determined by difference, but determinations of vapour pressure were also made, and whether the $\cdot NO_3$ groups present were ionogenic or not was discovered by titrations with sodium hydroxide, and by the behaviour of the compounds when dried over sulphuric acid. The four compounds are represented by the annexed formulæ (I, II, III, IV). The compound (I) is the first product; it is obtained when bismuth nitrate (see preceding abstract) is treated with very dilute nitric acid; when it is treated with a little warm water, or when bismuth nitrate itself is melted, the compound (II) is produced. This yields with much warm water the compound (III), and finally, by boiling any of the foregoing with water (IV), is obtained.



W. A. SILVESTER.

Hydroxynitrosylselenic acid. J. MEYER and W. GULBINS (Ber., 1926, **59**, [*B*], 456—457).—The blue colour formed by the action of nitrogen tetroxide on 83% selenic acid (cf. Lenher and Matthews, A., 1906, ii, 349) is not due to the formation of di- or mono-nitrosylselenic acid (cf. Meyer and Wagner, A., 1922, ii, 372), but is attributed to decomposition of the tetroxide by water into nitrogen trioxide and nitric acid. When either sulphuric or selenic acid is used, the mixture separates into two layers, the upper of which contains nitric acid and nitrogen trioxide, whereas the lower contains nitrogen trioxide. Sulphuric or selenic acid is present in each layer, but chiefly in the lower one, which solidifies when sufficiently cooled and decomposes into colourless nitrosylsulphuric or nitrosylselenic acid and nitric oxide when gently warmed.

A blue *compound*, apparently analogous to hydroxynitrosylsulphuric acid (cf. Scandola, A., 1911, ii, 273), is prepared by the addition of mercury to a solution of nitrosylselenic acid in selenic acid monohydrate or by reducing a solution of sodium nitrite in concentrated selenic acid by mercury. The blue coloration is greatly deepened by addition of copper selenate. Hydroxynitrosylselenic acid is stable only in the presence of concentrated selenic acid; it is very readily oxidised. H. WREN.

Action of hydrogen fluoride on compounds of selenium and tellurium. II. Tellurium dioxide. E. B. R. PRIDEAUX and J. O'N. MILLOTT (J.C.S., 1926, 520—522).—Hydrogen fluoride in the form of vapour or liquid when brought into contact with tellurium dioxide forms a liquid which in a vacuum desiccator forms white crystals. These have the composition TeF_4,TeO_2,H_2O, which, although similar in appearance, is not the same as the product obtained by Metzner (Ann. Chim. Phys., 1898, **15**, 203). A method of determining fluoride in the presence of tellurite depends on the fact that in the titration of hydrofluoric acid, tellurous acid also present can be disregarded at the *p*-nitrophenol end-point. W. THOMAS.

Reaction between manganese and iron sulphide. C. H. HERTY, jun., and O. S. TRUE (Blast Furnace and Steel Plant, 1925, **13**, 492).—Experiments in which manganese or manganese sulphide was added to molten electrolytic iron in a zirconia crucible show that manganese sulphide even with an excess of manganese forms ferrous sulphide. The reaction $Mn+FeS=MnS+Fe$ is reversible; as the concentration of manganese is raised, the ratio (MnS)metal/(FeS)metal must increase.

CHEMICAL ABSTRACTS.

Acid salts of the chloropentamminocobaltic radical. A. BENRATH (Z. anorg. Chem., 1926, **151**, 343—348; cf. A., 1924, ii, 557).—The solubilities of salts of the above radical in solutions of acids and salts have been measured. The results give no indication of the formation by the chloride of complex compounds with potassium chloride or hydrogen chloride, but the existence of Jörgensen's compounds,

$[Co(NH_3)_5Cl](SO_4)$, $[Co(NH_3)_5Cl](SO_4),2H_2O$,
$[Co(NH_3)_5Cl]_4(SO_4)_4,3H_2SO_4$, and
$[Co(NH_3)_5Cl]Cl_2,3HgCl_2$

(A., 1879, 597), has been confirmed. No compound with the formula $[Co(NH_3)_5Cl]_2(SO_4)_2,H_2SO_4$ (Biltz and Alefeld, A., 1906, ii, 859) has been obtained.

R. CUTHILL.

Preparation of *cis*-dinitrotetramminecobalt nitrite and some derivatives. C. DUVAL (Compt. rend., 1926, **182**, 636—637).—By passing air through an ammoniacal solution of cobalt acetate, sodium nitrite, and ammonium carbonate, cobaltitrinitrotriammine and cis-*dinitrotetramminecobalt nitrite* are formed. The last-named forms other salts when treated with the appropriate acids. The nitrite yields cis-*dichlorotetramminecobalt chloride* when treated with concentrated hydrochloric acid at −10°, and nitropentamminecobalt nitrite when treated with sodium nitrite. L. F. HEWITT.

Preparation of cyanogen. B. RICCA (Annali Chim. Appl., 1926, **16**, 83—88).—In Jacquemin's method of formation, from solutions of potassium cyanide and copper sulphate, a large quantity (30%) of carbon dioxide is formed at the same time, and the yield of cyanogen is only 60—65%. The carbon dioxide is not derived from impurities in the cyanide used, as is commonly stated, but by the oxidising action of the copper sulphate on the cyanide. Using potassium cyanide specially purified by alcohol, with carbon dioxide less than 2%, the gas collected had the composition : C_2N_2 62%, HCN 3%, CO_2 30%, air 5%. The gas was analysed by careful absorption in dilute sodium hydroxide solution and subsequent determination of the cyanide by Liebig's silver method and of the cyanate by hydrolysis with dilute acid to ammonia. It is not possible to remove the carbon dioxide easily without polymerising the cyanogen, hence this method of preparation is not convenient if a good yield of pure gas is required.

S. B. TALLANTYRE.

Preservation of gaseous cyanogen. B. RICCA (Annali Chim. Appl., 1926, **16**, 89—92).—Cyanogen is best collected over a saturated solution of sodium sulphate or sodium chloride containing 10 c.c. of hydrochloric acid per litre, since with neutral or alkaline solutions decomposition occurs, as shown by the formation of brown flocks. The solubility of the gas in the salt solutions is practically negligible. The pure cyanogen gas is preferably prepared (cf. preceding abstract) by heating mercuric cyanide, without the usual admixture of calomel, as any mercury vapour is absorbed by the salt solution. The gas (97—98·5% pure) is colourless and unaltered by light, and there is no reaction at the surface of the solution. Hydrocyanic acid was absent, and only a very small amount of carbon dioxide was present. The gas was unaltered after keeping for 2 weeks. S. B. TALLANTYRE.

Rare earths. XXII. Preparation and properties of metallic yttrium. A. P. THOMPSON, W. B. HOLTON, and H. C. KREMERS (Trans. Amer. Electrochem. Soc., 1926, **49**, 161—170; cf. A., 1925, ii, 588).—Metallic yttrium was prepared by the electrolysis of the fused chloride mixed with small amounts of sodium chloride. Graphite cells acting as cathodes, and graphite anodes were used, the metal being usually obtained as powder, but sometimes in coherent form. The powder would not coalesce on fusion. Yttrium is bright, lustrous, highly crystalline, and not malleable; d^{15} 4·57. The coherent mass is brittle and shows a bright crystalline fracture which tarnishes only after several days' exposure to air. Hot water has a slight action, but cold water has little effect on the metal, which is not affected by aqueous solutions of alkalis, although readily attacked by acids. It is not pyrophoric in air, although a vigorous reducing agent at high temperatures. The kindling temperatures in air, oxygen, and chlorine are 470°, 400°, and 200°, respectively, but vary to some extent with the fineness of division. The m. p. is probably between 1450° and 1500°. W. HUME-ROTHERY.

[Preparation of] stable solutions of unstable halogen compounds of heavy metals. H. TRUTTWIN.—See B., 1926, 237.

[Preparation of] metallic uranium. J. F. GOGGIN, J. J. CRONIN, H. C. FOGG, and C. JAMES.—See B., 1926, 244.

Qualitative [micro-]analysis. Micro-crystalloscopy. G. DENIGÈS (Mikrochem., 1926, **4**, 1—13).—A review showing how micro-crystalloscopy can be adapted to the detection of fractions of a mg. of a substance either alone or in admixture. Characteristic crystals which serve for the identification of the substance may be obtained by five methods, viz., extraction with suitable solvents and evaporation of the solvent, addition of suitable reagents to the solution to obtain crystalline compounds, action of reagents on insoluble compounds, sublimation, and, finally, crystallisation from fused salts, *e.g.*, the microcosmic salt or borax bead tests. Examples are given of the use of all these methods in their various modifications for identifying inorganic and organic compounds. A. R. POWELL.

Determination of perchloric acid. O. LOEBICH (Z. anal. Chem., 1926, **68**, 34—36).—A quantity of the substance containing about 0·1 g. of perchloric acid is dissolved in 60 c.c. of water, 1 c.c. of 2*N*-sulphuric acid is added, and the solution heated to boiling. Ten c.c. of a solution of 10 g. of " nitron " and 5 g. of glacial acetic acid in 85 c.c. of water are added and the mixture is placed in an ice chamber for 2—3 hrs. The precipitated " nitron " perchlorate is collected in a glass crucible with a porous glass bottom, washed rapidly 6 or 7 times with a small amount of ice-cold water, dried at 110°, and weighed. A. R. POWELL.

Determination of perchloric acid in organic perchlorates. F. ARNDT and P. NACHTWEY (Ber., 1926, **59**, [*B*], 446—448).—The organic perchlorate is treated with a large excess of a freshly-filtered solution of potassium acetate in absolute alcohol, saturated at the atmospheric temperature. The mixture is maintained at incipient ebullition for 15 min. and then at the atmospheric temperature for 1 hr., after which the precipitated potassium perchlorate is filtered off, washed with absolute alcohol, dried at 120°, and weighed. The success of the method depends on the solubility of the organic component of the perchlorate (or of its acetate or other transformation product) in alcohol. If this condition is not fulfilled, the precipitate is washed with chloroform or other suitable solvent.

The following m. p. have not been recorded previously : aniline perchlorate, decomp. above 180°; distyryl ketone perchlorate, m. p. 145—150° (decomp.); 1-phenylpyridone perchlorate, m. p. 164° after softening at 158°; 4-methoxy-2 : 6-dimethylpyroxonium perchlorate, m. p. 195—196° after softening at 192°. H. WREN.

Determination of perchlorate in Chile saltpetre. K. A. HOFMANN, F. HARTMANN, and U. HOFMANN.—See B., 1926, 292.

Hydrazine sulphate as a standardising reagent for iodine solutions. E. CATTELAIN (Ann. Falsif., 1926, **19**, 145—148).—Since hydrazine sulphate is readily obtained in the pure state and is quantitatively oxidised by iodine to hydriodic acid and

nitrogen, it forms a suitable standardising reagent for iodine solutions. D. G. HEWER.

Electrometric titration of oxidising acids. L. MALAPRADE (Bull. Soc. chim., 1926, [iv], **39**, 325—336).—A platinum electrode, coated electrolytically with gold, is suitable for the titration of oxidising acids. The *E.M.F.* is a linear function of the p_H value of the acid, but varies with different acids owing to the effect of the oxidising agent on the equilibrium of the reaction $O_2 \leftrightharpoons 2O'' + 4(+)$. The results are not reproducible with different electrodes. When chromic acid is titrated with sodium hydroxide, the potential curves obtained with the above electrode show sharp points of inflexion at the compositions of the salts $Na_2Cr_2O_7$ and Na_2CrO_4. With iodic acid, a single point of inflexion is shown at the composition $NaIO_3$, whilst with periodic acid the salts H_4NaIO_6 and $H_3Na_2IO_6$ are shown, but there is no indication of the salt $H_2Na_3IO_6$, showing that the last-named, whilst possibly existing, is extensively hydrolysed. When mixtures of iodic and periodic acids are titrated, two points of inflexion are found, the first corresponding with $H_4NaIO_6 + NaIO_3$, and the second with $H_3Na_2IO_6 + NaIO_3$. If n_1 and n_2 are the corresponding volumes of alkali which have been added, then $n_2 - n_1$ represents the H_5IO_6, and $2n_2 - n_1$ represents the HIO_3. When sensitised with traces of an oxidising acid, the gold-coated platinum electrode will also behave as an oxygen electrode in solutions of non-oxidising acids. In no case, however, does such an electrode give the true p_H value.
W. HUME-ROTHERY.

Detection of oxygen. A. H. MAUDE.—See B., 1926, 274.

Precipitation of tellurium from alkali sulphide solutions and its separation from heavy metals and from selenium. A. BRUKL and W. MAXYMOWICZ (Z. anal. Chem., 1926, **68**, 14—22).—Addition of sodium sulphite to solutions of tellurium in alkali sulphides results in complete precipitation of elementary tellurium after boiling for some time. Before treating solutions containing tellurium and heavy metals with hydrogen sulphide, the lead should be removed by evaporation with sulphuric acid and the bismuth by neutralising with sodium carbonate and boiling with a mixture of potassium bromide and bromate. Mercury is separated from tellurium by dissolving the mixed sulphides in sodium sulphide and hydroxide and boiling with ammonium chloride. Tellurium is separated from gold, copper, and selenium by treating the solution of the sulpho-salts with potassium cyanide and boiling with sodium sulphite. The precipitate is collected, dried at 110° in an atmosphere of nitrogen to prevent oxidation, and weighed as tellurium.
A. R. POWELL.

Determination of hydrogen cyanide in gaseous mixtures. G. E. SEIL.—See B., 1926, 271.

Determination of the strength of liquid hydrocyanic acid by specific gravity. M. WALKER and C. J. MARVIN.—See B., 1926, 271.

Use of powdered copper in analytical chemistry. [Determination of nitrogen, nitrate, chlorate, and perchlorate.] K. KÜRSCHNER and K. SCHARRER (Z. anal. Chem., 1926, **68**, 1—14).—Fuller experimental details are given of the modified Kjeldahl method previously described for determining the nitrogen content of organic compounds and nitrates, using copper powder in the sulphuric acid treatment (cf. B., 1926, 155). Chlorates and perchlorates may be reduced to chlorides by mixing them with at least ten times their weight of sodium nitrate, fusing the mixture in a nickel crucible, and dropping in 5—10 g. of copper powder a little at a time. The fused mass is leached with water and the chloride in solution determined as silver chloride in the usual way. A. R. POWELL.

Colorimetric determination of hydroxylamine. G. W. PUCHER and H. A. DAY (J. Amer. Chem. Soc., 1926, **48**, 672—676).—The neutral or slightly acid solution, containing 0·8—3·5 mg. of hydroxylamine in 4 c.c., is treated with 2 drops of benzoyl chloride, 4 c.c. of alcohol, and 2 c.c. of 2% (approx.) sodium acetate trihydrate solution. After shaking for 20—30 sec. and keeping for 2—3 min., 2 c.c. of ferric chloride solution (0·5 g. of the chloride and 2 c.c. of concentrated hydrochloric acid in 100 c.c.) are added; the whole is made up to 25 or 50 c.c. and compared with a standard in a colorimeter (cf. Bamberger, A., 1899, ii, 576). Temperatures up to 60° have no influence after development of the colour. The presence of a large excess of dextrose is immaterial at the ordinary temperature. S. K. TWEEDY.

Determination of phosphorous and hypophosphorous acids and calcium hypophosphite by oxidation with potassium permanganate. L. ZIVY (Bull. Soc. chim., 1926, [iv], **39**, 496—500).—The method of Gailhat (A., 1901, ii, 420) gives satisfactory results provided that, in effecting the oxidation, the mixture is boiled for not less than 25 min.
R. CUTHILL.

Determination of arsenic in organic compounds. H. TER MEULEN (Rec. trav. chim., 1926, **45**, 364—367).—An apparatus is described in which arsenic is removed from the sample in a stream of hydrogen as arsenious oxide, this being subsequently decomposed by heat, and the arsenic deposited in a tube which may be detached and weighed. In order to ensure that no arsenic is lost, a roll of platinum foil is inserted in the end of the collecting tube, and kept at red heat during the analysis. With certain organic compounds the tube must be washed with petroleum, whilst, in the presence of a metal, the sample is mixed with an equal volume of potassium hydrogen sulphate. The maximum error was 0·2%. J. GRANT.

Relative rates of certain ionic reactions. [Determination of arsenic acid.] A. W. FRANCIS (J. Amer. Chem. Soc., 1926, **48**, 655—672).—The relative rates of oxidation by bromine of ten inorganic reducing agents in aqueous solution were measured by making these oxidations compete with certain irreversible organic bromination or additive reactions. The ratios between the rates of the inorganic and the organic reactions are practically independent of

temperature and concentration. The reactivity of a solute reaches a maximum when the latter is present in a saturated solution; the reactivity increases when the solubility is decreased (*e.g.*, by the addition of another liquid). Reactivity is thus closely connected with thermodynamic activity. The high reactivity of certain compounds, inexplicable on grounds of chemical constitution, is partly explained with the aid of this principle. The velocity constants for the oxidation of the inorganic compounds vary between 10^4 and 10^8; sodium thiosulphate reacts more quickly with iodine than does sodium hydrogen sulphite. Arsenic acid may be determined by boiling with excess of standard titanous chloride solution in an atmosphere of carbon dioxide and titrating back with ferric alum solution. S. K. TWEEDY.

Determination of small quantities of potassium. M. DELAVILLE and P. CARLIER (Compt. rend., 1926, **182**, 701—703).—The method consists in the precipitation of the cobaltinitrite and the determination of the cobalt in the precipitate by means of nitroso-β-naphthol. Details of the micro-method are given. W. THOMAS.

Determination of potassium. M. WIKUL (Z. anorg. Chem., 1926, **151**, 338—342).—The potassium is precipitated from hot solution in presence of considerable amounts of sodium chloride by means of sodium cobaltinitrite, in the preparation of which tartaric acid has been substituted for the usual acetic acid. From the weight of the precipitate, which is a complex adsorption compound, the weight of potassium is obtained by multiplying by the empirical factor 0·1598. R. CUTHILL.

Determination of potassium by the cobaltinitrite method. L. LE BOUCHER (Anal. Fis. Quím., 1925, **23**, 540—550).—In order to obtain a precipitate of constant composition in the cobaltinitrite method for the determination of potassium, the cobaltinitrite reagent must be added drop by drop with continual agitation, which should be continued for half an hour after precipitation. After keeping over-night, the precipitate is filtered in a Gooch crucible, and washed with dilute acetic acid, ensuring that there is always some liquid in the crucible. After washing finally with 95% ethyl alcohol, the precipitate is dried in a current of dry air at 100—110°, and weighed. The composition of the precipitate corresponds with the formula $NaK_2Co(NO_2)_6,H_2O$. G. W. ROBINSON.

Determination of silver in lead. B. S. EVANS. See B., 1926, 278.

Determination of small amounts of silver in the presence of lead. E. DONATH (Chem.-Ztg., 1926, **50**, 222).—In order to separate a few mg. of silver from a large amount of lead, the nitrate solution of the metals is treated with 4—5 c.c. of glycerol, ammonia in excess, and 10—15 c.c. of a concentrated solution of sodium hydroxide. The mixture is boiled for a short time and allowed to cool completely, and the precipitate of metallic silver is collected, washed in succession with hot water, dilute acetic acid, and hot water again, dried, ignited, and weighed. The method is available also in the presence of copper, which is retained in solution by the glycerol. A. R. POWELL.

"Citarin" as a quantitative reagent. L. VANINO and O. GUYOT (Arch. Pharm., 1926, **264**, 98—99).—The sodium salt of anhydromethylenecitric acid ("citarin"), already used for preparing colloidal solutions of metals (Vanino, A., 1917, ii, 299), can also be used for the quantitative precipitation of silver and gold. The "citarin" liberates formaldehyde in hot alkaline aqueous solution and the reduction of silver nitrate or of gold chloride to the free metal takes place as with formaldehyde itself. W. A. SILVESTER.

Determination of calcium by conversion of the oxalate into carbonate. H. W. FOOTE and W. M. BRADLEY (J. Amer. Chem. Soc., 1926, **48**, 676—678).—Calcium oxalate is rapidly and quantitatively converted into the carbonate by heating in a current of dry carbon dioxide at 675—800°. This treatment enables calcium oxalate precipitates to be filtered in Gooch crucibles. S. K. TWEEDY.

Precipitation of magnesium with aluminium hydroxide. A. LASSIEUR (Ann. Chim. analyt., 1926, [ii], **8**, 97—98).—See this vol., 376.

Compounds of diphenylthiocarbazone with metals and their use in analysis. H. FISCHER (Wiss. Veröff. Siemens-Konz., 1925, **4**, 158—170).—Diphenylthiocarbazone (Fischer, A., 1878, 302; 1882, 1091) forms highly-coloured compounds with zinc, cadmium, copper, nickel, cobalt, manganese, lead, mercury, and silver, which are obtained as red, brown, or purple precipitates when its solution in alkali is added to a solution of a salt of the respective metal made alkaline with ammonia. No such compound is obtained with salts of iron, aluminium, chromium, or tin. With the exception of the mercurous and silver compounds, they are all soluble in chloroform and carbon disulphide. Sensitive and characteristic reactions for zinc and copper are based on the colours imparted by solutions of their salts to the green solution of diphenylthiocarbazone in carbon disulphide when the two are shaken together. Manganese and lead give a reaction similar to that of zinc, but are differentiated by adding a cobalt salt, which changes the colour, but not with zinc. Copper, mercury, silver, tin, and bismuth interfere with the zinc reaction and must be removed. The reaction for copper is unaffected by ammonia or tartrates, but is prevented by an excess of potassium cyanide. Somewhat less characteristic reactions are described for mercury, lead, cadmium, and cobalt. Zinc may be accurately determined gravimetrically by precipitating a cold solution containing 25% of acetic acid with a 3% solution of diphenylthiocarbazone in 10% ammonia, filtering, and finally weighing after ignition as zinc oxide. The method allows of an exact separation of zinc from manganese, precipitation being conducted as before in a solution containing not more than 0·05 g. of zinc per 100 c.c. G. M. BENNETT.

Determination of cadmium in copper. C. BLAZEY (Chem. Eng. Min. Rev., 1925, **17**, 502—503).—When copper is heated in hydrogen for several

hours, all the cadmium is volatilised; the condensed material is analysed. CHEMICAL ABSTRACTS.

Determination of copper, arsenic, and mercury. R. ROSENDAHL.—See B., 1926, 243.

Determination of mercury as metal in its organic and inorganic compounds. H. TER MEULEN (Rec. trav. chim., 1926, **45**, 368—370; cf. this vol., 490).—An apparatus and procedure are described similar to that used in the determination of arsenic. The sample is mixed with sodium sulphide and heated, the mercury being removed as mercuric sulphide in a current of hydrogen. It is subsequently reduced by heat, and the mercury deposited in a cooled, weighed U-tube. The sodium sulphide is omitted when sulphides or chlorides of mercury are being analysed. A maximum deviation of 0·3% from the theoretical mercury content is recorded. J. GRANT.

Determination of cerium in special steels. K. SWOBODA and R. HORNY.—See B., 1926, 242.

Rational analysis of clay. II. J. S. MCDOWELL.—See B., 1926, 240.

Use of pyrophosphates in micro-analysis. [Determination of manganese, zinc, and cobalt.] R. STREBINGER and J. POLLAK (Mikrochem., 1926, **4**, 15—18).—For the precipitation of manganese as the double ammonium phosphate in micro-analysis, 1—2 c.c. of the solution are neutralised with ammonia, and the solution is heated at 80° on a water-bath, treated with 2 c.c. of a 5% solution of diammonium hydrogen phosphate, stirred for 10 min. with a current of air to render the precipitate coarsely crystalline, cooled in water, and filtered through a Neubauer crucible. The precipitate is washed with a 1% ammonium nitrate solution and alcohol alternately, dried, and ignited to manganese pyrophosphate in an electric muffle. Zinc is determined in a similar way, except that the original solution is ammoniacal before adding the reagent and is subsequently made neutral to litmus with 0·02*N*-hydrochloric acid. To obtain a pink, crystalline deposit of cobalt ammonium phosphate on a micro-scale, the hot neutral solution is treated drop by drop with an equal volume of a hot 5% solution of diammonium hydrogen phosphate while a stream of air is being passed through the liquid. The precipitate is subsequently washed alternately with a 1% ammonium nitrate solution and 50% alcohol. A. R. POWELL.

Action of aliphatic and cyclic bases on salts of the metals. E. J. FISCHER (Wiss. Veröff. Siemens-Konz., 1925, **4**, 171—187).—Qualitative observations are recorded of the precipitates produced in solutions of the heavy metals by thirty-six different bases, including many primary, secondary, and tertiary aliphatic amines, quaternary ammonium bases, a sulphonium base, and a variety of heterocyclic nitrogen bases such as pyridines, piperazine, nicotine, glyoxaline, benziminazole, dimethylpyrazole, antipyrine, and urazole. Glyoxaline is recommended as a delicate reagent for cobalt, with which it yields a violet-blue precipitate. Possible applications of the results to the separation of various metals are discussed. G. M. BENNETT.

Volumetric determination of chromium and manganese by titration with permanganate in acetic acid solution. I. Chromium. B. REINITZER and P. CONRATH (Z. anal. Chem., 1926, **68**, 81—114).—In boiling solutions containing much sodium acetate and a little free acetic acid chromium salts are quantitatively oxidised to chromic acid by permanganate according to the equation:

$$Cr_2O_3+Mn_2O_7=2CrO_3+2MnO_2.$$

In order to get a good end-point, a barium salt must be added to the solution to precipitate the chromic acid as fast as it is formed. Chlorides do not interfere unless much iron is also present, but iron alone up to twenty times the weight of chromium does not affect the results. Manganese is quantitatively converted into dioxide in the process, so that, if present, it will be determined together with the chromium, but can be allowed for, if small, by determining it colorimetrically in the usual way. To determine chromium in ferro-alloys and steel containing more than 5% of Cr and only 0—0·3% of Mn, the metal is dissolved in the minimum quantity of dilute sulphuric acid, the iron oxidised with nitric acid, and the solution neutralised with sodium carbonate. An aliquot part is then treated with 7 g. of sodium acetate, diluted to 100—200 c.c., heated to boiling, treated with an excess of barium chloride, and titrated directly with 0·1*N*-permanganate, as in the Volhard method for manganese. If the steel contains less than 5% of Cr, it is dissolved in hydrochloric acid and the solution neutralised (without oxidising the iron) with sodium carbonate and agitated with finely-divided barium carbonate for 15 min. by passing a rapid current of air through the liquid. Chromium is completely precipitated as hydroxide, whilst the manganese and most of the iron remain in solution. The precipitate is dissolved in hydrochloric acid, the remaining iron oxidised, and the analysis finished as described above.

A. R. POWELL.

Determination of vanadium in ferrovanadium. K. SOMEYA.—See B., 1926, 278.

Separation of tantalum and niobium. G. W. SEARS.—See B., 1926, 282.

Benzoylmethylglyoxime as a precipitant of palladous salts. J. HANUŠ, A. JILEK, and J. LUKAS (Chem. Listy, 1926, **20**, 68—72, 133—137).—See this vol., 141.

Micro-burner. R. STREBINGER (Mikrochem., 1926, **4**, 14).—The jet of the burner consists of two concentric tubes, the inner tube having a relatively thick wall, so that the orifice is small. By means of a cock, the gas stream can be directed through the central jet or through the annular space between the two tubes to give a small, circular flame. A second stopcock serves to regulate the volume of gas supplied to the burner. A. R. POWELL.

Simple gas generator. J. CAMPARDOU (Bull. Soc. chim., 1926, [iv], **39**, 337—340).—A description of a simple generator working on the displacement system and suitable for the production of hydrogen, hydrogen sulphide, carbon dioxide, etc.

W. HUME-ROTHERY.

Sorption balance. J. W. McBain and A. M. Bakr (J. Amer. Chem. Soc., 1926, **48**, 690—695).—The balance consists of a delicate silica spring supporting a receptacle containing the adsorbent and enclosed in an evacuated sealed tube, which contains a bulb of the liquid being studied and a piece of iron. The tube is surrounded by an electric furnace. The bulb is broken by the application of a magnet to the iron. The balance is calibrated for a series of temperatures by observing microscopically the extensions produced by known weights (up to 0·6 g.) in the receptacle. The error in the determination of the ratio of the weight of sorbed substance to that of the sorbent is between 0·15 and 0·75%. Possible applications of the balance are mentioned (cf. Nature, 1925, **116**, 14). S. K. Tweedy.

Distillation of mercury containing gold. A. Miethe and H. Stammreich (Ber., 1926, **59**, [*B*], 359—362).—A reply to Riesenfeld and Haase (this vol., 264). Wetzel's apparatus as used by Riesenfeld and Haase affords only a limited protection against "pseudodistillation" of gold with the mercury. The second form of apparatus appears more satisfactory, but it is pointed out that the weight of gold found in the distillate lies within the experimental error of the balance used and that proof is not adduced that the residue actually consists of gold. In any case, the results have no bearing on the observations of Miethe and Stammreich, who used gold-free mercury in their experiments. H. Wren.

Photometric and spectrophotometric studies. V. Tube photometer for ultra-violet spectrophotometry. K. Schaum and H. M. Kellner (Z. wiss. Phot., 1926, **24**, 85—90).—A tube photometer with quartz optical parts for use in conjunction with a large Steinheil quartz spectrograph is described in detail, and the method of use is discussed. Intensity in the comparison beam is varied by means of diaphragms. The light source is a high-frequency aluminium spark under water, arranged to illuminate both tubes of the photometer equally. Data are given of measurements made of the absorption spectra of potassium nitrate and sucrose. The measurements on the former agree with those of Glatzel (Physikal. Z., 1899, **1**, 173). W. Clark.

Ultra-violet filter. C. Winther and E. H. Mynster (Z. wiss. Phot., 1926, **24**, 90—96).—A simple ultra-violet filter is described, and full transmission data of its components are given. The filter is suitable for demonstration purposes and for the study of luminescence, and consists of 1 cm. of a 2·6% solution of copper sulphate with six times the quantity of ammonia necessary to redissolve the precipitate, combined with 1 cm. of 0·045% diamond-fuchsine in water. The maximum transmissivity is at 375 μμ, and the range extends from about 405 to 320 μμ. In another filter, the dye is replaced by a 0·1215% solution of potassium chromate, the maximum transmission in this case being at 313 μμ. With increasing excess of ammonia, copper sulphate solution becomes more transparent, especially in the ultra-violet; the maximum transparency is attained when the ammonia present is four times the quantity necessary to redissolve the precipitated copper hydroxide, and then extends from about 450 to 300 μμ. This solution is suitable for a standard light source for photographic sensitometry. W. Clark.

Production of copper mirrors on glass. K. Bamberger and R. Schweizer.—See B., 1926, 241.

New notation. R. Saxon (Chem. News, 1926, **132**, 197—203).—An attempt to augment the information conveyed by ordinary chemical symbols by means of signs used in conjunction therewith. A. A. Eldridge.

Use of subscript and superscript exponents in chemistry. E. Q. Adams (J. Amer. Chem. Soc., 1926, **48**, 708—709).—It is proposed to use a superscript exponent in chemistry to denote the repetition of a symbol (*e.g.*, H^2O for HHO), and a subscript exponent to designate the separate members of a series of related substances (*e.g.*, Li_6 and Li_7 to represent the two isotopes of lithium). This is in accordance with usual algebraic practice. S. K. Tweedy.

Anticipation of modern physico-chemical views. E. O. von Lippmann (Z. physikal. Chem., 1926, **119**, 275—276).—An appreciation of the views expressed in R. Grassmann's "Das Weltleben oder die Metaphysik" (Stettin, 1881). L. F. Gilbert.

Mineralogical Chemistry.

Ozone in the earth's atmosphere and its relation to other geophysical conditions. G. M. B. Dobson and D. N. Harrison (Proc. Roy. Soc., 1926, **A**, **110**, 660—693; cf. this vol., 140).—Details are given of the apparatus and method for determining the ozone content of the atmosphere by measuring the absorption coefficient in the region of the ultra-violet absorption band of ozone (3000—3300 Å.). In a long method, the actual atmospheric absorption coefficients for a number of wave-lengths are determined by making observations at various altitudes of the sun. This requires a number of photographs and is impracticable for routine observations in a cloudy climate. In a short method, the intensities of two wave-lengths near the edge of the absorption band are measured on a single photograph, and it is assumed that the ratio of the intensities of these wave-lengths as emitted by the sun remains constant. In order to avoid fogging of the plates by scattered light, it is necessary to cut out light of wave-lengths not used, and this is effectively done by a tube containing gaseous chlorine and bromine. The chief source of error in the determinations is change in the atmosphere; any error due to absorption of the wave-lengths used by gases other than ozone is small. It is estimated that the probable error of a single determination is not more than the amount that would form a layer on the earth's surface 0·005 cm.

thick at *N.T.P.*, excluding systematic errors. Data are given for each day in 1925 when observation was possible. There is a close relation between the amount of ozone and the barometric pressure at the earth's surface, although it is probable that the ozone is situated above the troposphere. The amount of ozone is greatest when the pressure is lowest and *vice versa*, but the ozone variations appear to lag a few days behind those of pressure. The ozone content is greatest in the spring and least in the late autumn, and it is known that the ultra-violet light reaching the earth is a minimum in April and a maximum in December. High sun-spot numbers are associated with low ozone values. It is probable that ozone is formed at heights above 40 km. by ultra-violet light from the sun or by electric discharges in the aurora, but the correlation with surface pressure indicates that it must afterwards sink to much lower levels. A. GEAKE.

Atmospheric ozone and terrestrial magnetism. C. CHREE (Proc. Roy. Soc., 1926, **A**, **110**, 693—699).—The ozone content of the atmosphere, as determined by Dobson and Harrison (see preceding abstract), is related to the magnetic character figure, the ozone content being greater the greater the magnetic disturbance. A. GEAKE.

Condensation of water from the air on hygroscopic crystals. J. S. OWENS (Proc. Roy. Soc., 1926, **A**, **110**, 738—752).—Deliquescence of small crystals of pure or mixed salts commences under definite conditions of temperature and humidity, depending on the vapour pressure of the saturated solution at the temperature concerned. By observations with a microscope of crystals derived from atmospheric dust, the conditions when deliquescence commences may be determined, and some information is thus obtained as to the nature of the salt, when the amount is too small for micro-chemical or crystallographic examination. Natural variations of humidity and temperature were usually relied on, but the crystals may also be enclosed in a small, air-tight cell over the saturated solution of a pure salt. Crystals obtained from atmospheric dust are usually impure, and this greatly increases the difficulty of interpreting the results; the conditions under which a haze of solid particles would be converted into a fog of liquid drops may, however, be determined. A. GEAKE.

Nomenclature of the banded constituents of coal. C. A. SEYLER (Nature, 1926, **117**, 486).—A comparison of the nomenclature due respectively to Stopes and Thiessen. A. A. ELDRIDGE.

Volcanic rocks of Christmas Island (Indian Ocean). W. C. SMITH [with E. D. MOUNTAIN] (Quart. J. Geol. Soc., 1926, 82, 44—66).—Petrographical descriptions and seven detailed analyses are given of basaltic rocks. Plotting molecular percentages of the bases against those of silica, there is with increasing silica a decrease in magnesia, lime, and ferrous oxide, and an increase in alumina, soda, potash, and titania. L. J. SPENCER.

Chlorite as a polycomponent system. A. N. WINCHELL (Amer. J. Sci., 1926, [v], **11**, 283—300).—Tschermak's end-members $H_4Mg_3Si_2O_9$ (antigorite) and $H_4Mg_2Al_2SiO_9$ (amesite) are accepted with the addition of the corresponding iron compounds, $H_4Fe^{II}{}_3Si_2O_9$ (ferro-antigorite) and $H_4Fe^{III}{}_2Al_2SiO_9$ (daphnite), and in some cases small amounts of $H_4Fe^{II}{}_2Fe^{III}{}_2SiO_9$ (cronstedtite), $H_4Mg_2Fe^{III}{}_2SiO_9$ (magnesio-cronstedtite), and $H_4Mg_2Cr_2SiO_9$ (kämmererite). Published analyses are plotted on a square with the first four of these compounds at the corners, and also for six components on a triangular prism. The optical data plotted on the same square show a relation with the chemical composition. It is suggested that there may be a change in the state of oxidation of the iron in ferriferous chlorites without destroying the crystalline structure.

L. J. SPENCER.

Pickeringite from Portland, Connecticut. J. F. SCHAIRER and C. C. LAWSON (Amer. J. Sci., 1926, [v], **11**, 301—304).—Pickeringite as masses of minute white needles is now forming near the contact of pegmatite and schist in the Strickland quarry. The needles show an extinction-angle of 28°, very low birefringence, and refractive indices slightly above and below 1·485. Analysis gave SO_3 36·86, Al_2O_3 11·64, Fe_2O_3 0·24, MgO 4·16, MnO 1·02, CuO 0·17, NiO trace, H_2O 46·10, insol. 0·24, total 100·43, agreeing with the formula $MgSO_4,Al_2(SO_4)_3,22H_2O$. Published analyses of pickeringite plotted on a graph also indicate $22H_2O$, rather than $24H_2O$.

L. J. SPENCER.

Genesis of sulphide ores. H. FREEMAN (Eng. Min. J.-Press, 1925, **120**, 973—975).—The reactions of alkali sulphides with alkaline-earth and heavy metal sulphides explain the mode of formation of primary sulphide ore deposits and associated non-metallic minerals. The following m. p. were determined: lead sulphide, 1130°; ferrous sulphide, 1000°; zinc sulphide, 1650°; cuprous sulphide, 1100°; the compounds PbS,Na_2S, 650°; FeS,Na_2S, 660°; ZnS,Na_2S, 620°; Cu_2S,Na_2S, 560°. Alkaline-earth sulphates and carbonates originate from the sulphides. Colloidal silica is obtained from the compound Na_2S,SiO_2 by oxidation of the sodium sulphide.

CHEMICAL ABSTRACTS.

Alkali sulphides as collectors of metals. J. E. SPURR (Eng. Min. J.-Press, 1925, **120**, 975—977).—Water is not believed to have been the universal solvent of ore magmas; fluorine and boron were not the principal carriers. Formation of double sulphides of heavy metals with alkali metals, followed by hydrolysis and deposition of the heavy metal sulphides, is considered to be a possible explanation of the origin of sulphide ore deposits.

CHEMICAL ABSTRACTS.

Atomic weight of uranium lead and the age of an ancient uraninite. T. W. RICHARDS and L. P. HALL.—See this vol., 449.

Rock-lead, ore-lead, and the age of the earth. A. HOLMES.—See this vol., 449.

Radioactive manganiferous nodules from Tanokami, Japan. S. IIMORI (Bull. Chem. Soc. Japan, 1926, **1**, 43—47).—See this vol., 380.

Organic Chemistry.

ββ-Dimethylpentane and γ-methylhexane. H. DE GRAEFF (Bull. Soc. chim. Belg., 1926, **34**, 427—433).—ββ-Dimethyl-Δ$^{\gamma}$-pentinene, b. p. 82·9—83°/760 mm., d_4^{15} 0·7224, $n_D^{20\cdot1}$ 1·4071, is hydrogenated in the presence of platinum-black to ββ-dimethylpentane, b. p. 79·3°/760 mm., m. p. −137°, d_4^{16} 0·6780, $n_D^{20\cdot5}$ 1·3820, which closely resembles βδ-dimethylpentane. γ-Methylhexane, obtained by dehydration of methylethylpropylcarbinol by Wuyts' method and hydrogenation of the heptene fraction, b. p. 95·5—96°, d_4^{20} 0·7133, has b. p. 91·8°/760 mm., d_4^{15} 0·6909, $n_D^{20\cdot4}$ 1·3884, critical solution temperature in aniline, 70·5°. R. BRIGHTMAN.

Electronic interpretation of the ethylenic linking. H. GILMAN and J. M. PETERSON (J. Amer. Chem. Soc., 1926, **48**, 423—429; cf. A., 1923, i, 285).—A quantitative study has been made of the reaction between ethereal magnesium ethyl bromide and eighteen ethylenic compounds, as well as of that between αα-diphenylethylene and Grignard reagents containing magnesium attached to oxygen, sulphur, and nitrogen, and between diphenylethylene and zinc ethyl iodide. In no case was appreciable reaction observed which could be ascribed to addition of the Grignard reagent to the ethylenic linking. It is concluded that, under the conditions of experiment, active or polar forms of the ethylenic linking are absent or present only in very small concentration, or, if present, they are not sufficiently active to react additively with Grignard reagents. The electronic structure of the ethylenic linking is discussed, and a comprehensive bibliography appended. F. G. WILLSON.

Polymerisation and hydrogenation of ethylene by means of excited mercury atoms. A. R. OLSON and C. H. MEYERS.—See this vol., 364.

Synthesis of Δ$^{\alpha\beta}$-pentadiene. M. BOUIS (Compt. rend., 1926, **182**, 788—790).—When γ-hydroxy-Δ$^{\alpha}$-pentene is treated with phosphorus tribromide, *α-bromo-Δ$^{\beta}$-pentene*, b. p. 123—124°, d^{20} 1·2545, n_D^{20} 1·4731, is formed instead of the γ-bromo-isomeride. The α-bromo-compound on bromination forms αβγ-tribromopentane, and this, when treated with solid potassium hydroxide, gives *βγ-dibromo-Δ$^{\alpha}$-pentene*, b. p. 173° (partial decomp.), 75—76°/12 mm., d^{12} 1·7442, n_D^{19} 1·5316, which with zinc dust and alcohol yields *Δ$^{\alpha\beta}$-pentadiene*, b. p. 44—45°, d^{20} 0·6890, n_D^{20} 1·4149. With bromine, Δ$^{\alpha\beta}$-pentadiene forms *αββγ-tetrabromopentane*, b. p. 120°/3 mm., d^{22} 2·2839, n_D^{22} 1·5916. B. W. ANDERSON.

Identification of monosubstituted acetylenes. Derivatives of mercury diethinyl. J. R. JOHNSON and W. L. MCEWEN (J. Amer. Chem. Soc., 1926, **48**, 469—476).—Monosubstituted acetylene derivatives can be identified by their characteristic mercury derivatives, $(CR{:}C\cdot)_2Hg$, which are precipitated in crystalline form when alcoholic solutions of the hydrocarbons are added to aqueous alkaline mercuric iodide or cyanide. Mercury dipropinenyl has m. p. 203—204° (cf. Kutscheroff, A., 1883, 172). *Mercury di-*n*-butinenyl*, m. p. 162—163°, *mercury di-γγ-dimethylpentinenyl*, m. p. 91—92°, and *mercury di-*n*-heptinenyl*, m. p. 61°, are described. Treatment of magnesium *n*-heptyl bromide with βγ-dibromo-Δ$^{\alpha}$-propene affords *β-bromo-Δ$^{\alpha}$-decene*, b. p. 76—77°/3 mm., 115—116°/22 mm., d_4^{20} 1·0844, n_D^{20} 1·46290, which, on treatment with sodamide, affords the corresponding decinene (cf. Picon, A., 1919, i, 429) (*mercury* derivative, m. p. 83—84°). Mercury diphenylacetylenyl has m. p. 124·5—125° (cf. Nef, A., 1900, i, 20). Phenylpropiolanilide, m. p. 126—127° (cf. Stockhausen and Gattermann, A., 1892, i, 163), is obtained by condensing magnesium ethyl bromide with phenylacetylene and treating the reaction product with phenylcarbimide. *Mercury di-γ-phenyl-Δ-propinenyl* (cf. Lespieau, A., 1921, i, 656) has m. p. 106·5—107·5°. Condensation of magnesium benzyl chloride with βγ-dibromo-Δ$^{\alpha}$-propene affords *β-bromo-δ-phenyl-Δ$^{\alpha}$-butene*, b. p. 117—118°/21 mm., 77—78°/5 mm., d_4^{20} 1·2901, n_D^{20} 1·5450, which, when treated with a suspension of sodamide in liquid paraffin, yields δ-phenyl-Δ$^{\alpha}$-butinene (cf. André, A., 1913, i, 1065) (*mercury* derivative, m. p. 83·5—84·5°). *Mercury di-*p*-tolylacetylenyl*, m. p. 199—202°, *mercury di-*p*-anisylacetylenyl*, m. p. 207—209° (after darkening if heated slowly), *mercury dicyclohexylacetylenyl*, m. p. 104°, and *mercury di-γ-phenoxy-Δ$^{\alpha}$-propinenyl*, m. p. 120·5—121°, are described. F. G. WILLSON.

Producing chloro-derivatives of methane. S. KARPEN AND BROS.—See B., 1926, 253.

Mechanism of the action of bromine on the stereoisomeric *s*-dichloroethylenes. I. (MLLE.) D. VERHOOGEN (Bull. Soc. chim. Belg., 1926, **34**, 434—456; cf. *ibid.*, **33**, 249).—The results obtained by Chavanne (A., 1914, i, 1045) are confirmed, but the ratio of the reaction velocities of the two stereoisomeric forms of *s*-dichloroethylene and bromine is shown to depend directly on the oxygen present. Oxygen markedly retards the addition of bromine; in pure nitrogen the reaction constants for the *cis*- and *trans*-forms are approximately the same, and for the *cis*-isomeride about twice as great as in "crude" nitrogen from liquefied air; the reaction velocity in the latter case is twenty-five to thirty times as great as in air. In an atmosphere of carbon dioxide, the addition of bromine is about five times as rapid as in pure nitrogen, whilst in oxygen the reaction velocity is only one-fifth of that in air and the reaction constant for the *trans*- is double that for the *cis*-form. *s*-Dichlorodibromoethane is without influence on the reaction constant, and the nature of the influence exerted by hydrogen bromide has not been determined. Addition of substances of the "antioxygen" class, such as iodine and quinol, or the dichloroaldehyde resulting from the oxidation of *s*-dichloroethylene has no retarding influence on the addition of bromine either in air or in nitrogen. It is suggested that the formation of *s*-dichlorodibromoethane takes place in two stages, the first involving

the formation of an unstable molecular complex, and the second its rearrangement into the stable saturated compound. In this complex, the two ethylenic carbon atoms would be relatively mobile and in rearrangement would tend to yield the *cis*- rather than the *trans*-isomeride. The observations indicate that only a small number of the complex molecules undergo rearrangement to the stable ethane derivative, the majority dissociating into the halogen again, and it is concluded that the isomerisation of the *trans*-form is four times as rapid as that of the *cis*-form. The retarding influence of oxygen is attributed to a decrease in the number of active ethylene molecules produced by the formation of an unstable primary peroxide, which in an atmosphere of nitrogen or carbon dioxide tends to be destroyed by dissociation (cf. Bruner and Kozak, Bull. Acad. Sci. Cracovie, 1925, 211; 1920, 103).

R. BRIGHTMAN.

Stereoisomerides of chloroiodoethylene. H. VAN DE WALLE and A. HENNE (Bull. Soc. chim. Belg., 1925, **34**, 399—410; cf. A., 1921, i, 491).—Chloroiodoethylene prepared from acetylene and iodine monochloride (Plimpton, J.C.S., 1881, **41**, 392) is a mixture of two stereoisomerides which are separated by fractional distillation of their mixture with *n*-propyl alcohol. Two azeotropic mixtures are obtained from which the chloroiodoethylenes are recovered by dilution: *cis*, b. p. 116—117°, m. p. −36·4°, d_4^0 2·2399, d_4^{15} 2·2080, n_D 1·58288, dielectric constant, ε, 2·72, forming an azeotropic mixture, b. p. 93·6—94·0°, containing 44·4% of *n*-propyl alcohol; *trans*, b. p. 113—114°, m. p. −41·0°, d_4^0 2·1355, d_4^{15} 2·1048, n_D 1·57146, ε 2·95, forming an azeotropic mixture, b. p. 87·5—88·5°, containing 4% of *n*-propyl alcohol. The liquids are unstable to air and light. After 1 hr. of exposure to sunlight they revert to the equilibrium mixture containing 82·5% of the *cis*-isomeride, this being also the composition of the original crude mixture. The configurations are deduced from the fact that the *trans*-isomeride reacts 0·55 times as rapidly as the *cis* with alcoholic potassium hydroxide solution to yield chloroacetylene, the removal of hydrogen iodide being assumed to take place more readily in a *trans* sense. The molecular absorption coefficient for ultra-violet light is 10·400 for the *trans*- as compared with 7·000 for the *cis*-isomeride. The physical constants are reviewed in comparison with those of other halogenated ethylenes. The *cis*-compound is normal in having the higher b. p. and density and the lower molecular refraction of the two.

G. M. BENNETT.

Action of bromine on chloroiodoethylene. H. VAN DE WALLE and A. HENNE (Bull. Soc. chim. Belg., 1926, **35**, 29—38; cf. preceding abstract).—Bromination of chloroiodoethylene as described by Plimpton (J.C.S., 1881, **41**, 392) gives chlorobromoethylene in 13% yield together with α-chloro-αββ-tribromoethane, but if the reaction is conducted under water with careful cooling, the yield of chlorobromoethylene is 70%, which rises to 89% if alcohol be substituted for water. Under these controlled conditions, the chief by-product is *α-chloro-αβ-dibromo-β-iodoethane*, b. p. 75°/1 mm., 110°/10 mm., d_4^{15} 2·9858, solidifying at the temperature of solid carbon dioxide. This substance is best prepared by the addition of iodine monochloride to dibromoethylene, chlorobromoethylene and chlorotribromoethane being produced at the same time. The fact that the same three compounds are obtained in this reaction as in the bromination of chloroiodoethylene is due to the first step in each process being a simple addition to give the same product. This partly breaks down to give chlorobromoethylene, and some addition of free bromine to the latter also occurs. The effect of cooling in improving the yield of chlorobromoethylene is attributed to the decrease of this latter addition at low temperatures. This is confirmed by the observation that bromine and dichloroethylene do not react at the ordinary temperature, but the additive reaction occurs on warming.

A similar reaction occurs between iodine monochloride and dichloroethylene, which unite to give a 70% yield of trichloroiodoethane, b. p. 77°/9 mm., d_4^{15} 2·2760 (cf. Howell and Noyes, A., 1920, i, 469). This substance breaks down in a similar manner when distilled at the ordinary pressure, the products being dichloroethylene and tetrachloroethane, resulting from the addition of chlorine to it.

G. M. BENNETT.

Alcohols containing the trichloromethyl group. J. W. HOWARD (J. Amer. Chem. Soc. 1926, **48**, 774—775).—The following alcohols were prepared by condensing chloral with the requisite Grignard reagent: *trichloromethylethylcarbinol*, b. p. 99°/680 mm., d_{20}^{20} 1·488 (*acetate*, b. p. 164—165°/680 mm.; *benzoate*, b. p. 217—218°/680 mm.); *trichloromethylpropylcarbinol*, b. p. 115°/686 mm., d_{20}^{20} 1·481 (*acetate*, b. p. 168—169°/686 mm.; *benzoate*, b. p. 197—198°/686 mm.), and *trichloromethylbenzylcarbinol*, b. p. 97°/686 mm., d_{20}^{20} 1·365 (*acetate*, b. p. 159—160°/686 mm.; *benzoate*, b. p. 210—211°/680 mm.).

F. G. WILLSON.

Catalytic dehydration of alkylvinylcarbinols. C. PRÉVOST (Compt. rend., 1926, **182**, 853—855).—Ethylvinylcarbinol yields 60—70% of $\Delta^{\alpha\gamma}$-pentadiene, d_4^{18} 0·683, n_D^{18} 1·428, and some Δ^{β}-penten-α-ol (cf. Delaby, A., 1923, i, 753), when dehydrated at 350—365° in presence of fresh alumina, prepared by the passage of carbon dioxide through an aluminate. $\Delta^{\alpha\gamma}$-Pentadiene yields two *dibromides*, b. p. 70°/11 mm. and 88°/11 mm., respectively; the glycol derived from the latter gives a *diacetate*, b. p. 112·5°/11 mm. $\Delta^{\alpha\gamma}$-Pentadiene also gives a tetrabromide, m. p. 114·5°, and a liquid, b. p. 121—125°/3 mm., probably a mixture of isomerides. The tetrabromides lose 2 mols. of hydrogen bromide when treated with alcoholic sodium hydroxide, yielding *βγ-dibromo-$\Delta^{\alpha\gamma}$-pentadiene*, b. p. 64·5°/12 mm., and 4 mols. of hydrogen bromide when treated with excess of alcoholic potassium hydroxide, giving *$\Delta^{\alpha\gamma}$-pentadiinene*. Propylvinylcarbinol is similarly dehydrated, and on hydrolysis of the tetrabromides of the hydrocarbon formed, a mixture of *$\Delta^{\alpha\gamma}$-hexadi-inene*, b. p. 80°, and $\Delta^{\beta\delta}$-hexadi-inene is obtained. Butylvinylcarbinol gives $\Delta^{\beta\delta}$-heptadiene when dehydrated, and the tetrabromides when treated with alcoholic

potassium hydroxide give a small amount of $\Delta^{\alpha\gamma}$-heptadi-inene and a *hydrocarbon*, b. p. 143°, possibly $\Delta^{\beta\delta}$-heptadi-inene. L. F. HEWITT.

Attempted catalytic hydrogenation of ethylene oxide. P. SABATIER and J. F. DURAND (Compt. rend., 1926, **182**, 826).—When treated with hydrogen in the presence of reduced nickel at 125—150°, ethylene oxide yields acetaldehyde and a small amount of crotonaldehyde. The nickel therefore lowers the temperature at which ethylene oxide is transformed into acetaldehyde without promoting hydrogenation. L. F. HEWITT.

Pyrogenic decomposition of ethylene oxide and the mean temperature at which the decomposition reactions occur. E. PEYTRAL (Bull. Soc. chim., 1926, [iv], **39**, 206—214).—The decomposition products obtained on passing ethylene oxide through a heated platinum tube are water containing a small amount of acetaldehyde together with a gas of the composition: carbon monoxide, 45·7; hydrogen 26; methane, 17·7; acetylene, 4·2; ethylenic hydrocarbons, 6·4%. The rise of temperature due to evolution of heat during the decomposition is 629° and, as the temperature of the tube is about 1200°, this corresponds with a sudden heating through 571° to bring about the decomposition. H. J. EVANS.

Organic phosphoric acid derivatives. II. Esters of β-nitro-β-hydroxymethylpropane-αγ-diol. F. ZETZSCHE and E. ZURBRÜGG (Helv. Chim. Acta, 1926, **9**, 297—300).—β-Nitro-β-hydroxymethylpropane-αγ-diol in dry pyridine solution reacts with phosphoryl chloride, giving in 62% yield the *dicyclic phosphate*, $NO_2\cdot C(CH_2\cdot O)_2(CH_2\cdot O)P{:}O$, m. p. 243°, very stable towards acids, hydrolysed by cold alkalis. In moist pyridine solution, esterification of only one hydroxyl group takes place. The product can be isolated in 22% yield as the *barium phosphoric* ester, very readily hydrolysed by alkalis with simultaneous decomposition of the diol formed. Reaction with phenoxyphosphoryl dichloride (A., 1925, i, 1468) gives the *phenyl* cyclo*phosphate*,

$$C(NO_2)(CH_2\cdot OH)<\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}>PO\cdot OPh,$$

hydrolysed by alkali with accompanying decomposition of the diol. Reaction with anilinophosphoryl dichloride gives the *anilido*cyclo*phosphate*, $C(NO_2)(CH_2\cdot OH)<\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}>PO\cdot NHPh$, m. p. 192—194° (decomp.) after softening at 190°. M. CLARK.

Action of sodium on alkyl disulphides. C. G. MOSES and E. E. REID (J. Amer. Chem. Soc., 1926, **48**, 776—777).—Metallic sodium is without appreciable action on alkyl sulphides in anhydrous ether, but the alkyl disulphides are decomposed with formation of the corresponding sodium alkyl mercaptides, this reaction proceeding equally well in absolute alcohol. Magnesium is without action on alkyl disulphides under similar conditions. *iso*Butyl 1-anthraquinonyl sulphide has m. p. 116° (cf. Reid, Mackall, and Miller, A., 1922, i, 154).
F. G. WILLSON.

Basis for the physiological activity of certain -onium compounds. IV. Sulphur analogue of choline. R. R. RENSHAW, N. BACON, and J. H. ROBLYER (J. Amer. Chem. Soc., 1926, **48**, 517—520; cf. this vol., 155).—*Dimethyl-β-hydroxyethylsulphonium iodide* is obtained when a mixture of methyl sulphide and β-iodoethyl alcohol is kept in the dark for several days at the ordinary temperature. It decomposes when kept. *Dimethylacetoxymethylsulphonium bromide*, m. p. 104°, is obtained similarly in about 30 min. from a mixture of methyl sulphide and bromomethyl acetate. This compound has a muscarine action only slightly less intense than that of the nitrogen analogue (cf. Hunt and Renshaw, A., 1925, i, 861), but, even in large doses, does not show any stimulating nicotine effect. These results indicate that the -onium element of these sulphur and nitrogen compounds determines the extent of their physiological activity, if not actually the type of action. F. G. WILLSON.

Reactions of carbon disulphide. I. E. WERTHEIM (J. Amer. Chem. Soc., 1926, **48**, 826—830).—When carbon disulphide (40 c.c.) is shaken with aqueous ammonia (200 c.c.; *d* 0·90) the red, aqueous solution affords, when shaken with methyl iodide, methyl trithiocarbonate, b. p. (decomp.) 110—111°/18 mm., 219—220°/760 mm. *Ethyl trithiocarbonate*, b. p. (decomp.) 102—104°/7 mm., 241—244°/717 mm., and *benzyl trithiocarbonate*, b. p. 240—260°/55—60 mm. (decomp.), are obtained similarly. When the above aqueous extract is kept for longer than 1 month, it yields, on treatment with benzyl chloride, benzyl mercaptan (*silver* salt, amorphous). When benzaldehyde (20 g.), carbon disulphide (20 g.), and aqueous ammonia (150 c.c.; *d* 0·90) are mixed and kept for 24 hrs. in a closed container, thiobenzaldin is precipitated. This has m. p. 131° or, when heated rapidly, m. p. 136—137° (cf. Laurent, Annalen, 1841, **38**, 323; Baumann and Fromm, A., 1891, 1050). F. G. WILLSON.

Derivatives of ethyl selenomercaptan. E. H. SHAW, jun., and E. E. REID (J. Amer. Chem. Soc., 1926, **48**, 520—528).—A completely enclosed apparatus is figured, suitable for the preparation of 100 g. batches of ethyl selenomercaptan by an adaptation of Siemans' method (Annalen, 1847, **61**, 360) from aluminium selenide. Condensation of ethyl selenomercaptan with the requisite ketones in presence of hydrogen chloride affords *ββ-diethylselenolpropane*, b. p. 81°/4 mm., d_{25}^{25} 1·4329, *ββ-diethylselenolbutane*, b. p. 91·5°/3·5 mm., d_{25}^{25} 1·4064, and *γγ-diethylselenolpentane*, b. p. 104·5°/3·5 mm., d_{25}^{25} 1·3608. Oxidation of these selenomercaptoles with dilute nitric acid yields ethylseleninic acid nitrate, $EtSeO_2H,HNO_3$, m. p. 80°, decomp. 100°. Hydrochloric acid converts this nitrate into the corresponding *hydrochloride*, $EtSeO_2H,HCl$, m. p. 100—107° (decomp.), depending on the rate of heating, whereas hydrobromic acid affords *selenium ethyl tribromide*, $EtSeBr_3$, decomp. 73° after darkening at about 50° (rapid heating), whilst hydriodic acid affords a dark, viscous *oil*. Oxidation of the selenomercaptoles with hydrogen peroxide affords ethylseleninic acid, whilst treatment with free halogens results in decomposition

with formation of selenium halides. Sodium ethylselenomercaptide condenses in alcoholic solution with ββ′-dichlorodiethyl sulphide, sulphone, and sulphoxide, yielding, respectively, *di-β-ethylselenolethyl sulphide*, $(EtSeC_2H_4)_2S$, m. p. 15°, b. p. 171°/4 mm., d_{25}^{25} 1·4724, and the corresponding *sulphone*, m. p. 72·5°, and *sulphoxide*, an oil decomposing on distillation at 4 mm. (cf. Helferich and Reid, A., 1920, i, 524). Condensation with sodium anthraquinone-1-butylsulphone-5-sulphonate yields similarly *5-ethylselenol-1-n-butylsulphoneanthraquinone*, m. p. not below 300°.

F. G. Willson.

Action of formic acid on methylalkylglycerols. R. Delaby and G. Morel (Bull. Soc. chim., 1926, [iv], **39**, 416—421; cf. A., 1923, i, 753).—If αγ-dimethylglycerol is boiled with 2·5 times its weight of 96% formic acid, a mixture is obtained, a fraction of which, b. p. 151·5—153·5°/19 mm., consists mainly of the *diformate*. When this mixture is gradually heated to 200°, decomposition ensues, leaving *dimethylglyceryl triformate*, m. p. 85°, b. p. 130—134°/15 mm. The distillate contains Δ^{γ}-penten-β-ol and its formic ester, and yields this alcohol (*allophanate*, m. p. 158—159°) on hydrolysis. The mixture of formates, b. p. 150—156°/18 mm., similarly obtained from formic acid and α-methyl-γ-ethylglycerol yields, on heating to 220°, a non-volatile residue of *methylethylglyceryl triformate*, m. p. 94·5°. The distillate is a mixture of alcohols and formates and gives, on hydrolysis, a mixture of Δ^{β}-hexen-γ-ol, b. p. 135—138°, and Δ^{δ}-*hexen-β-ol*, b. p. 138—143°, in quantity insufficient for complete characterisation.

H. E. F. Notton.

Complex formato- [and henzoato-]ferri-bases containing pyridine; formatoferric chloride and bromide. R. Weinland and L. Engel (Arch. Pharm., 1926, **264**, 33—45; cf. A., 1923, i, 291; 1913, i, 644).—The formic and benzoic acid analogues of the acetato-compounds already described (Weinland and Beck, *loc. cit.*, 1913) have been investigated. When aqueous (not anhydrous as with the acetato-compounds) ferric chloride is mixed with pyridine and formic acid, a deep red solution is produced, from which red crystals of *hydroxyhexaformatopyridine-triferric diformate*, $Fe_3(H{\cdot}CO_2)_8(OH),C_5H_5N,2H_2O$, separate. Other compounds isolated are as follows: the greyish-green *dichloride*,

$$Fe_4(H{\cdot}CO_2)_6(OH)_4Cl_2(C_5H_5N)_6,$$

by adding lithium chloride to a solution of ferric formate in pyridine, or by dissolving formatoferric chloride (see below) in pyridine; a greenish-black *perchlorate*, $Fe_8(H{\cdot}CO_2)_{16}(OH)_5(ClO_4)_3(C_5H_5N)_{10}$, the *benzoato*-analogues, *viz.*,

$$Fe_8(BzO)_{18}(OH)_3(ClO_4)_3(C_5H_5N)_{12},$$

and $Fe_6(BzO)_{12}(OH)_4(ClO_4)_2(C_5H_5N)_5$, greyish-green and dark brown, respectively, and an orange-coloured *thiocyanate*, $Fe_3(BzO)_6(OH)_2(CNS),C_5H_5N$.

When hydrated or anhydrous ferric chloride is dissolved in formic acid, a yellowish-green powder, *formatoferric chloride*, $Fe(H{\cdot}CO_2)_2Cl,H_2O$, separates. The hot aqueous solution of this compound is deep red, and therefore is presumed to contain the hexaformatotriferric cation. The analogous *bromide* is a dark brown powder. The compounds are almost insoluble in cold water.

W. A. Silvester.

Complexes of formic acid and thorium. Aluminium and manganese formates. R. Weinland and A. Stark (Ber., 1926, **59**, [*B*], 471—479; cf. Weinland and Reihlen, A., 1913, i, 1300).—*Ammonium hexaformatothorate* $[Th(H{\cdot}CO_2)_6](NH_4)_2$, is prepared by the action of a large excess of ammonium formate on thorium formate in aqueous solution; the corresponding *barium* $(+2H_2O)$ and *strontium* $(+2H_2O)$ salts are described. Under similar conditions, potassium formate yields *potassium pentaformatothorate*, $[Th(HCO_2)_5]K$, whereas pyridine and formic acid afford *pyridine hydrogen hexaformatothorate*. All the salts are stable and may be recrystallised from water. Thorium formate and sodium perchlorate yield the *salt*, $\left[Th_3\frac{(HCO_2)_6}{(OH)_5}\right]ClO_4,12H_2O$; the corresponding *nitrate* $(+12H_2O)$, *chlorate* $(+16H_2O)$, and *thiocyanate* $(+7H_2O)$ are prepared in a similar manner, whilst also the nitrate is formed by double decomposition between the thiocyanate and sodium nitrate. A corresponding *basic formate*, $Th_3(HCO_2)_7(OH)_5,2H_2O$, is prepared by the cautious addition of ammonia to a solution of thorium formate. *Manganese formate* is prepared by the action of cold, 90% formic acid on manganese dioxide. It is decomposed by water, alcohol, or concentrated alkali formate solution into hydrated manganese sesquioxide; the constitution $[Mn_3(HCO_2)_6](HCO_2)_3,2H_2O$ is suggested. Freshly-precipitated aluminium hydroxide and warm 90% formic acid afford *basic aluminium formate*, $Al(HCO_2)_2(OH),H_2O$, from which complex salts, analogous to those derived from thorium, could not be prepared.

H. Wren.

Saturated acids of highest melting point from arachis oil. D. Holde and N. N. Godbole (Z. Deuts. Oel- und Fett-Ind., 1926, **46**, 129—130, 145—146, 163—165, 179—180).—A more detailed account of work the results of which have been published previously (cf. this vol., 268).

Catalytic hydrogenation of highly unsaturated acids. I. Course of hydrogenation of methyl esters of highly unsaturated acids in the presence of nickel catalyst. Y. Toyama and T. Tsuchiya. —See B., 1926, 286.

Chinese wood oil. W. Nagel and J. Grüss (Wiss. Veröff. Siemens-Konz., 1925, **4**, 284—320; cf. B., 1926, 164).—The following derivatives of α-elæostearic acid are described: *potassium*, *sodium*, and *copper* salts; methyl ester, b. p. 214°/12 mm. (with conversion into the β-isomeride), η_{25}^{0} 0·109 (as compared with 2·019 for the tung oil), obtained by the action of diazomethane on the acid or of methyl-alcoholic potassium hydroxide on the original tung oil; ethyl and iso*amyl* esters prepared in a similar manner, b. p. 229—232°/17·5 mm. and 260—280°/40—70 mm. (decomp.), respectively; *glycol* ester (β-hydroxyethyl ester), decomposed on distillation, obtained by heating the acid with ethylene glycol at 180—200°. The following deriv-

atives of β-elæostearic acid are described: *amide*, m. p. 111—112°; *hydrazide*, m. p. 128—129°, obtained from the methyl ester; ethyl ester, b. p. 225—240°/15 mm. G. M. BENNETT.

Manufacture of lactic acid. S. E. FAITHFULL.—See B., 1926, 252.

Equilibrium of lactic acid and lactic anhydride in commercial lactic acid. R. EDER and F. KUTTER (Helv. Chim. Acta, 1926, **9**, 355—364).—Ullmann's conclusion ("Enzyk. der tech. Chem.," 1920, VIII, 135) that the lactyl-lactic acid content of aqueous solutions of commercial lactic acid depends on the acid concentration is confirmed. At the ordinary temperature, an equilibrium between the acid and anhydride is reached in 100 days, the time being shortened to 12 hrs. when the solutions are heated at 100°. Solutions in equilibrium contain for an 80% acid concentration 62% of acid and 18% of anhydride, for a 50% acid concentration 46·5% of acid and 3·5% of anhydride, and for a 20% acid concentration 19·6% of acid and 0·4% of anhydride. When the equilibrium is once attained, it is not altered by raising the temperature, provided that the concentration of the solution is unaltered (cf. Dietzel and Krug, A., 1925, i, 1036).

M. CLARK.

Ferric salts of malonic and substituted acetic acids and their constitution. R. WEINLAND and O. LOEBICH (Z. anorg. Chem., 1926, **151**, 271—288).—*Hexamonochloroacetatodihydroxytriferric perchlorate*, $[Fe_3(CH_2Cl{\cdot}CO_2)_6(OH)_2]ClO_4,9H_2O$, red, is obtained from sodium perchlorate or perchloric acid, ferric chloride, and sodium monochloroacetate. The *nitrate* has $4H_2O$. The *trichloroacetate*,

$$[Fe_3(CCl_3{\cdot}CO_2H)_6(OH)_2](CCl_3{\cdot}CO_2),2H_2O,$$

red leaflets from hydrated ferric oxide and boiling trichloroacetic acid solution, when heated in dilute aqueous solution, yields the *salt*,

$$Fe_3(CCl_3{\cdot}CO_2)_6(OH)_3,7H_2O;$$

excess of trichloroacetic acid yields the *salt*,

$$[Fe_3(CCl_3{\cdot}CO_2)_6(OH)](CCl_3{\cdot}CO_2)_2,4H_2O,$$

which may be obtained anhydrous from hydrated ferric oxide and an ethereal solution of trichloroacetic acid. *Basic ferric iodoacetate*,

$$[Fe_3(CH_2I{\cdot}CO_2)_6(OH)_2](CH_2I{\cdot}CO_2),$$

orange, *hexacyanoacetatodihydroxytriferric perchlorate*, $[Fe_3(CH_2CN{\cdot}CO_2)_6(OH)_2]ClO_4,8H_2O$, red, *trimalonatodihydroxytriferric perchlorate*,

$$[Fe_3(CO_2{\cdot}CH_2{\cdot}CO_2)_3(OH)_2]ClO_4,$$

rose-red, and a double *salt* of *hexaglycollatodihydroxytriferric perchlorate* and sodium perchlorate,

$$[Fe_3\{CH_2(OH){\cdot}CO_2\}_6(OH)_2]ClO_4,NaClO_4,4H_2O,$$

are described. *Pyridine triglycollatoferriate*,

$$\left[Fe\left(<\!\!\begin{matrix}O{\cdot}CH_2\\ O{\cdot}C{\cdot}O\cdot\end{matrix}\!\!\right)_3\right]H_3,C_5H_5N,$$

and *diglycollatoferriate*,

$$\left[\begin{matrix}H_2C-O\\ OC-O\end{matrix}\!\!>Fe<\!\!\begin{matrix}O-CH_2\\ O=C{\cdot}O\cdot\end{matrix}\right]H,C_5H_5N,$$

are green powders obtained from ferric chloride, glycollic acid, and pyridine in methyl alcohol. Ferric perchlorate yields a yellow *nonahydrate*. Weinland and Ensgraber's method (A., 1914, ii, 132) gives a hexahydrate. R. CUTHILL.

Polymethylenedicarboxylic acids containing 11—19 carbon atoms and their derivatives. P. CHUIT (Helv. Chim. Acta, 1926, **9**, 264—278).—Polymethylenedicarboxylic acids, containing 11—19 carbon atoms in the chain and designed for conversion into the corresponding cyclic ketones, were prepared by methods clearly indicating their constitution. Nonane-αι-diol, prepared by the action of sodium and ethyl or amyl alcohol on the dimethyl or diethyl esters of azelaic acid, and decane-ακ-diol (A., 1903, i, 371) were converted into the corresponding bromides, and thence, through the cyanides or by condensation with malonic ester, into higher carboxylic acids. The esters of these were reduced to the corresponding glycols, which furnished new starting points for similar syntheses. In certain cases, the glycol stage was omitted, and the dibromo-compounds, by the action of monochlorodimethyl ether on their magnesium derivatives, were converted into the dimethoxy-derivatives of the hydrocarbons containing two more carbon atoms in the chain, $MgBr[CH_2]_nBrMg+2CH_2Cl{\cdot}OMe=2MgBrCl+MeO{\cdot}[CH_2]_{n+2}{\cdot}OMe$. By the action of dry hydrogen bromide, the dimethoxy-compounds are readily converted into the corresponding dibromo-derivatives. The following compounds are described: *monomethyl* ester, m. p. 25°, b. p. 185°/15 mm., d^{15} 1·033, *dimethyl* ester, b. p. 140°/8 mm., d^{15} 1·006, *monoethyl* ester, b. p. 187—192°/15 mm., d^{15} 1·020, and *diethyl* ester, b. p. 154—155°/8 mm., d^{15} 0·9756, of azelaic acid; αι-dibromononane, b. p. 147—149°/9 mm., 121°/2 mm., d^{15} 1·415; *ακ-dibromodecane*, m. p. 27·4°, b. p. 161·1—162·4°/9 mm., d^{30} 1·335, n_D^{30} 1·49051; *α-bromodecanol*, b. p. 153—155°/8 mm., d^{15} 1·188; *ακ-dicyanodecane*, m. p. 16°, b. p. 195°/8 mm.; nonane-αι-dicarboxylic acid (*dimethyl* ester, b. p. 140—141/3 mm., d^{15} 0·990; *diethyl* ester, b. p. 165—166°/5 mm., 173—175°/13 mm., d^{15} 0·957); *undecane-αλ-diol*, m. p. 62—62·5° (*diacetyl* derivative, b. p. 181—183°/13 mm., d^{15} 0·964); αμ-dibromoundecane, b. p. 179°/12 mm., d^{15} 1·332; decane-ακ-dicarboxylic acid, m. p. 127·8—128° (*dimethyl* ester, m. p. 31°, b. p. 167—169°/9 mm.; *diethyl* ester, m. p. 16°, b. p. 165—166°/3·5 mm., d^{20} 0·849); *dodecane-αμ-diol*, m. p. 80·8°, b. p. 185°/8 mm. (*diacetyl* derivative, m. p. 36°, b. p. 189—190°/10 mm.); *αμ-dimethoxydodecane*, b. p. 155—160°/15 mm.; *αμ-dibromododecane*, m. p. 36·8°, b. p. 177—180°/8 mm.; undecane-αλ-dicarboxylic acid (*dimethyl* ester, m. p. 32°, b. p. 192—194°/11 mm.; *diethyl* ester, m. p. 20°, b. p. 204°/12 mm.); *tridecane-αν-diol*, m. p. 76·4°, b. p. 195—197°/10 mm.; *αν-dibromotridecane*, m. p. 8—10°, b. p. 185—187°/9 mm., d^{15} 1·276; dodecane-αμ-dicarboxylic acid (*dimethyl* ester, m. p. 43°, b. p. 193—194°/8 mm.); *tetradecane-αξ-diol*, m. p. 84·8°, b. p. 200°/9 mm.; *αξ-dibromotetradecane*, m. p. 50·4°, b. p. 190—192°/8 mm.; *αξ-dimethoxytetradecane*, m. p. 23·3°, b. p. 170—171°/10 mm.; *tridecane-αν-dicarboxylic acid*, m. p. 114·6—114·8° (*dimethyl* ester, m. p. 43°, b. p. 203—205°/11 mm.; *diethyl* ester, m. p. 30°, b. p. 192—193°/3 mm.); *pentadecane-αο-diol*, m. p. 87°; *αο-dibromopentadecane*, m. p. 15°, b. p. 215—225°/15 mm.; *α-bromopentadecan-ο-ol*, m. p. 59—60°; tetradecane-αξ-dicarboxylic acid (*dimethyl* ester, m. p. 51·6°);

hexadecane-απ-diol, m. p. 91·4°, b. p. 195—200°/4 mm. (*diacetyl* derivative, m. p. 47·2°); *απ-dimethoxyhexadecane*, m. p. 32°, b. p. 174—176°/3 mm.; *απ-dibromohexadecane*, m. p. 56·2°, b. p. 204—205°/4 mm.; *pentadecane-αo-dicarboxylic acid*, m. p. 118° (*dimethyl* ester, m. p. 52·3°, b. p. 235°/15 mm.; *diethyl* ester, m. p. 41·6°, b. p. 209—210°/3 mm.); hexadecane-απ-dicarboxylic acid, m. p. 124·8° (*dimethyl* ester, m. p. 60°, b. p. 205—207°/3 mm.; diethyl ester, m. p. 48·2°, b. p. 201—204°/1·5 mm.); heptadecane-αρ-dicarboxylic acid, m. p. 119·2° (*dimethyl* ester, m. p. 60·2°, b. p. 212—213°/3 mm.; *diethyl* ester, m. p. 49·2°, b. p. 212—213°/1·5 mm.). The m. p. of the even-numbered dicarboxylic acids fall from one acid to the next, whilst the m. p. in the odd-numbered series rise, so that the smooth curves on which the m. p. lie tend to converge for the higher members. The m. p. of the methyl esters of the even series lie on a curve which ascends with increasing number of carbon atoms, and is approximately parallel to the corresponding curve for the esters of the odd-numbered series. The diethyl esters give similar curves. In the glycol series, the ascending curves, parallel at first, rapidly converge, the even-numbered glycols having the higher m. p. M. CLARK.

Salts of anhydromethylenecitric acid. L. VANINO and O. GUYOT (Arch. Pharm., 1926, **264**, 113—117; cf. A., 1919, i, 9).—By double decomposition of the sodium salt (" citarin ") the following are obtained: as immediate precipitates the silver, bismuth, *copper*, *beryllium*, *barium*, *mercuric*, *mercurous*, *aluminium*, *lead*, *ferric*, and *stannous* salts; on keeping, the *magnesium*, *calcium*, *strontium*, *zinc*, and *cadmium* salts. Precipitates are also produced by interaction with chromium potassium sulphate and ferrous ammonium sulphate. The *lithium* ($+3H_2O$), *magnesium* ($+2H_2O$), *cupric* ($+2H_2O$), *manganous* ($+3H_2O$), *chromic* ($+2H_2O$), *cobalt* ($+3H_2O$), and *nickel* ($+3H_2O$) salts are described in detail. W. A. SILVESTER.

Selective reduction of citral by means of platinum oxide–platinum-black and a promoter. XII. R. ADAMS and B. S. GARVEY (J. Amer. Chem. Soc., 1926, **48**, 477—482; cf. this vol., 165).—When treated with hydrogen in presence of platinum oxide–platinum-black, citral is partly reduced to tetrahydrogeraniol. Reactivation of the catalyst by shaking with air causes the reaction to go further, but the reduction cannot be completed, as successive reactivations cause coagulation of the catalyst. In presence of a trace of ferrous sulphate, reduction proceeds progressively to tetrahydrogeraniol. If the reaction is interrupted when successive mols. of hydrogen have been absorbed, the products are pure geraniol, citronellol, and tetrahydrogeraniol, respectively. The action of zinc acetate is similar to that previously reported (*loc. cit.*) in the reduction of cinnamaldehyde, and the concentration of this promoter can be adjusted to cause the reaction to cease when either 1 or 2 mols. of hydrogen have been absorbed by the citral, but in such cases the rate of reduction is considerably reduced. F. G. WILLSON.

Action of acraldehyde on the mixed dimagnesium derivative of acetylene. LESPIEAU (Compt. rend., 1926, **182**, 637—638; cf. A., 1925, i, 225).—Acraldehyde reacts with the dimagnesium derivative of acetylene, yielding the *alcohol*, $CH{:}C{\cdot}CH(OH){\cdot}CH{:}CH_2$, b. p. 128·5—129°, d^{23} 0·9175, n_D^{23} 1·4525; *hexabromide*, m. p. 77—79°, and the glycol, $[CH_2{:}CH{\cdot}CH(OH){\cdot}C{:}]_2$ (Dupont, Diss., Paris, 1912), *hexabromide*, m. p. 196—197·5°. L. F. HEWITT.

Zinc chloride compounds of oximes. P. BILLON (Compt. rend., 1926, **182**, 584—586).—By the interaction between ketones and the zinc chloride compound of hydroxylamine, or by the action of zinc chloride on 2 mols. of a ketoxime, compounds of the type $(R'R''C{:}N{\cdot}OH)_2,ZnCl_2$ are formed. When treated with water, these compounds yield the oxime. The *compounds* derived from acetone, methyl ethyl ketone, methyl *n*-propyl ketone, methyl *iso*propyl ketone, dipropyl ketone, have m. p. 104°, 71°, 51°, 94°, and 42°, respectively. The other ketoximes investigated do not yield crystalline zinc chloride compounds. Acetylacetone reacts with the zinc chloride compound of hydroxylamine, giving *bisdimethylisooxazole zinc chloride*, $\left(CH\ll\begin{matrix}CMe{\cdot}O\\ CMe{:}N\end{matrix}\right)_2,ZnCl_2$, m. p. 92—93°, which yields dimethyl*iso*oxazole when treated with water. L. F. HEWITT.

Molecular transformations of α-keto-alcohols. A. FAVORSKI [with E. VÉNUS-DANILOV, M. WASSILIEV, A. OUMNOV, and E. KOTCHERGINE] (Bull. Soc. chim., 1926, [iv], **39**, 216—220).—When alcoholic solutions of keto-alcohols are heated at 120—130° in a sealed tube with a few drops of sulphuric acid, molecular rearrangement takes place in such a manner that the carbonyl group tends to take up a position near the end of the chain, if possible to form part of an acetyl group. The following transformations were studied: (1) butyrylethylcarbinol into propionylpropylcarbinol, (2) propionylmethylcarbinol into acetylethylcarbinol, (3) trimethylacetylmethylcarbinol into acetyl*tert.*-butylcarbinol, (4) *iso*butyryldimethylcarbinol into acetylmethyl*iso*propylcarbinol, (5) oxoctenol (cf. Boutleroff, A., 1882, 936) into acetylmethyl*tert.*-butylcarbinol, (6) benzoylmethylcarbinol into acetylphenylcarbinol. The transformation mechanism is applied theoretically to the case of alcoholic fermentation. H. J. EVANS.

[Hydroxymethylene ketones.] E. BENARY (Ber., 1926, **59**, [*B*], 600).—Benary, Meyer, and Charisius (this vol., 272) have overlooked the fact that the compound obtained from methyl ethyl ketone and ethyl formate has the constitution $COMe{\cdot}CMe{:}CH{\cdot}OH$, as established previously by Claisen and by Diels and Ilberg (A., 1916, i, 372); the benzeneazo-derivative cannot therefore have the constitution ascribed to it. The next higher homologue from methyl *n*-propyl ketone must, however, possess the assigned constitution, since it is transformed by ammonia into 5-butyryl-2-propylpyridine (cf. Charisius, Diss., Berlin, 1925). H. WREN.

Relations between rotatory power and structure in the sugar group. XII. Preparation and properties of pure α-methyl-*d*-lyxoside. F. P. PHELPS and C. S. HUDSON (J. Amer. Chem. Soc., 1926, **48**, 503—507; cf. Pringsheim and Leibowitz, this vol., 275).—Pure α-methyl-*d*-lyxoside has now been prepared, both by the method of Van Eckenstein and Blanksma (Z. Ver. deut. Zuckerind., 1908, **58**, 114), and by treating pure α-*d*-lyxose with boiling absolute methyl-alcoholic 1·5% hydrogen chloride (cf. Bourquelot, A., 1915, i, 703). It has m. p. 108—109°, $[\alpha]_D^{20}$ +59·4° in water, the latter constant being in close agreement with that previously calculated (cf. Hudson, A., 1925, i, 233). The (unimolecular) reaction constants for the hydrolysis of the following carbohydrates at 98° in presence of 0·05*N*-hydrochloric acid decrease in the order α-methyl-*d*-lyxoside, lactose, maltose, and α-methyl-*d*-mannoside. The prediction of Armstrong and Caldwell (A., 1904, i, 957) that lactose should hydrolyse faster than maltose at temperatures above 77° has thus been verified. F. G. WILLSON.

Action of almond emulsin on *l*-arabinose in ethyl-alcoholic solution of different concentrations. M. BRIDEL and C. BÉGUIN (Compt. rend., 1926, **182**, 659—661; cf. A., 1923, ii, 882).—The diminution in rotatory power and amount of arabinose present in solutions of arabinose and almond emulsin increases with increasing concentration of ethyl alcohol; *e.g.*, in 40% ethyl alcohol 3·9% of arabinose disappeared in 280 days, whilst in 95% alcohol 68·3% of arabinose disappeared, on incubation at 33°. The phenomenon is ascribed to the formation of α-ethyl-*l*-arabinoside, using Hudson's nomenclature (cf. A., 1925, i, 232, and following abstract). L. F. HEWITT.

Biochemical synthesis of α-ethyl-*l*-arabinoside, using almond emulsin. M. BRIDEL and C. BÉGUIN (Compt. rend., 1926, **182**, 812—814).—After prolonged action of almond emulsin on an alcoholic solution of arabinose, pure *α-ethyl*-l-*arabinoside*, m. p. 122—123°, α_D +9·95°, may be isolated. This compound has no reducing properties, and is readily hydrolysed by 3% sulphuric acid or in aqueous solution by almond emulsin, yielding arabinose and ethyl alcohol. B. W. ANDERSON.

Constituent sugars of some lichens. E. VOTOČEK and J. BURDA (Bull. Soc. chim., 1926, [iv], **39**, 248—254).—Examination of several species of lichens shows that almost all contain polyoses soluble in hot water, but insoluble in alcohol; these are present chiefly as glucosans. The hemicelluloses are mainly derivatives of mannose and galactose, whilst the true celluloses are all derived from dextrose. H. J. EVANS.

2 : 4-Dibromophenylhydrazine, the three iodophenylhydrazines, and their aldehydic and ketonic compounds. E. VOTOČEK, V. ETTEL, and B. KOPPOVA (Bull. Soc. chim., 1926, [iv], **39**, 278—285).—The following are described: 2 : 4-dibromophenylhydrazone of *arabinose*, m. p. 161°, of *xylose*, m. p. 127—128°, of *rhamnose*, m. p. 150°, of galactose, m. p. 190° (*monohydrate*, m. p. 178°); o-*iodophenylhydrazine*, m. p. 29—30°, yielding *compounds* with benzaldehyde, m. p. 66°, galactose, m. p. 196°, dextrose, m. p. 125°, osazone of dextrose, m. p. 169°; m-*iodophenylhydrazine*, yielding *compounds* with benzaldehyde, m. p. 146—147°, salicylaldehyde, m. p. 133°, galactose, m. p. 148°, dextrose, m. p. 162—163°, rhamnose, m. p. 161°, furfuraldehyde, m. p. 74°, and *osazones* of dextrose, m. p. 198—199°, lævulose, m. p. 198—200°, galactose, m. p. 168°, and rhamnose, m. p. 142°; p-*iodophenylhydrazones* of benzaldehyde, m. p. 118°, salicylaldehyde, m. p. 181°, dextrose, m. p. 169°, galactose, m. p. 179°, rhamnose, m. p. 167°, and *osazones* of galactose, m. p. 154—156°, and of rhamnose, m. p. 190°. 2 : 4-Dibromophenylhydrazine furnishes a means of quantitative separation of galactose from xylose, rhamnose, dextrose, lævulose, maltose, and lactose, but not from arabinose. Osazones derived from the iodophenylhydrazines are of no value analytically. H. J. EVANS.

Interaction of amino-compounds and carbohydrates. I. Action of carbamide on dextrose, lævulose, and mannose. II. Preparation of glucoseureide. A. HYND (Biochem. J., 1926, **20**, 195—204; 205—209).—I. The addition of carbamide to an alcoholic or aqueous solution of dextrose causes a fall in the optical activity of the solution without altering its copper-reducing value. The decrease in the optical activity is accompanied by an increase in the p_H of the solution and by development of a positive Selivanov test. With the aqueous solution of dextrose the results were obtained at p_H 6·0, 7·42, and 7·0. Most marked results were recorded in a few hours at about 80°. The reaction was less marked when the mixture was kept for several days at 50°, whilst several months were required to obtain a change at 37°. Similar results were obtained with lævulose and mannose. The above changes are not due to the action of micro-organisms and the formation of ureide is probably also excluded. The mechanism of these changes is discussed. The specificity of Selivanov's reaction for ketones is questioned. The presence of reducing sugars accelerates the decomposition of carbamide.

II.—By using an excess of carbamide in Schoorl's method for the preparation of glucoseureide, a much better yield (66% against 10%) of the compound is obtained. By this modified method an additive *compound* of glucoseureide and carbamide, m. p. 170—171°, is obtained. The additive molecule of carbamide is removed slowly by boiling alcohol. By crystallising glucoseureide in presence of carbamide, the additive compound is obtained. A dextrorotatory substance is also obtained in this reaction. S. S. ZILVA.

Partial bromination of phloridzin. I, II. Bromophlorin and bromo-*p*-hydroxyphenylpropionic acid, cleavage products of dibromophloridzin. K. MISAKI (J. Biochem. [Japan], 1925, **5**, 1—7; 9—12).—I. Treatment of phloridzin in anhydrous methyl alcohol at −5° to −10° with bromine water affords dibromophloridzin, $C_{21}H_{22}O_{10}Br_2$, m. p. 160°, $[\alpha]_D$ −35·8°. Further bromination yields hexabromophloretin and dextrose.

II. Hydrolysis of dibromophloridzin with boiling barium hydroxide yields bromo-*p*-hydroxyphenylpropionic acid, m. p. 90°, bromophlorin, and bromophloretinic acid. CHEMICAL ABSTRACTS.

Decomposition of xylan by enzymes. M. EHRENSTEIN (Helv. Chim. Acta, 1926, 9, 332—336).—The optimum p_H for hydrolysis of xylan (cf. A., 1922, i, 113, 323) to xylose by vineyard-snail enzyme (A., 1906, ii, 101) is 4·65, using a citrate buffer solution and 5·28 with a sodium phosphate buffer. The citrate buffer solution induces greater activity, a maximum transformation of 69% being obtained. When the enzyme concentration is doubled, the amount of hydrolysis is increased only by 20%; the rate of hydrolysis obeys neither the unimolecular equation nor Schutz's rule. Colloidal solutions of xylan containing the same relative amounts of xylan, enzyme, and buffer show little change in the rate of reaction under progressive dilution with water, whereas when the xylan is held in suspension, a retardation is produced. Xylan, like reserve cellulose, is hydrolysed by an aqueous extract of malt, although in less degree than by the snail enzyme.

M. CLARK.

Mechanical liquefaction of starch. P. PETIT and RICHARD (Compt. rend., 1926, **182**, 657—659; cf. A., 1925, i, 967).—When starch paste is passed six times in the form of a spray into carbon dioxide or hydrogen, a soluble starch, $[M]_D$ 210°, is obtained, but, when kept under sterile conditions, the solution becomes progressively more cloudy. When centrifuged, a limpid, soluble starch solution is obtained, together with a deposit containing starch granules and cellulose. When treated with amylase at 20°, starch gives 0·91% of an insoluble material which yields soluble starch on treatment with warm water, 61·4% of dextrose when boiled with dilute hydrochloric acid, 100·5% of dextrose when hydrolysed with dilute hydrochloric acid after previous boiling, and 73·9% of maltose when treated with amylase at 50° after previous boiling. Some cellulose is found after the previous boiling treatment. Starch after treatment with light petroleum readily gives soluble starch. L. F. HEWITT.

Action of concentrated sulphuric acid on cellulose and extraction of cellulose from wood. K. ATSUKI and T. MINAKE.—See B., 1926, 266.

Polysaccharides. XXXIV. Hydro- and oxycelluloses. P. KARRER and T. LIESER.—See B., 1926, 267.

Depolymerisation of cellulose. E. HEUSER and N. HIEMER (Cellulosechem., 1925, **6**, 101—122, 125—132, 153—166; cf. A., 1925, i, 1387).—Cellulose is generally regarded as a polymerisation product of an anhydro-monose, -biose, or -triose, which by various treatments may be gradually depolymerised. The degree of depolymerisation of cellulose itself cannot be determined cryoscopically, on account of its insolubility, and the solvents for cellulose esters are unsuitable, on account of their associating properties. By exhaustive methylation, products are obtained which are completely soluble in water and suitable for cryoscopic measurements. When pure Egyptian cotton is dissolved in cuprammonium hydroxide, reprecipitated with carbon dioxide, and methylated with methyl sulphate and sodium hydroxide, a methoxyl content of 44·9% (trimethylcellulose= 45·6%) is obtained after twenty-two operations. For the later methylations, a solution containing 50—60% of sodium hydroxide and a large excess of methyl sulphate are used. The solubility in water increases to a maximum of 64% at 22·4% methoxyl and then diminishes to zero at 42% methoxyl. The solubility in glacial acetic acid remains nearly constant at about 33% between 10% and 32% methoxyl (dimethylcellulose = 32·6%) and then increases to 100% at 40·8%. The end-product is also completely soluble in chloroform, dichloroethane, tetrachloroethane, and pyridine. Cuprammonium staple fibre is more readily methylated, and after five methylations contains 35·7% of methoxyl. This dissolves to the extent of 80% in water at 15—17°, and is completely soluble at 8—12°. It is also completely soluble in pyridine and 50% soluble in glacial acetic acid. After purification by repeated dissolution in cold water and reprecipitation by heating, the methoxyl content rises to 37·5%. Cellulose regenerated from "viscose" or from cellulose acetate, hydrocelluloses prepared from these with gaseous hydrogen chloride, and cellulose dextrin prepared with sulphuric acid are more readily methylated, and a methoxyl content of 35—40% is generally obtained after three methylations. These products are all soluble in cold water, the highest temperature at which dissolution is complete varying up to 75° for the cellulose dextrin. The softening temperature, which is about 350° for the product from pure cotton cellulose, varies down to 203° for the methylated dextrin. The mol. wts. of these substances were determined in aqueous solution by the cryoscopic method. The concentrations of the solutions were varied between 0·12% and 1·9% and the f.-p. depressions were 0·001—0·014°. The mol. wts. found are independent of the concentration, and the ash content, which is usually about 0·1%, is shown to be without significant influence. The results for cuprammonium staple fibre were irregular, but the hydrocellulose prepared from it, having a corrected copper number (Schwalbe) of 6·8, has a mol. wt. of 2700, corresponding with 13·5 dimethylanhydroglucose residues. The lowest mol. wts. are 800 for a hydrocellulose, having a copper number of 8, prepared by the action of gaseous hydrogen chloride on viscose staple fibre, and 900 for the cellulose dextrin with a copper number of 16·6. The mol. wt. rises with diminishing hydration temperature (temperature of complete dissolution in water), and with increasing softening temperature, but is not directly related to the copper number. Since depolymerised cellulose is more readily methylated than cellulose itself, it is to be expected that it may be possible to obtain trimethylcellulose more readily from such substances. After nine methylations of hydrocellulose from viscose staple fibre, the methoxyl content is 45·42%, trimethylcellulose requiring 45·5%. The same methoxyl content is also obtained when dimethylcellulose from viscose cellulose is acetylated to dimethylcellulose monoacetate and then twice

methylated. The product is completely soluble in glacial acetic acid and chloroform, but insoluble in water. After six methylations, cellulose triacetate from cotton linters contains 45·0% of methoxyl; it is soluble in glacial acetic acid and chloroform and is mostly dissolved by cold water. A. GEAKE.

Nitration of cellulose. [**Cellulose pernitrates.**] E. CARRIÈRE (Bull. Soc. chim., 1926, [iv], **39**, 438—443).—Analyses of the spent acids and wash waters obtained in the nitration of cotton in Selwig centrifugals indicate that an intermediate cellulose pernitrate, which breaks down during washing and stabilisation with liberation of nitric acid, is formed. For example, in the preparation of "CP_1," $C_{24}H_{29}O_9(NO_3)_{11}$, and "$CP_2$," $C_{24}H_{31}O_{11}(NO_3)_9$, the intermediate compounds are $C_{24}H_{24}O_5(NO_3)_{14}$ and $C_{24}H_{30}O_{10}(NO_3)_{10},2HNO_3$, respectively. The instability of unwashed cellulose nitrate is due to these products, whilst the greater ease of stabilisation of CP_2 by washing is due to the different mode of attachment of the excess of nitric acid in the two cases. CP_1 nitrated by Thomson's method is more easily stabilised than that from Selwig's, because the pernitrate is more readily destroyed by the warm acid wash water used in the former than by pure water. Selwig's product is more easily stabilised if it is treated after nitration with sulphuric acid of d 1·58. The formation of cellulose pernitrates also explains the fact that cellulose nitrates of the same nitrogen content may have different physical properties (cf. A., 1908, i, 504). H. E. F. NOTTON.

Stereoisomeric diaryl-βγ-diamino-*n*-butanes. G. T. MORGAN, W. J. HICKINBOTTOM, and T. V. BARKER (Proc. Roy. Soc., 1926, **A, 110**, 502—523).—*dl*- and *meso*-Di-*p*-tolyl-βγ-diamino-*n*-butanes, prepared by the interaction of βγ-dibromobutane with *p*-toluidine, were separated and purified by means of the *picrate* and hydrochloride. Resolution of the *dl*-diamine into its enantiomerides was effected by *d*-α-bromocamphor-π-sulphonic acid, by alternate inoculation of the diamine solution with *d*- and *l*-diamines, and by selection of one crystal from the conglomerate and separate identification of the remaining crystals by a mixed m. p. method. No evidence was obtained for the formation of a racemoid compound over the range −15° to +30°. The axial ratios of the orthorhombic enantiomerides are $a:b:c=0{\cdot}3531:1:0{\cdot}2710$, whilst the monoclinic *meso*-isomeride has $a:b:c=1{\cdot}498:1:1{\cdot}049$, β=103° 23′. Formaldehyde condenses with the four isomeric di-*p*-tolyl-βγ-diamino-*n*-butanes to yield: dl-cyclo*methylene*di-p-*tolyl*-βγ-*diamino*-n-*butane*,

$$C_6H_9Me\cdot N\begin{<}CH_2\\CHMe\cdot CHMe\end{>}N\cdot C_6H_4Me,$$

m. p. 107°, crystallising as a true racemoid compound in the monoclinic system, $a:b:c=1{\cdot}026:1:1{\cdot}300$, β=102° 43′; meso-*isomeride*, m. p. 94°, monoclinic, $a:b:c=0{\cdot}3092:1:0{\cdot}2848$, β=96° 23′; d-*isomeride*, m. p. 65—66°, $[M]_D$ −9·2°, monoclinic, $a:b:c=0{\cdot}7075:1:0{\cdot}8646$, β=102° 59′; and the l-*isomeride*, m. p. 65—66°, $[M]_D$ +11·2°. Ethylene dibromide in the presence of anhydrous sodium carbonate condenses with the di-*p*-tolyl-βγ-diaminobutanes to give dl-1 : 4-*di*-p-*tolyl*-2 : 3-*dimethylpiperazine*, m. p. 110—111°, which crystallises as a pseudo-racemoid, and the meso-*isomeride*, m. p. 83—84°, anorthic system, $a:b:c=0{\cdot}6814:1:0{\cdot}6867$, α=95° 13′, β=92° 56′, γ=62° 5′. These substances were purified through their *hydrochlorides* and *picrates*, decomp. 203—205° after softening at 200°, and m. p. 194—195° (decomp.), respectively. The d- and l-*isomerides*, m. p. 138·5°, were prepared both by the interaction of the optically active diamine with ethylene dibromide and by resolution of the *dl*-piperazine by *d*-camphor-β-sulphonic acid; the *d*-enantiomeride has $[M]_D$ −116·1° and the *l*-enantiomeride $[M]_D$ +114·4°. The monoclinic crystals have $a:b:c=3{\cdot}711:1:1{\cdot}894$, β=115° 13′.

The diphenyl-βγ-diaminobutanes were obtained as uncrystallisable oils.

The following derivatives of the *dl*-bases were prepared: *hydrochloride*, m. p. 205—208°; *sulphate*; *nitrate*, decomp. 170—173°; *picrate*, m. p. 136°; dl-n-*butylene*-βγ-*diphenyldinitrosoamine*, m. p. 101°; dl-*di*-p-*nitrosodiphenyl*-βγ-*diamino*-n-*butane*, m. p. 205° (decomp.), and its *hydrochloride*; dl-cyclo*methylene*-*diphenyl*-βγ-*diamino*-n-*butane*, m. p. 99—100°; r-1 : 4-*diphenyl*-2 : 3-*dimethylpiperazine*, m. p. 89—90°, and its picrate, m. p. 202—205° (decomp.). The *r*-1 : 4-diphenyl-2 : 3-dimethylpiperazine is a true racemoid compound, the crystals being monoclinic with $a:b:c=1{\cdot}750:1:0{\cdot}8939$, β=95° 49′. It was resolved into its *enantiomerides* by *d*-camphor-β-sulphonic acid, the dextrorotatory amine having m. p. 87°, $[\alpha]_D$ + 44·8° in alcohol, $a:b:c=2{\cdot}401:1:1{\cdot}076$, β=104° 47′, and the lævorotatory amine m. p. 87°, $[\alpha]_D$ −36·8°. The *meso*-diphenyl-βγ-diamino-*n*-butane, which is produced in small yield simultaneously with the *dl*-form, was converted into meso-n-*butylene*-βγ-*diphenyldinitrosoamine*, m. p. 125°, and recovered pure by reduction. It gives a *dihydrochloride* and a *dibenzoyl* derivative, m. p. 250—251°. F. G. SOPER.

Aminoethers of the ephedrine group. Alkyl α-phenylpropylamine oxides. W. DULIÈRE (Bull. Soc. chim., 1926, [iv], **39**, 285—292).—The following were prepared by the action of dialkylamines on α-phenyl-γ-chloropropyl alkyl ethers: *methyl* α-*phenyl*-γ-*dimethylaminopropyl ether*, m. p. 112—115°; *methyl* α-*phenyl*-γ-*diethylaminopropyl ether*, b. p. 170°/12 mm., d^{20} 0·971; *methyl* α-*phenyl*-γ-*dipropylaminopropyl ether*, d^{20} 0·942; *methyl* α-*phenyl*-γ-*diethylaminopropyl ether*, d^{20} 0·921 (*hydrochloride*, m. p. 74°); *propyl* α-*phenyl*-γ-*diethylaminopropyl ether* (*hydrochloride*, m. p. 94)°; α-*phenyl*-γ-*diethylaminopropyl* iso*butyl ether*, d^{20} 0·927 (*hydrochloride*, m. p. 125°); α-*phenyl*-γ-*dimethylaminopropyl* iso*amyl ether*, d^{20} 1·011. H. J. EVANS.

Derivatives of γ-aminobutaldehyde and γ-aminobutyl alcohol. C. MANNICH and P. HORKHEIMER (Arch. Pharm., 1926, **264**, 167—180).—Crotonaldehyde interacts with aliphatic amines; it also dissolves with interaction in solutions of their salts; but from neither reaction is a homogeneous product obtainable. γ-Aminobutaldehyde derivatives may, however, be prepared by way of the

corresponding halogenoacetals. Crotonaldehyde and hydrogen bromide in cold alcohol give *γ-bromobutacetal*, b. p. 80—83°/12 mm., an unstable compound, less convenient to use in synthetic work than the corresponding chloro-compound. The latter, when treated with alcoholic ammonia at 125°, gives (yield 20%) *γ-aminobutacetal*, b. p. 72—75°/13 mm. (*hydrochloride*, m. p. 74°; *benzylidene* derivative, b. p. 140°/12 mm.). Similarly with methylamine, *γ-methylaminobutacetal*, b. p. 77—79°/12 mm. (N-*benzoyl* derivative, an oil), is obtained (yield 70%). This compound is so sensitive towards acids that a hydrochloride cannot be directly obtained; it is hydrolysed by cold concentrated hydrochloric acid to *γ-methylaminobutaldehyde* (*chloroaurate*, m. p. 96°). When the acetal is treated with ethyl chloroacetate, its *hydrochloride* is produced, together with *γ-methylcarbethoxymethylaminobutacetal* (b. p. 133—135°/13 mm.), which is split up by cold concentrated hydrochloric acid; the identified product of the reaction is sarcosine, and no heterocyclic compound is formed by intramolecular condensation. With ethyl β-chloropropionate the acetal similarly reacts, giving β-methyl-β′-carbethoxyethylaminobutacetal, b. p. about 150°/13 mm. This also cannot be caused to undergo intramolecular condensation; when heated alone at 200°, it is decomposed into β-methylaminobutacetal and a *compound* containing no nitrogen. γ-Methylaminobutyl alcohol (b. p. 65°/14 mm.) is obtained when the aldehyde (above) is reduced with sodium amalgam and dilute acetic acid.

The chloroacetal and dimethylamine interact in alcohol at 120—130° to give (yield 50%) *γ-dimethylaminobutacetal*, b. p. 92°/15 mm. (*methiodide*, m. p. 133°), which is hydrolysed by cold concentrated hydrochloric acid to the corresponding *aldehyde* (*chloroaurate*, m. p. 173°). The syrupy *hydrochloride*, as obtained from the preceding hydrolysis, when reduced as described above, affords *γ-dimethylaminobutyl alcohol*, b. p. 78°/14 mm. (*chloroaurate*, m. p. 131—132°; *methiodide*, m. p. 242°). The *benzoate* (m. p. 105°) is a very weak anæsthetic. *γ-Diethylaminobutacetal*, b. p. 105°/15 mm. (*methiodide*, m. p. 98—100°), similarly yields eventually *γ-diethylaminobutyl alcohol*, b. p. 85°/13 mm., the *benzoate* (m. p. 161°) of which has distinct anæsthetic potency. *γ-Piperidinobutacetal*, obtained by direct interaction of piperidine and the chloroacetal at 150—160°, has b. p. 125—135°/13 mm. It likewise eventually affords, by way of the *aldehyde* (*chloroaurate*, m. p. 97°), *γ-piperidinobutyl alcohol* (b. p. 110°; *chloroaurate*, m. p. 81°; *methiodide*, m. p. 112°); the *benzoate* (m. p. 159°) of which also has anæsthetic properties.

When β-chlorobutacetal is heated with aminoacetal at 125°, *γ-β′-diethoxyethylaminobutacetal*, b. p. 140—145°/14 mm., is obtained. This compound is rapidly decomposed when treated with hydrochloric acid, a mixture of products being formed.

W. A. Silvester.

Condensation of ammonium chloride with formaldehyde and acetone. C. Mannich and K. Ritsert (Arch. Pharm., 1926, **264**, 164—167; cf. A., 1917, i, 634).—The products obtained when ammonium chloride, formaldehyde, and acetone interact have been re-examined in the light of more recent experience with the corresponding products from methylamine hydrochloride (cf. this vol., 522). This product is a complex mixture; more than 50% (the residuum from a vacuum fractionation) is a resin. The distillate (b. p. 125—135°/15 mm.) tends to resinify on keeping or on re-distillation. It yields when treated with hydroxylamine (the only reagent giving a crystalline derivative) the *trioxime* (m. p. 132°; *hydrochloride*, m. p. 177—178°) of *tri-γ-keto*-n-*butylamine*. When the crude basic mixture is treated, without previous distillation, with cold alcoholic hydrogen chloride and afterwards distilled, the distillate (about 60% of the oily product; b. p. 60—130°/18 mm.) takes up methyl iodide to yield the methiodide (m. p. 173°) of 3-acetyl-1 : 4-dimethyltetrahydropyridine (cf. this vol., 523). Evidently the formaldehyde in excess has brought about methylation.

W. A. Silvester.

Mechanism of the synthesis of α-amino-acids by means of Strecker's reaction. II. Disappearance of ammonia and the intermediate reactions. III. C. Sannié (Bull. Soc. chim., 1926, [iv], **39**, 254—274; 274—278; cf. this vol., 276).—II. Disappearance of the ammonia is irregular, the form of the curve indicates the occurrence of consecutive reactions, and after a certain time ammonia reappears in the solution. At 20°, the variation in the constant $K=1/t \cdot x/a(a-x)$ is linear except for the first hour. In the case of the reaction between hydrocyanic acid and acetaldehydeammonia, the disappearance of the reactants takes place in a different manner. The curve representing the disappearance of ammonia in the action between this substance and α-hydroxypropionitrile confirms the hypothesis that the latter is the intermediate product in the course of Strecker's reaction. A study of the decomposition of α-aminopropionitrile and of its combination with lactonitrile seems to indicate that its decomposition is the chief perturbation factor in the disappearance of the ammonia. Two molecules of the aminonitrile condense to one of iminonitrile, liberating 1 mol. of ammonia. In all the reactions dealt with fresh perturbations are observed at the end of the second or third day.

III. The formation of hydroxynitriles, which is catalysed by hydroxyl ions, seems to take place in two stages, $R\cdot CHO+H_2O \longrightarrow R\cdot CH(OH)_2$ and $R\cdot CH(OH)_2+HCN \longrightarrow R\cdot CH(OH)\cdot CN+H_2O$. In the first reaction, ammonia is a better catalyst than stronger bases; this is ascribed to additional catalytic action on the part of ammonium ions. In Strecker's reaction the velocity is directly proportional to the rate of formation of the intermediate substance and thus directly proportional to the quantity of ammonia present. This quantity at time t depends on its initial concentration and on the amount formed by reason of the decomposition of the aminonitrile, so that there should be a double variation on calculating the velocity constant for the disappearance of hydrocyanic acid. K should decrease to a minimum in proportion to the diminution in the original concentration and increase towards the end of

the reaction. This accords with the experimental results. H. J. EVANS.

Configuration of *d*-glutamic acid, *d*-ornithine, and *d*-lysine. P. KARRER, K. ESCHER, and R. WIDMER (Helv. Chim. Acta, 1926, **9**, 301—323).—Attempts to prepare an active glutamic acid from an optically active serine gave, in every case, a racemic product. Benzoylation of the methyl ester hydrochloride of *d*-β-chloro-α-aminopropionic acid (A., 1907, i, 900) gives *methyl* d-β-*chloro-α-benzamidopropionate*, m. p. 114°, $[\alpha]_D^{18}$ +16·2° in absolute alcohol, which condenses with ethyl sodiomalonate to give inactive glutamic acid.

l-Benzoylasparagine, like *l*-acetylasparagine (A., 1923, i, 660), on treatment with bromine in barium hydroxide solution gives *l*-glyoxalid-2-one-5-carboxylic acid, converted by heating with hydrochloric acid into *d*-αβ-diaminopropionic acid monohydrochloride. *d*-Glutamine is similarly converted through the *acetyl* derivative, m. p. 199°, $[\alpha]_D^{21}$ −12·5° in water, into d-α*γ*-*diaminobutyric acid*, isolated as *oxalate*, decomp. at 205°, $[\alpha]_D^{18}$ +7·8° in water [cf. racemic oxalate (+2H_2O), m. p. 219°]. The *hydrochloride* has $[\alpha]_D$ +8·2° in water. The optical properties of the homologous series formed by the active diaminopropionic and diaminobutyric acids, *d*-ornithine, and *d*-lysine were examined for evidence of similar configuration in these compounds. In order to eliminate the complications introduced by salt-formation, the methyl and ethyl esters of the *N*-dibenzoyl derivatives were prepared. The hydrochlorides of all four acids are dextrorotatory. The esters of the *N*-dibenzoyl derivatives show uniformly negative rotations, differing little from each other in value in the two series. The ethyl ester shows in each case the smaller rotation. It is concluded that *d*-αβ-diaminopropionic acid, *d*-α*γ*-diaminobutyric acid, *d*-ornithine, and *d*-lysine are of similar configuration, that of *l*-asparagine. *d*-Glutamic acid, *d*-glutamine, *d*-ornithine, and *d*-lysine must accordingly possess the same configuration as *d*-alanine, *l*-serine, *l*-cystine, *l*-aspartic acid, *l*-histidine, and *l*-leucine (A., 1925, i, 1046). Evidence is adduced in support of the assumption that *l*-proline, and therefore *l*-hygrinic acid, *l*-stachydrine, and *l*-nicotinic acid, must also be included in this group. A third sub-group of naturally-occurring amino-acids of like configuration, *l*-phenylalanine, *l*-tyrosine, and *l*-dihydroxyphenylalanine (A., 1921, i, 788; 1924, i, 1068), remains as yet unrelated, whilst the configurations of valine, *iso*leucinc, tryptophan, and hydroxyproline are not yet established. Comparison of the specific rotations of alanine, leucine, and tyrosine with those of the *N*-acetyl derivatives and their methyl esters (cf. Clough, J.C.S., 1918, **113**, 526) shows that in *d*-alanine and *l*-leucine conversion into the acetamido-derivative is accompanied by diminished rotation, whilst in tyrosine the rotation is increased. The difference in chemical constitution must, however, be taken into account. It becomes increasingly probable that these natural constituents of albumin, together with the simpler alkaloids, possess a uniform configuration.

d-Dibenzoyl-αβ-diaminopropionic acid has m. p. 156—157° (cf. Fischer, A., 1907, i, 394, m. p. 171—172°), $[\alpha]_D^{18}$ −28·06° in sodium hydroxide solution (cf. Fischer, *loc. cit.*, $[\alpha]_D^{20}$ −35·76°), $[\alpha]_D^{15}$ −23·9° in methyl alcohol (*methyl* ester, m. p. 153—154°, $[\alpha]_D^{16}$ −21·58° in methyl alcohol; *ethyl* ester, m. p. 151°, $[\alpha]_D^{18}$ −13·3° in ethyl alcohol). d-*Dibenzoyl-α*γ*-diaminobutyric acid* has m. p. 149° (cf. inactive acid, m. p. 200—201°), $[\alpha]_D^{18}$ −18·15° in sodium hydroxide solution, $[\alpha]_D^{15}$ −16·36° in methyl alcohol (*methyl* ester, $[\alpha]_D^{17}$ −22·74° in methyl alcohol; *ethyl* ester, m. p. 133—134°, $[\alpha]_D^{18}$ −11·74° in ethyl alcohol). *d*-Ornithuric acid has $[\alpha]_D^{18}$ +10·1° in sodium hydroxide solution, $[\alpha]_D^{15}$ +1·6° in methyl alcohol (*methyl* ester, m. p. 145—146°, $[\alpha]_D^{17}$ −13·24° in methyl alcohol; *ethyl* ester, m. p. 155°, $[\alpha]_D^{19}$ −8·64° in ethyl alcohol). *d*-Lysuric acid has $[\alpha]_D^{20}$ +3·07° in sodium hydroxide solution, $[\alpha]_D^{15}$ −8·59° in methyl alcohol (*methyl* ester, m. p. 114°, $[\alpha]_D^{17}$ −18·62° in methyl alcohol; *ethyl* ester, m. p. 101°, $[\alpha]_D^{19}$ −16·24° in ethyl alcohol). Rotation dispersions are given for each ester. *d*-Alanine has $[\alpha]_D^{16}$ +14·07° in dilute hydrochloric acid, giving for the base $[\alpha]_D^{16}$ +10·0°. d-*Acetylalanine*, m. p. 116° after sintering, has $[\alpha]_D^{16}$ −45·59° in water (*methyl* ester, $[\alpha]_D^{16}$ −64·30° in water). *Acetyl-leucine*, sintering at 155°, m. p. 167°, remelting at 155°, has $[\alpha]_D^{16}$ −12·09° in alcohol (*methyl* ester, m. p. 74—75°, $[\alpha]_D^{16}$ −17·22° in water).

d-αβ-Diaminopropionic acid gives the *methyl* ester *hydrochloride*, decomp. 183° after softening at 170°, $[\alpha]_D^{15}$ +18·51° in water. The free ester, kept for 5 days at the ordinary temperature, gives a white *dipeptide*, $[\alpha]_D^{20}$ +20° in water [*picrate*, m. p. 200—210° (decomp.)]. d-*Acetylglutamic acid* has m. p. 195° after sintering.

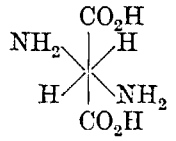
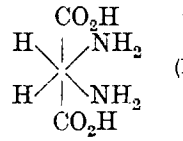
It is suggested that the new symbols, λ and ϱ, might with advantage be used to indicate lævo- and dextro-configuration in optically active compounds, reserving the symbols *l* and *d* for observed sign of rotation. M. CLARK.

Formation of anhydrides of amino-acids and peptides.—K. SHIBATA (Bull. Chem. Soc. Japan, 1926, **1**, 19—21).—A reply to Abderhalden and Schwab. A. DAVIDSON.

Identification of creatine. R. J. WILLIAMS and P. A. LASSELLE (J. Amer. Chem. Soc., 1926, **48**, 536—537).—When heated so that the temperature rises about 10° per min., creatine darkens and finally decomposes with effervescence at about 291°. Its identification is assisted by its quantitative loss of water of crystallisation (12·082%) at 100°, and by its conversion into creatinine, the latter being identified by the m. p. of the pierate and by the Jaffe reaction. F. G. WILLSON.

Stereochemistry of the tetrahedral carbon atom. III. Configuration of the diaminosuccinic acids. II. R. KUHN and F. ZUMSTEIN (Ber., 1926, **59**, [*B*], 479—488; cf. A., 1925, i, 780, 1249). *meso*-αβ-Diaminosuccinic acid is smoothly converted by an excess of concentrated hydrochloric acid into a sparingly soluble *dihydrochloride*, whereas, under similar conditions, the *dl*-acid remains dissolved, but yields a monohydrochloride on addition of alcohol to the solution. meso-αβ-*Diaminosuccinic acid*

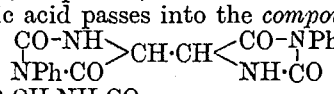
dihydrobromide, decomp. 204°, and dl-αβ-*diaminosuccinic acid monohydrobromide*, decomp. about 205°, are similarly obtained. Very energetic treatment with the halogen acid transforms the *dl*-acid into the *dihydrochloride*, decomp. about 180°, and *dihydrobromide*, decomp. about 180°, but these salts are unstable. meso-αβ-*Diaminosuccinic acid sulphate* decomposes at about 203°. The preparation of a monohydrochloride or monohydrobromide of the *meso*-acid has not been achieved. The differing ease with which the two acids form salts is attributed to the differing basicity of the amino-groups, the assumption being made that salt formation is rendered more difficult by the close proximity of the second amino-group to the group $\cdot NH_3^+$. The projection formulæ (I) and (II) are attributed to the *meso*- and

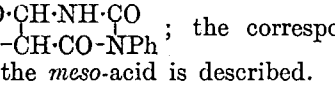
(I.)  (II.) 

dl-acid, respectively. Direct confirmation of this hypothesis by determination of the dissociation constants of the two acids has not proved possible, but support for it is forthcoming from observations on other diamines (this vol., 513). The isomerisation of the *dl*- to the *meso*-acid by protracted heating with 15% hydrochloric acid and failure to effect the reverse transformation under far more drastic conditions is in harmony with the suggested formulæ.

Hydrolysis of *l*-dibenzamidosuccinic acid with 15% hydrochloric acid affords a mixture of *meso*-αβ-diaminosuccinic acid and l-αβ-*diaminosuccinic acid*, $[\alpha]_D^{20}$ −18·9° in 10% hydrochloric acid, $[\alpha]_D^{20}$ −10·1° in 0·3*N*-potassium hydroxide solution. Treatment of the optically active acid with nitrosyl bromide yields impure *d*-dibromosuccinic acid, but it is uncertain whether partial racemisation occurs, since the optical homogeneity of the diamino-acid is not established. The *r*-acid is transformed by nitrosyl chloride or bromide into the corresponding *r*-halogeno-acid, whereas the *meso*-acid affords the *meso*-dibromo- and dichloro-acids in which the presence of the racemic form could not be detected. Similar results are obtained by the addition of silver nitrite to solutions of the diaminosuccinic acids in concentrated hydrochloric or hydrobromic acid. Nitrous acid converts *dl*-diaminosuccinic acid exclusively into *r*-tartaric acid. In all cases, replacement of the $\cdot NH_2$ group by ·OH, Cl, or Br occurs without change of configuration or a Walden inversion takes place simultaneously at each asymmetric centre. The action of sodium, barium, or silver nitrite (1 mol.) in hydrochloric or sulphuric acid solution on the diaminosuccinic acids yields about 50% of unchanged acid and 50% of tartaric or dichlorosuccinic acid; the formation of aminohydroxysuccinic acid could not be detected.

The action of naphthalene-2-sulphonyl chloride dissolved in ether on a solution of *meso*-diaminosuccinic acid in aqueous alkali hydroxide affords meso-αβ-*di*-2-*naphthalenesulphonamidosuccinic acid*, m. p. 234°; dl-αβ-*di*-2-*naphthalenesulphonamidosuccinic acid* has m. p. 200°. The *dl*-acid is transformed by phenylcarbimide into dl-αβ-*diphenylcarbamidosuccinic acid*, m. p. 200°, which when evaporated with hydrochloric acid passes into the *compound*



or  ; the corresponding *derivative* from the *meso*-acid is described. H. WREN.

Benzoylation of diacetomethylenediamide. P. KNUDSEN (Ber., 1926, **59**, [*B*], 367).—The product obtained by the benzoylation of diacetomethylenediamide (cf. A., 1915, i, 220) is identified as benzoic anhydride instead of as methylene dibenzoate; the anhydride appears to retain formaldehyde with great tenacity, thus accounting for the results of previous analyses. H. WREN.

Hydrolysis of cyanic acid. W. R. FEARON and G. C. DOCKERAY (Biochem. J., 1926, **20**, 13—16).—In the hydrolysis of potassium cyanate, carbamic acid is formed in concentrations greater than would be required if it were produced from ammonium carbonate as an equilibrium component. It is concluded that carbamic acid represents the first stage in the hydrolysis of cyanic acid and that it is probably formed by direct hydration of the ketonic form of cyanic acid. S. S. ZILVA.

Applicability of lithium in place of sodium for organic syntheses. C. A. ROJAHN and J. SCHULTEN (Ber., 1926, **59**, [*B*], 499—501).—The possibility of substituting lithium or lithium alkoxide for sodium or its derivative has been tested for the following reactions: etherification (benzyl ethyl ether); Fittig's hydrocarbon synthesis (ethylbenzene); preparation of acid anhydride from acid chloride and lithium or sodium salt of the acid (acetic anhydride); introduction of an alkyl group into ethyl malonate or ethyl acetoacetate; condensation by means of lithium or sodium alkoxide (acetoacetic ester; ethylmalonic ester); Perkin's cinnamic acid synthesis; pinacone synthesis; preparation of ethyl orthoformate; synthesis of ketones from salts of aliphatic and aromatic acids (acetone, benzophenone); Grignard's reaction with lithium in place of magnesium. In general, the yields are lower with lithium than with sodium except in the alkylation of ethyl acetoacetate and the preparation of ketones by the dry distillation of lithium salts. H. WREN.

Luminescent Grignard compounds. W. V. EVANS and E. M. DIEPENHORST (J. Amer. Chem. Soc., 1926, **48**, 715—723; cf. A., 1923, ii, 714).—Of ninety Grignard compounds examined, all except twenty-one showed chemiluminescence on oxidation. Of the latter, eleven were chlorides where formation of the Grignard compound was not certain, and nine contained radicals of low mol. wt. The observation of Dufford (*loc. cit.*) that luminescence does not appear except when the magnesium is attached to an unsaturated carbon atom, was not confirmed, whilst luminescence is shown, as stated by Moeller (Arch. Pharm. Chem., 1914, **21**, 449), by magnesium propyl, *iso*amyl, and benzyl bromides, but not by magnesium

ethyl bromide. The brightness of the luminescence is in proportion to the mol. wt. of the halogen derivative so long as the nature of this remains unaltered, or, in the case of aromatic derivatives, the position of substituents remains unchanged. Generally, the bromides show strong luminescence, whilst the iodides are weak, in this respect. *p*-Substituted derivatives show markedly greater luminescence than *o*- and *m*-. The last two stand in this order, with only slight difference between them. Luminescence from magnesium phenyl halides is dim. One substituent in the phenyl group increases the luminescence, whilst the introduction of a second group again decreases it. In the case of phenyl radicals containing two alkyl substituents, brightness of luminescence is in the decreasing order 3 : 4-, 2 : 4-, and 3 : 5-, these positions being relative to the magnesium atom. The solvent influences the luminescence only in proportion to its solvent power for the Grignard compound, and accordingly as the rate of oxidation is reduced by the viscosity of the solution. Photographs of the chemiluminescence spectra of a number of Grignard compounds are included. As oxidation proceeds, the light emitted moves towards the red end of the spectrum, an effect possibly attributable to the superimposition, on the luminescence, of the fluorescence of the compound produced by oxidation. F. G. WILLSON.

Oxidation of magnesium aryl halides. H. GILMAN and A. WOOD (J. Amer. Chem. Soc., 1926, **48**, 806—810).—In the production of phenol by the oxidation, with pure or atmospheric oxygen, of magnesium phenyl bromide in ethereal solution, the yield is limited on account of the simultaneous formation of up to 18% of phenylmethylcarbinol, as well as benzene and diphenyl (cf. Wuyts, A., 1909, i, 448). The production of phenylmethylcarbinol is ascribed to the interaction of the Grignard compound with acetic acid or its acetal, derived from decomposition of the α-ethoxyethyl hydrogen peroxide (cf. Clover, A., 1924, i, 363), whilst the benzene is formed by reduction of the Grignard derivative by hydrogen from the above peroxide, or from the monoacetal, ethyl alcohol, or acetic acid, into which the peroxide may also decompose. As the production of secondary alcohols is much greater than would correspond with the amount of peroxide which can be isolated from the oxidation of ether alone, it appears that the oxidations are mutually autocatalytic. Phenol is obtained in good yield by this method when phenetole, which does not undergo autoxidation, is used as the solvent. In ether, an average yield of phenol of 26% was obtained at 0°, cooling below this temperature showing little advantage. When ethereal magnesium phenyl bromide is boiled under reflux in the ordinary apparatus into which air can diffuse through the calcium chloride–soda-lime drying tube, a 6·8% yield of phenol is obtained in 8 hrs. When most of the ether was replaced by benzene or toluene, the yield of phenol rose, under the same conditions, to 16·1% and 21·9%, respectively.

When the magnesium phenyl bromide was hydrolysed immediately after its preparation in ethereal solution, 2·9% of phenol was obtained (cf. Porter and Steel, A., 1921, i, 140), whilst if the ether had been previously treated with dry oxygen at 0° for 7 hrs., the yield of phenol was 6·9%, and 16·4% when oxygen was passed in during the formation of the Grignard compound. The yield of phenol is only slightly affected by varying the rate of adding oxygen or the quantity of ether present. Oxidation of magnesium *p*-tolyl bromide gave *p*-cresol (15·3%), di-*p*-tolyl (16%), toluene (11%), and *p*-tolylmethylcarbinol (11%). When an ether–toluene solution of magnesium phenyl bromide was boiled for 19 hrs. at 108° with yellow mercuric oxide, the yield of phenol was 15·1%. In ethereal solution, boiling for 10 hrs. with silver oxide gave phenol in 18% yield, whilst boiling for 5 hrs. with sodium peroxide gave phenol in 14·5% yield. F. G. WILLSON.

Asymmetric dialkylarsinic acids. Methylethylarsinic acid. M. GUERBET (Compt. rend., 1926, **182**, 638—640).—Ethyl chloride reacts with methylarsenious oxide in presence of alcoholic potassium hydroxide, giving *methylethylarsinic acid*, m. p. 120—121°, which behaves as a weak monobasic acid, stable to mild reducing agents, reduced by phosphorous acid, forming probably the arsenious oxide, whilst hypophosphorous acid liberates free arsenic. Crystalline *sodium* and *potassium* salts have been obtained. α-Chloropropane reacts similarly with methylarsenious oxide, giving *methyl-n-propylarsinic acid*. L. F. HEWITT.

Antimonial analogues of the cacodyl series. G. T. MORGAN and G. R. DAVIES (Proc. Roy. Soc., 1926, **A**, **110**, 523—534).—When trimethylstibine dibromide is distilled under reduced pressure in a current of carbon dioxide, methyl bromide and *dimethylstibine bromide*, m. p. 89°, are formed. *Dimethylstibine chloride*, b. p. 155—160°/750 mm., and *iodide*, m. p. 86°, are prepared by analogous reactions. The corresponding oxyhalides are produced by regulated oxidation of the dimethylstibine halides, the *oxychloride* and *oxybromide* being white and the *oxyiodide* yellow. *Methylstibine dichloride*, b. p. 115—120°/60 mm., *dibromide*, m. p. 42°, and *diiodide*, m. p. 110°, were prepared from the dimethylstibine series by halogenation and demethylation. *Dimethylstibine trichloride*, m. p. 105—110° (decomp.), *tribromide*, and the unstable *tri-iodide* are described. The monomethylated antimonials are far less oxidisable than the dimethyl compounds and are not spontaneously inflammable in air. Dimethylstibine oxybromide is slowly hydrolysed in boiling water to *dimethylstibinic acid*, and dimethylstibine bromide in alkaline solution to *dimethylstibine oxide*, a colourless oil. Hydrolysis of the monomethyl dihalides yields *methylstibine oxide*, and their treatment with hydrogen sulphide gives *methylstibine sulphide*, m. p. 70°. Attempts to prepare *tetramethyldistibine* (*antimony cacodyl*) were only partly successful. In addition to the desired reaction, $2SbMe_2Br+M=MBr_2+Sb_2Me_4$, a reversion to trimethylstibine also occurred. The presence of antimony cacodyl was demonstrated, however, by the yellow complex *compound*,

$$2SbMe_2I,SbMe_4I,MeI,$$

formed with methyl iodide. F. G. SOPER.

Dimethylstibine cyanide, an analogue of cacodyl cyanide. G. T. MORGAN and V. E. YARSLEY (Proc. Roy. Soc., 1926, **A**, **110**, 534—537).—*Trimethylstibine cyanobromide*, prepared by the action of cyanogen bromide on trimethylstibine, is readily hydrolysed to *trimethylstibine hydroxybromide*, but when heated at 160—180° under reduced pressure, the cyanobromide loses methyl bromide and yields *dimethylstibine cyanide*, m. p. 113—114°; this readily oxidises in the air, forming *dimethylstibine oxycyanide*. Treatment of trimethylstibine hydroxybromide with silver oxide yielded *trimethylstibine dihydroxide*, and this on addition of concentrated hydrochloric acid gave *trimethylstibine hydroxychloride*.

F. G. SOPER.

Geometrical stereoisomerism in the *cyclo*hexane series. IV. Action of magnesium phenyl bromide on *cyclo*hexene oxide; *o*-phenyl-*cyclo*hexanols; *cyclo*hexane-1 : 2-diol bromohydrin; Δ^{β}-*cyclo*hexenol. P. BEDOS (Bull. Soc. chim., 1926, [iv], **39**, 292—305; cf. Godchot and Bedos, this vol., 164, 280).—The action of magnesium phenyl bromide on *cyclo*hexene oxide, followed by treatment of the product with water, results in the formation of cyclo*hexane*-1 : 2-*diol bromohydrin*, b. p. 87—88°/9 mm., d_{12}^{12} 1·402, n_D^{12} 1·528 (*phenylurethane*, m. p. 87—88°), and Δ^{β}-*cyclo*hexenol, b. p. 65°/7 mm., together with some diphenyl, an *o*-*phenyl*cyclo*hexanol*, b. p. 138—140°, d_{16}^{16} 1·035, n_D^{16} 1·5415, and a small quantity of a hydrocarbon. The *o*-phenol-*cyclo*hexanol yields a *phenylurethane*, m. p. 135—136°, and a *hydrogen phthalate*, m. p. 185—186°, and thus appears to be distinct from that prepared by Braun, Gruber, and Kirschbaum (A., 1923, i, 107). The latter is regarded as the *trans*-isomeride, as the above method of formation indicates that the compound, b. p. 138—140°, has the *cis*-structure. The Δ^{β}-*cyclo*hexenol appears to be identical with that described by Brunel (A., 1905, i, 869). The author regards its formation as due to decomposition of the bromohydrin and not as a result of a reaction taking place according to the method suggested by Blaise (A., 1902, i, 357). Attempts to hydrogenate the *cis*-compound failed, and both chromic and permanganic oxidation yielded no definite results. The general conclusion is reached that a halogen compound of the aromatic series may replace an aliphatic compound without changing the general character of the reaction.

H. J. EVANS.

Nitration of decahydronaphthalene. S. NAMETKIN and O. MADAEFF-SSITSCHEFF (Ber., 1926, **59**, [*B*], 370—374).—Technical decahydronaphthalene is converted by prolonged boiling with dilute nitric acid (*d* 1·2) into a mixture of nitro-compounds which are separated from one another by means of alcoholic potassium hydroxide. The insoluble portion consists mainly of 9-*nitrodecahydronaphthalene*, b. p. 96—97°/2 mm., d^{20} 1·0847, n^{20} 1·4944, with some 9 : 10-*dinitrodecahydronaphthalene*, m. p. 164° (decomp.). The mononitro-compound is reduced by zinc dust in acetic acid solution to 9-*aminodecahydronaphthalene*, b. p. 98°/15 mm., d_4^{20} 0·9435, n^{20} 1·4932 (*hydrochloride*; *benzoyl* derivative, m. p. 148—149°), which is converted by potassium nitrite into 9-*hydroxydecahydronaphthalene*, m. p. 65°, and an *octahydronaphthalene* ($\Delta^{9:10}$ or $\Delta^{1:9}$), b. p. 88—89°/14 mm., d_4^{20} 0·9200, n^{20} 1·4979. The part of the nitro-product soluble in alkali hydroxide affords 1-*nitrodecahydronaphthalene*, b. p. 108—109°/14 mm., d_4^{20} 1·0825, n^{20} 1·4978; the position of the nitro-group is established by oxidation of the compound in alkaline solution by potassium permanganate to α-ketodecahydronaphthalene which gives a mixture of the semicarbazones of the *cis*- and *trans*-forms.

H. WREN.

Formation of triphenylmethyl in the ethyl acetoacetate synthesis. F. F. BLICKE (J. Amer. Chem. Soc., 1926, **48**, 738—739).—Triphenylmethyl bromide reacts quantitatively with ethyl sodioacetoacetate in ether–benzene (cf. Allen and Kölliker, A., 1885, 655), with formation of triphenylmethyl and the triphenylmethyl derivative of ethyl acetoacetate. The former imparts a deep orange colour to the reaction mixture, which disappears on shaking with air, and the product, after removal of the solvent and hydrolysis with alcoholic sodium hydroxide, affords triphenylmethyl peroxide and ββ′β″-triphenylpropionic acid, m. p. 177—178° (cf. Henderson, J.C.S., 1887, **51**, 226).

F. G. WILLSON.

Action of α-particles on benzene vapour. W. MUND and E. BOGAERT (Bull. Soc. chim. Belg., 1925, **34**, 410—415).—The α-radiation from niton acts on liquid benzene to produce a small quantity of a gas not liquefied at −78°, together with a viscous, non-volatile substance with a bitter, penetrating odour. From observations of the fall of pressure in benzene vapour at 100° subjected to the action of the same α-radiation, it is calculated that $2{\cdot}1\times10^5$ mols. of gas are removed by each α-particle, a figure identical with that assigned by Bragg to the number of pairs of ions produced in benzene by one α-particle from niton.

G. M. BENNETT.

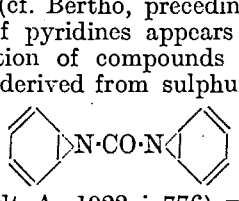
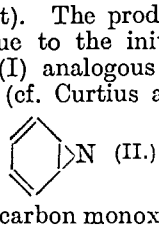
Behaviour of hydrazoic acid and ammonium azide in benzene and *p*-xylene under pressure. A. BERTHO (Ber., 1926, **59**, [*B*], 589—595; cf. Schmidt, A., 1924, i, 721).—Hydrazoic acid in benzene at about 200—210° or in *p*-xylene at about 150° undergoes thermal decomposition into nitrogen and ammonium azide. The possible introduction of the imino-group into the benzene ring can therefore only be effected at higher temperatures at which ammonium azide decomposes in accordance with the scheme: $N_4H_4 = NH_3 + {:}NH + N_2$. In *p*-xylene at 200—210°, disappearance of ammonium azide is observed, but the production of a primary amine could not be established in consequence of experimental difficulties. More definite results are obtained by the use of pre-formed ammonium azide in benzene at 260—280° or *p*-xylene at 250—260°, the higher temperature appearing necessary on account of the smaller pressure developed during the change. Under these conditions, the imino-group is mainly hydrogenated to ammonia, partly in accordance with the scheme $3NH{:} = NH_3 + N_2$, partly by hydrogen withdrawn from the hydrocarbons, which are consequently converted into substances resembling humus. To a smaller extent, it becomes attached to the benzene ring with production of aniline and *p*-xylidine, respectively. The

bases have an odour of pyridine, which, however, cannot be present in more than minimal amount.

H. WREN.

Action of carbonyl azide, CON_6, on aromatic hydrocarbons. T. CURTIUS and A. BERTHO (Ber., 1926, **59**, [*B*], 565—589).—The action of carbonyl azide on benzene, toluene, *p*-xylene, and *p*-cymene has been investigated. For this purpose, the concentrated aqueous solution of carbohydrazide hydrochloride is treated with sodium nitrite and the azide is extracted directly from the solution by the hydrocarbon under investigation. The extract is dried for a short time over calcium chloride and subsequently heated in an enamelled iron autoclave at about 150°. The procedure is rendered necessary by the highly explosive nature of carbonyl azide, but suffers from the drawbacks that more moisture than is desirable is present during the experiments and that hydrazodicarbonazide (obtained as by-product of the action of nitrous acid on carbohydrazide) may be introduced in small amount although it is sparingly soluble in aromatic hydrocarbons. In all cases, the product of the reaction is a brown liquid containing a considerable quantity of brown humus. The basic components are separated from one another by fractional precipitation of their ethereal solutions by ethereal picric acid or by fractional crystallisation of their picrates from alcohol. The yield of bases is small. Benzene gives pyridine and very little aniline, toluene affords 4-methylpyridine and a little *o*-toluidine, 2 : 5-dimethylpyridine and *p*-xylidine are derived from *p*-xylene, whereas *p*-cymene yields carvacrylamine and 2-methyl-5-*iso*propylpyridine (or 5-methyl-2-*iso*propylpyridine). The humus contains a considerable proportion of nitrogen. When hydrolysed with hydrochloric acid, it affords ammonia, very small quantities of the appropriate bases, and carbon dioxide. It appears, therefore, to consist of compounds of high mol. wt. derived from undecomposed azide residues and hydrocarbon molecules.

Since the gases evolved during the action of carbonyl azide on hydrocarbons consist of nitrogen, carbon monoxide, and carbon dioxide, the formation of amines may be explained by assuming that the azide immediately loses 2 mols. of nitrogen with production of the "fixed residue," :N·CO·N:, which unites with two benzene nuclei, giving diarylcarbamides. These have not been isolated, and appear to be hydrolysed by water to carbon dioxide and the corresponding primary amine. This conception is in harmony with the observed ratio of carbon dioxide to *p*-xylidine in experiments with *p*-xylene. The production of primary amines in this manner has nothing in common with their formation from aromatic hydrocarbons and azoimide or ammonium azide (cf. Bertho, preceding abstract). The production of pyridines appears to be due to the initial formation of compounds of type (I) analogous to those derived from sulphuryl azide (cf. Curtius and

(I.)   (II.)

Schmidt, A., 1922, i, 776), which lose carbon monoxide and yield two residues of type (II). The nitrogen of the latter compounds then appears to pass into the ring with extrusion of a methine group the fate of which could not be determined.

The following new or amended data are incidentally recorded : 2 : 5-dimethylpyridine picrate, m. p. 163·5° (corr.) ; 2 : 5-*dimethylpyridine chloroplatinate* ($+2H_2O$), m. p. 191° (decomp.), which does not appear to be identical with the salt of the same composition, m. p. 194°, obtained by Garrett and Smythe (Proc. C.S., 1902, **18**, 47); p-*xylidine chloroplatinate*, m. p. (indef.) 195—198° (decomp.) after softening ; 4-methylpyridine picrate, m. p. 164° ; 2(?5)-*methyl*-5(?2)-iso*propylpyridine picrate*, m. p. 167·5° ; 2(?5)-*methyl*-5(?2)-iso*propylpyridine chloroplatinate*, m. p. 131°.

H. WREN.

Dependence of rotatory power on chemical constitution. XXVIII. *d*-*sec*.-Butylbenzene. P. W. B. HARRISON, J. KENYON, and J. R. SHEPHERD (J.C.S., 1926, 658—663).—*sec*.-Butylbenzene has been prepared in apparently an optically pure condition. The inactive hydrocarbon was nitrated and gave principally *p*-nitro-*sec*.-butylbenzene. This was reduced to *p*-amino-*sec*.-butylbenzene and this converted into the *hydrogen tartrate*, which was fractionally crystallised. Elimination of the amino-group from the optically active base obtained by decomposing the salt gave optically active *sec*.-butylbenzene. *d*-*p*-Amino-*sec*.-butylbenzene has $[\alpha]^{20}_{5461}$ +41°, whilst *d*-*sec*.-butylbenzene has $[\alpha]^{20}_{5461}$ +33·15°, n^{25}_{5461} 1·4915, d^{20}_4 0·8639. Both the amine and the hydrocarbon have very high optical rotatory dispersive powers : $\alpha_{4359}/\alpha_{5461}=1{\cdot}87$ and 1·81, respectively.

A. E. MITCHELL.

1-Phenylnaphthalene. R. WEISZ and K. WOIDICH (Monatsh., 1926, **46**, 453—458).—When 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene is treated with magnesium phenyl bromide, the intermediate compound readily loses water with formation of 1-*phenyl*-3 : 4-*dihydronaphthalene*, b. p. 175—177°/12 mm., which is converted by sulphur at 250° into 1-*phenylnaphthalene*, b. p. 334°/770 mm. This hydrocarbon is also obtained by the dehydrogenation of 1-α-*naphthyl*-2 : 3 : 4 : 5-*tetrahydrobenzene*, m. p. 36°, which is obtained by the action of magnesium α-naphthyl bromide on *cyclo*hexanone. When 1-phenylnaphthalene (*bromo*-derivative, m. p. 70°, and *sodium monosulphonate* are described) in acetic acid solution is treated with nitric acid, it yields 5(or 8)-*nitro*-1-*phenylnaphthalene*, m. p. 132°, which is readily reduced to 5(or 8)-*amino*-1-*phenylnaphthalene* [*hydrochloride*, m. p. 234° (decomp.); *acetyl* derivative, m. p. 169—170°]. Since this base couples with diazotised *p*-nitroaniline to yield p-*nitrobenzeneazo*-5(or 8)-*amino*-1-*phenylnaphthalene*, m. p. 220—222°, which reduces to a *p*-diamine, p-*diamino*-1-*phenylnaphthalene* (*diacetyl* derivative, m. p. 278°), it follows that the original nitro-group must occupy either the 5- or 8-position.

R. W. WEST.

Electrochemical oxidation of aromatic hydrocarbons containing nuclear chlorine. F. FICHTER and M. ADLER (Helv. Chim. Acta, 1926, **9**, 279—287 ; cf. A., 1922, i, 37 ; 1925, i, 1055).—Electrolytic oxidation of chlorobenzene in an emulsion with aqueous

sulphuric acid, using a lead dioxide anode and no diaphragm, gives *p*-benzoquinone and, thence, succinic acid. The intermediate formation of *p*-chlorophenol is postulated. This substance undergoes electrolytic oxidation to *p*-benzoquinone more readily than chlorobenzene. The efficiency of the oxidation is increased in either case by use of a diaphragm. Oxidation of *p*-chlorotoluene under similar conditions gives *p*-chlorobenzaldehyde and *p*-chlorobenzoic acid. The yield of aldehyde increases with rising current density, reaching a maximum (10%) at 0·009 amp./cm.^{2} and afterwards falling off. The yields of acid (33·6% at 0·0018 amp./cm.^{2} and 10·5% at 0·0126 amp./cm.^{2}) and of acid and aldehyde combined diminish throughout the rise in current density. In alkaline emulsion at 60°, the product is exclusively *p*-chlorobenzoic acid. This substance is not readily susceptible to electrolytic oxidation. In alkaline solution, it is scarcely attacked. In acetic acid solution containing a little dilute sulphuric acid, using a platinum electrode and a diaphragm, it yields at 60—70° *p*-chlorosalicylic acid. It was hoped that electrolysis of the sodium salt of *p*-chlorobenzoic acid might give indications of a Kolbe hydrocarbon synthesis or of intermediate peroxide formation. Electrolysis of the sodium salt in aqueous solution is, however, immediately checked by precipitation of the free acid. In presence of excess of alkali, further oxidation takes place, apparently in the nucleus, since no product which might be produced by a Kolbe synthesis can be isolated. Electrolytic oxidation of 2 : 4-dichlorotoluene in an emulsion with aqueous sulphuric acid, using a lead dioxide anode and no diaphragm, gives 2 : 4-dichlorobenzoic acid (maximum yield 6·5%). Oxidation of the sodium salt of this acid in aqueous or alkaline solution fails to give any trace of a Kolbe synthesis. Oxidation of the acid in sodium sulphate solution at 60° gives almost complete breakdown into carbon dioxide. These failures are not due to abnormal breakdown of *p*-chlorobenzoyl peroxide (A., 1925, i, 379) or of 2 : 4 : 2′ : 4′-tetrachlorodibenzoyl peroxide, since 4 : 4′-dichlorodiphenyl and 2 : 4 : 2′ : 4′-tetrachlorodiphenyl, respectively, are obtained by decomposition of these substances. M. CLARK.

Action of sodium ethoxide on *s*-trichlorodinitro- and -trinitro-benzene and of hydroxylamine on *s*-trinitrotrimethoxy(phenoxy)benzene. P. J. VAN RIJN (Rec. trav. chim., 1926, **45**, 257—266).—With the object of preparing hexanitrobenzene, *s*-trinitrotrimethoxybenzene was treated with hydroxylamine. The reaction observed by Borsche (A., 1923, i, 780, 1091) does not take place to any appreciable extent, the main product in ethyl-alcoholic solution being *s*-trinitrotriethoxybenzene. *s*-Trinitrotriphenoxybenzene behaves similarly, and it thus appears that in highly nitrated benzenes exchange of alkoxy- for the hydroxylamino-group does not take place.

1 : 3 : 5-Trichloro-2 : 4-dinitrobenzene is converted by 2 mols. of sodium methoxide at the ordinary temperature into a mixture of 1-*chloro*-2 : 6-*dinitro*-3 : 5-*dimethoxybenzene*, m. p. 218°, and 1-*chloro*-2 : 4-*dinitro*-3 : 5-*dimethoxybenzene*, m. p. 102°, with a little 1 : 3 : 5-trichloro-2-nitro-6-methoxybenzene, m. p. 45·5° (cf. Hugounenq, A., 1890, 241). The reaction is thus much more complex than the analogous reactions described by Jackson (A., 1897, i, 29) and Hüffer (A., 1921, i, 459). The structure of the two isomeric chlorodinitrodimethoxybenzenes follows (1) from the conversion of the isomeride, m. p. 218°, on heating with aniline into 4 : 6-dinitro-5-anilino-1 : 3-dimethoxybenzene (Blanksma, A., 1908, i, 147), the isomeride, m. p. 102°, similarly yielding 2 : 4-*dinitro*-1-*anilino*-3 : 5-*dimethoxybenzene*, red, m. p. 189°; and (2) from their nitration to the same 1-chloro-2 : 4 : 6-trinitro-3 : 5-dimethoxybenzene, m. p. 85°. The latter substance on treatment with sodium methoxide in benzene yields 2 : 4 : 6-*trinitro*-1 : 3 : 5-*trimethoxybenzene*, m. p. 75°. With hydroxylamine hydrochloride and sodium ethoxide in alcohol, this yielded, besides *s*-trinitrotriethoxybenzene, traces of a yellow substance, decomp. 200°, possibly $C_6(NO_2)_3(NH{\cdot}OH)_2{\cdot}OEt$. 1 : 3 : 5-Tribromo-2 : 4 : 6-trinitrobenzene, obtained by Jackson's method together with a substance, m. p. 233—234° (cf. A., 1888, i, 1276), was converted by sodium phenoxide in benzene (cf. Jackson, A., 1891, i, 1024) into 2 : 4 : 6-trinitro-I : 3 : 5-triphenoxybenzene, m. p. 181°. Hydroxylamine in ethyl-alcoholic solution converts the latter into the corresponding 1 : 3 : 5-triethoxy-compound, in methyl alcohol into the analogous methoxy-derivative. R. BRIGHTMAN.

Standardisation of the Sandmeyer reaction, with special applications. H. S. FRY and I. W. GROTE (J. Amer. Chem. Soc., 1926, **48**, 710—714).—The following procedures have been applied to the preparation of a number of halogen-substituted benzene derivatives by the Sandmeyer reaction, and the yields compared. The amine ($\frac{1}{8}$ mol.) is dissolved in 50% acetic acid (250 c.c.), the solution cooled to 0°, and 50 g. of ice are added. Sodium nitrite solution (15%; 70 c.c.) is then slowly introduced below the surface of the acetate solution, with mechanical stirring, which is continued for 10—30 min. after completion of the mixing. The diazonium acetate solution is then added, slowly and with agitation, to a solution (250 c.c.) of cuprous halide ($\frac{1}{8}$ mol.) and the corresponding halogen acid (1·5 mols.), either at 0—5°, in which case 50 g. of ice are added to the cuprous solution (" cold procedure "), or at the b. p., in which case the temperature is maintained at 100—105° by blowing in steam (" hot procedure "). Recovery of product from the reaction mixture is effected, in both cases, by steam distillation. Yields of the six *p*-dihalogenobenzenes, obtained as above in all possible ways from *p*-chloro-, bromo-, and iodo-aniline, varied from 67% to 83%, and from 67% to 81%, by the cold and hot procedures, respectively, the former giving the same or higher yields than the latter in all cases except in the preparation of *p*-chloroiodobenzene from *p*-chloroaniline. Substitution of cuprie for cuprous halide in the cold procedure gave considerably lower yields in the preparation of *p*-dichlorobenzene, and of *p*-chlorobromobenzene from *p*-bromoaniline, but appreciably higher yields in the preparation of the latter from *p*-chloroaniline, and of *p*-dibromobenzene. Yields

of dichloro-, chlorobromo-, chloronitro-, and bromonitro-benzenes from the corresponding chloro- and nitro-anilines were in the order: *para* (75—90%), *ortho* (48—80%), and *meta* (49—75%), except in the case of the dichlorobenzenes, where the *meta* stands second. The use of hot cupric solutions in the hot procedure affords yields of the order of 10%, with formation of azo-compounds and tar. Substitution of the chlorides of iron, cobalt, nickel, and manganese for the cuprous salt is equally unsatisfactory in the case of *p*-chloroaniline, except that ferrous chloride gave a 43% yield. From the point of view of the halogen atom introduced by the above standard procedures, yields are in the relative order Br>I>Cl.

F. G. WILLSON.

Hydrolysis of substituted benzyl chlorides and the theory of steric hindrance. S. C. J. OLIVIER (Rec. trav. chim., 1926, **45**, 296—306; cf. A., 1922, i, 646; 1923, i, 197, 769, 908).—From a study of the rates of hydrolysis of 2 : 4-, 2 : 6-, and 3 : 5-dibromobenzyl chlorides in aqueous alcohol at 83° and at 30°, in comparison with earlier results on the hydrolysis of the monobromo-derivatives, the author concludes that steric considerations play no part in the hydrolysis of the substituted benzyl chlorides. The velocity coefficients found, 0·00289 for the 2 : 4-, 0·00187 for the 2 : 6-, and 0·00084 for the 3 : 5-derivative at 83°, are slightly greater than the coefficients obtained by multiplying the velocity coefficient for benzyl chloride itself by the respective ratios representing the effect of *o*-, *m*-, and *p*-monobromination on the rate of hydrolysis, the bromine atoms in the dibromo-compounds being considered independently.

2 : 4-Dibromotoluene, b. p. 243·5—244·5°/761 mm., obtained from 4 : 6-dibromo-*p*-toluidine by the method previously described (this vol., 161), yields on chlorination only a crude dibromobenzyl chloride. Bromination at the b. p. yields 2 : 4-*dibromobenzyl bromide*, m. p. 40—41°, hydrolysed by potassium hydroxide to 2 : 4-*dibromobenzyl alcohol*, m. p. 81—81·5° (yielding on oxidation 2 : 4-dibromobenzoic acid, m. p. 172·5—173·5°), together with a *substance*, probably the corresponding dibromobenzyl ether, since on fractional distillation dibromotoluene and a dibromobenzaldehyde apparently result. 2 : 4-*Dibromobenzyl chloride* has m. p. 33·5—34°. 2 : 6-Dibromotoluene, b. p. 242·5—243·5°/753 mm.; 2 : 6-*dibromobenzyl bromide*, m. p. 80°; 2 : 6-*dibromobenzyl alcohol*, m. p. 110—110·5° (oxidised to 2 : 6-dibromobenzoic acid, m. p. 150—151°), and 2 : 6-*dibromobenzyl chloride*, m. p. 65—66°, were similarly obtained. Dibromo-*p*-toluidine has m. p. 73·5—74·5° (cf. Fries, A., 1906, i, 644), 3 : 5-*dibromobenzyl alcohol*, m. p. 107—107·5°, 3 : 5-*dibromobenzyl chloride*, m. p. 50—50·5°.

R. BRIGHTMAN.

Arylsulphuric acids. G. N. BURKHARDT and A. LAPWORTH, with F. ASHWORTH (J.C.S., 1926, 684—690).—Sodium phenyl sulphate is prepared in 90% yield by interaction of phenol with chlorosulphonic acid, dialkylaniline and carbon disulphide, followed by treatment with alkali (cf. Verley, A., 1901, i, 143) and a 60% yield is obtained when, instead of chlorosulphonic acid, a solution of sulphuric anhydride in liquid sulphur dioxide is used. Pyridine sulphuroanhydride has been employed in preparing potassium *p*- and *o*-nitrophenyl sulphates and potassium eugenyl sulphate, whilst good yields of arylsulphuric acids are obtained by means of potassium pyrosulphate and dialkylaniline (cf. Baumann, A., 1879, 148). The potassium, sodium ($+3H_2O$), barium, ammonium, and magnesium phenyl sulphates are described. Salts of the tolylsulphuric acids have been prepared; oxidation of potassium *m*-tolyl sulphate gives *potassium* m-*carboxyphenyl sulphate*; the potassium tolyl sulphates may be converted into *p*-toluidine tolyl sulphates. By these methods of obtaining arylsulphuric acids have been obtained *potassium α-naphthyl sulphate*, *potassium β-naphthyl sulphate* ($+4H_2O$), and potassium *iso*eugenyl sulphate.

F. M. HAMER.

Action of sulphur on the monochloroanilines. Mechanism of aromatic thionation and structure of sulphide dyes. H. H. HODGSON (J. Soc. Dyers and Col., 1926, **42**, 76—80; cf. A., 1925, i, 1104).—The main products formed by the action of sulphur on the chloroanilines are green, insoluble sulphurised complexes in each case, but under certain conditions small quantities of simpler intermediate substances have been isolated which throw light on the mechanism involved. Reaction between *o*-, *m*-, and *p*-chloroanilines and sulphur commences at about 170° and then proceeds so rapidly that after about 6 hrs. only the intractable complex results. The initial reaction, most marked in the case of the *o*-compound, is a condensation to a diphenylamine derivative as indicated by the appearance of a sublimate of the hydrochloride of the chloroaniline. Subsidiary reactions in the case of the *o*- and *m*-chloroanilines result in the formation of dichlorodiaminodiphenyl mono- and di-sulphides, whilst with the *o*- and *p*-chloroanilines the diphenylamine condensation is followed by thionation, and small amounts of the respective chloroaminothiodiphenylamines have been isolated, that from the *p*-compound being always found in greatest amount.

Acid extraction of the reaction mixture from *o*-chloroaniline yielded 3 : 3′-*dichloro*-4 : 4′-*diaminodiphenyl sulphide* (which on diazotisation and coupling with β-naphthol gave a red *azo* compound, $C_{32}H_{20}O_2N_4Cl_2S$) and the corresponding *disulphide*, which also gave a red *azo* compound, $C_{32}H_{20}O_2N_4Cl_2S_2$, under the same conditions. From *m*-chloroaniline were obtained 4 : 4′-*dichloro*-2 : 2′-*diaminodiphenyl sulphide*, and *disulphide* (relatively large in amount). The disulphide on diazotisation yielded 4-chlorobenzthiodiazole (cf. A., 1925, i, 532). From *p*-chloroaniline no simple thioamines were obtained. The respective residues left after acid extraction were washed with aqueous ammonia and water and then extracted with a mixture of ether and chloroform. This extract in the case of *o*-chloroaniline contained a *chloroaminothiodiphenylamine*, $C_{12}H_9NClS$, m. p. about 130° (indefinite), forming a *hydrochloride*, readily hydrolysed; diazotisation and coupling with β-naphthol gave a red *azo* compound, $C_{22}H_{16}ON_3ClS$. Only traces of such compounds were found in the case of *m*-chloroaniline. With *p*-chloroaniline the

main product is 3-*chloro*-9-*aminothiodiphenylamine*, the amount being at a maximum after 6 hrs.' heating and totally disappearing after about 12 hrs. The *hydrochloride*, greenish-white, readily hydrolysed solid, the *sulphate*, the *acetyl* derivative, $C_{14}H_{11}ON_2ClS$, softens at 120°, m. p. about 160°, and the *azo*-β-*naphthol* derivative are described. The final green complexes possess the characteristics of sulphide dyes in all but solubility in sodium sulphide and dissolve only in concentrated sulphuric acid. They have, so far, defied resolution. A. COULTHARD.

Abnormal course of Grignard reactions. G. STADNIKOV and A. WEIZMANN (J. pr. Chem., 1926, [ii], **112**, 177—186; cf. Stadnikov, A., 1915, i, 372; 1924, i, 388).—Magnesium is not attacked by a mixture of ethyl iodide and dimethylaniline, only the quaternary iodide being formed. If benzene be present, however, the quaternary iodide reacts slowly with the magnesium, and in the course of several years the metal dissolves completely, forming the compound $NPhMe_2EtMgI,C_6H_6$. Decomposition of this with water yields no ethane, but dimethylaniline and a little tertiary aliphatic amine. By the action of the magnesium compound on benzaldehyde, a complex is formed which when treated with water gives no secondary alcohol, but regenerates benzaldehyde. The etherate obtained by the action of magnesium propyl iodide in benzene on diphenylmethyl butyl ether similarly reacts with benzaldehyde to give a complex which regenerates benzaldehyde and diphenylmethyl butyl ether, together with a little α-phenylbutyl alcohol, when decomposed with water. Abnormal reaction seems to be an effect of high mol. wt. of the final complex. C. HOLLINS.

Conditions of formation of rings attached to the *o*-, *m*-, and *p*-positions of the benzene nucleus. II. Reduction of *m*- and *p*-phenylenediacetonitrile. A. F. TITLEY (J.C.S., 1926, 508—519).—Re-examination of the work of von Braun, Karpf, and Garn, concerning substances in which a heterocyclic ring is joined to the benzene ring in the *m*-position (A., 1920, i, 251) shows that in fact no ring formation takes place, for the amine described is in reality β-*m*-tolylethylamine, and the unsaturated hydrocarbon derived from it is *m*-methylstyrene. Reduction of *m*-phenylenediacetonitrile (b. p. 230—231°/20 mm., m. p. 27°) with sodium and alcohol gives *m*-tolylacetonitrile (*m*-tolylacetamide has m. p. 141—142°), *m*-xylene, hydrogen cyanide, and *m*-phenylene-ββ′-diethylamine, b. p. 162°/18 mm., together with a 40% yield of β-*m*-tolylethylamine, b. p. 97—98°/15 mm., 101—102°/18 mm. [hydrochloride, m. p. 160°; picrate, m. p. 174°; *benzoyl* derivative, m. p. 72°; *phenylthiocarbamide*, m. p. 86—87°, *platinum* salt, m. p. 246° (decomp.); quaternary *methiodide*, m. p. 237°], which is also obtained, together with *m*-xylene, by reduction of *m*-tolylacetonitrile [b. p. 245—247°/745 mm. (decomp.), 133°/15 mm.]. The condensation *compound* of β-*m*-tolylethylamine and piperonal, $C_{17}H_{17}O_2N$, m. p. 53—54°, by heating with methyl iodide and subsequent treatment with aqueous alcohol is converted into *methyl*-β-m-*tolylethylamine hydriodide*, m. p. 104° (or 107°?), which gives the *base*, b. p. 88—89°/12 mm. (*hydrochloride*, m. p. 134°; *picrate*, m. p. 126—127°). By boiling with methyl-alcoholic potassium hydroxide, the quaternary methiodide of β-*m*-tolylethylamine is converted into trimethylamine and *m*-methylstyrene, b. p. 61—62°/18 mm., d^{16} 0·906 (αβ-dibromo-α-*m*-tolylethane has m. p. 47°).

Reduction of *p*-phenylenediacetonitrile, m. p. 96°, gives *p*-xylene, with a 50% yield of β-*p*-tolylethylamine, b. p. 94—95°/13 mm. (also prepared by reduction of *p*-tolylacetonitrile, b. p. 135°/14 mm., m. p. 17°), hydrochloride, m. p. 216°; *picrate*, m. p. 155°; *platinum* salt, m. p. 234°; *benzoyl* derivative, m. p. 89°; quaternary *methiodide*, m. p. 244°. The base is converted by nitrous acid into β-p-*tolylethyl alcohol*, b. p. 112°/12 mm. (p-*nitrobenzoate*, m. p. 91°). With piperonal the base gives a *compound*, m. p. 107°, which on treatment with methyl iodide and aqueous alcohol yields *methyl*-β-p-*tolylethylamine hydriodide*, m. p. 149°; the *base* has b. p. 96°/12 mm. (*hydrochloride*, m. p. 191°; *picrate*, m. p. 135°). The quaternary methiodide of β-*p*-tolylethylamine is converted by methyl-alcoholic potassium hydroxide into *p*-methylstyrene, b. p. 59—60°/12 mm. (αβ-dibromo-α-*p*-tolylethane has m. p. 45—46°).

F. M. HAMER.

Catalytic reduction of α-nitronaphthalene to α-naphthylamine. A. N. PARRETT and A. LOWY (J. Amer. Chem. Soc., 1926, **48**, 778—782).—α-Nitronaphthalene is reduced to α-naphthylamine in ethylene glycol solution at 70° by hydrogen in presence of palladium-black. Using a pressure of 100 lb./sq. in., 5 g. of nitronaphthalene in 100 c.c. of solvent, and 0·2 g. of catalyst, a yield of 98·44% of amine was obtained in 3 hrs. In a given time, the yield of amine is increased as the temperature of reduction is raised from 50° to 100°. The yield of naphthylamine under the same conditions with different solvents increases in the order: glycerol, glycol, water, and *iso*propyl alcohol. Platinum and palladium oxide catalysts gave slightly better yields of naphthylamine than palladium-black in half the time, whilst nickel gives much lower yields, at temperatures varying from 70° to 240°, in various solvents. Pure nitronaphthalene gave a 93·9% yield of naphthylamine in presence of 1% of palladium oxide in 3 hrs. with hydrogen at 100 lb./sq. in. at 100—110°, whilst 4% of nickel at 250° yielded similarly 14·32% of the amine. F. G. WILLSON.

Chlorination and bromination of 4-aminodiphenyl. H. A. SCARBOROUGH and W. A. WATERS (J.C.S., 1926, 557—562).—N-*Chloro*-4-*acetamidodiphenyl*, m. p. 129·5° (obtained by the action of aqueous sodium hypochlorite on 4-acetamidodiphenyl in presence of sodium hydrogen carbonate), is converted, by addition of water to the alcoholic acetic acid solution, into 3-*chloro*-4-*acetamidodiphenyl*, m. p. 147°, which may be hydrolysed to 3-*chloro*-4-*aminodiphenyl*, m. p. 71° [*hydrochloride*, m. p. 217° (decomp.)]; 3 : 4-*dichlorodiphenyl* has b. p. 195—200°/15 mm., m. p. 46°, and gives 3 : 4-dichlorobenzoic acid on oxidation. 3-Chloro-4-acetamidodiphenyl may be converted into impure 3-*chloro*-4-*chloroacetamidodiphenyl*, but attempts to bring about a rearrangement of this have resulted only in loss

of chlorine. Chlorination of 4-acetamidodiphenyl in glacial acetic acid yields (impure) 3-chloro-4-acetamidodiphenyl and 3 : 5 : 4′-*trichloro-4-acetamidodiphenyl*, m. p. 236°, which is hydrolysed to 3 : 5 : 4′-*trichloro-4-aminodiphenyl*, m. p. 128°. Bromination of 4-aminodiphenyl gives 3 : 5-*dibromo-4-aminodiphenyl*, m. p. 119° (3 : 5-*dibromo-4-acetamidodiphenyl*, m. p. 162°; 3 : 5-*dibromodiphenyl*, b. p. 208°/15 mm., m. p. 15°, is oxidised to 3 : 5-dibromobenzoic acid); this is further brominated to 3 : 5 : 4′-*tribromo-4-aminodiphenyl*, m. p. 149° (*acetyl* derivative, m. p. 256°), which is also obtained by bromination of 4-acetamidodiphenyl, and is oxidised to *p*-bromobenzoic acid. Less vigorous bromination of 4-acetamidodiphenyl yields 4′-*bromo-4-aminodiphenyl*, m. p. 145°, and a little 3 : 4′-*dibromo-4-acetamidodiphenyl*, m. p. 197°, which on hydrolysis and subsequent bromination gives 3 : 5 : 4′-tribromo-4-aminodiphenyl. Suggestions are made to account for the orientation of substituents in the diphenyl molecule. All m. p. recorded are corrected. F. M. HAMER.

Stereochemistry of aromatic compounds. II. Dissociation constants of aromatic diamines and the spatial configuration of benzidine. R. KUHN and F. ZUMSTEIN (Ber., 1926, **59**, [*B*], 488—498; cf. A., 1925, i, 1249).—The first and second dissociation constants of *o*-, *m*-, and *p*-phenylenediamine have been deduced from measurements of the hydrogen-ion concentration in approximately equimolecular mixtures of free base and monohydrochloride and mono- and di-hydrochloride, respectively; the solvents used are water and approximately 50% aqueous methyl alcohol. The basicity of the first amino-group is increased 2·5-fold by transition from the *o*- to the *m*-compound and 16-fold by transition from the *m*- to the *p*-derivative. The acidity of the first carboxyl group in the benzenedicarboxylic acids is affected in the reverse order. Again, whereas benzoic acid is appreciably weaker than terephthalic acid in the first phase, aniline occupies a place between *o*- and *m*-phenylenediamine. The second dissociation constants of the phenylenediamines increase in the same sequence as the first constants, the behaviour being the opposite of that observed with the benzenedicarboxylic acids. The calculated and observed values for the distances between the ionogenic groups of the acids and amines are in harmony only in the case of *iso*phthalic acid. With the diamines, the distances between the amino-groups are uniformly less than expected from the röntgenometric data. If, with Bjerrum, the difference is attributed to the electron displacements in the carbon chain, it follows that the effect in benzene is influenced greatly by the nature of the substituent.

From the dissociation constants of benzidine in 50% methyl alcohol the distance between the amino-groups is calculated to be 7·5 Å.; this figure, considered in the light of observations with the diamines and dicarboxylic acids, must be regarded as a minimum value. This does not agree with Kaufler's formula, $\begin{matrix}C_6H_4\cdot NH_2\\ C_6H_4\cdot NH_2\end{matrix}$, for benzidine, but is compatible with the more usual conception, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NH_2$. Possibly a fixed formula cannot be assigned to the compound, which in the crystal lattice may exist as Kaufler's form, whereas the benzene nuclei are repelled from one another in solution and particularly in the salts in consequence of the mutual repulsion of the charged amino-groups. H. WREN.

Colouring matters derived from thiocarbodibenzidine. II. G. ROSSI and B. CECCHETTI (Gazzetta, 1925, **55**, 872—875).—The compound previously referred to (A., 1925, i, 701), now named thiocarbodibenzidine, readily yields *tetrazothiocarbodibenzidine chloride*, $CS(NH\cdot C_6H_4\cdot C_6H_4\cdot N{:}NCl)_2$. With sodium phenoxide in alkaline solution, this gives *bisphenolazothiocarbodibenzidine*,

$$CS(NH\cdot C_6H_4\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot OH)_2,$$

which decomposes without melting at 300° and acts as a yellow substantive dye for wool, silk, and cotton. The dilute solution of its sodium salt serves as an indicator, the orange-yellow colour disappearing when the reaction becomes acid. *Bis-β-naphtholazothiocarbodibenzidine*, similarly prepared, crystallises with 2 mols. of xylene; it is violet and does not melt, but decomposes, below 300°. T. H. POPE.

Reduction of aromatic nitro-compounds and action of alcoholic potassium hydroxide on arylhydroxylamines. E. BAMBERGER [with E. ORMEROD and E. REBER] (Ber., 1926, **59**, [*B*], 418—431).—The reduction of aromatic nitro-compounds in neutral solution to nitroso-, hydroxylamino-, and amino-compounds ("straight reduction") and in alkaline solution as a consequence of side reactions to azoxy-, azo-, hydrazo-, and amino-substances ("branched reduction") does not proceed so definitely as has been assumed generally. Thus nitrobenzene, when treated with zinc dust and water, affords azoxy- and azo-benzene and ammonia, in addition to phenylhydroxylamine (cf. Blaskopf, Diss., Zürich, 1895), and *p*-bromonitrobenzene in alcoholic solution is transformed by zinc amalgam in the presence of aqueous alum into 4 : 4′-dibromo-azo-, -hydrazo-, and -azoxy-benzene, in addition to *p*-bromophenylhydroxylamine (Stiegelmann, *ibid.*, 1896). Similarly, *p*-nitrotoluene is reduced by zinc and calcium chloride to *p*-tolylhydroxylamine, azoxy- and azo-toluene (L'Orsa, *ibid.*). In the expectation that the tendency towards "branched reduction" would be restricted by the presence of anti-reactive substituents in the molecule, the action of zinc dust and boiling alcoholic potassium hydroxide on nitrobenzene and its methyl derivatives containing the methyl groups in positions 2-, 3-, 4-, 2 : 3-, 2 : 4-, 2 : 5-, 3 : 4-, 2 : 6-, and 2 : 4 : 6- has been examined under comparative conditions. With the first eight compounds reduction affords preponderatingly azoxy-compounds or, if more drastic, azo- and hydrazo-derivatives. In general, amines are not produced, or only traces are formed; in a few instances, the production is somewhat greater, but even then is relatively subordinate. Addition of water appears to facilitate reduction. With the two di-*o*-methyl nitro-compounds the case is different, since the nitroxylene affords the very stable nitroso-xylene and xylylhydroxylamine, whilst nitromesitylene gives mesitylhydroxylamine and, apparently,

traces of nitrosomesitylene. Azoxyxylene is produced in small quantity from the nitroxylene, but nitromesitylene yields azoxymesitylene in such small amount that its presence could not be established with certainty. The proportion of amine obtained from the nitroxylene or nitromesitylene is much greater than that produced from the other eight nitro-compounds.

Aromatic azoxy-compounds are reduced by zinc dust and boiling alcoholic potassium hydroxide solution to azo- and hydrazo-compounds, the yields being so nearly quantitative that amines cannot be formed in more than minor amount. In this connexion, the di-*o*-substituted azoxyxylene is exceptional, since it is reduced with great difficulty and yields appreciable amounts of an amine; the production of azoxylene could not be detected. The behaviour of azoxymesitylene has not been examined.

The action of alcoholic potassium hydroxide at the atmospheric temperature on arylhydroxylamines generally leads predominatingly to azoxy-compounds; in certain cases, azo-derivatives result in appreciable amount and, occasionally, nitro- and amino-aryls. The formation of amines is particularly noticeable with the di-*o*-methylated nitro-compounds. Presumably in all cases the azoxy-compounds are formed from the nitroso- and hydroxylamino-derivatives, but it is remarkable that the very stable di-*o*-methylated nitroso-compounds could not be isolated in this reaction. The preponderance of azoxyaryls from the di-*o*-methylated arylhydroxylamines is worthy of comment and appears to be due to the catalytic acceleration by hydroxyl ions of the reaction between nitroso- and hydroxylamino-derivative; if this is the case, it is difficult to explain why azoxyaryls are formed in such modest yield by the reduction of the di-*o*-methylated nitro-compounds with zinc and alcoholic potassium hydroxide.

Azoxymesitylene, m. p. 87—87·5°, is incidentally described. H. WREN.

Influence of sulphur on the colour of azo dyes. G. D. PALMER and E. E. REID (J. Amer. Chem. Soc., 1926, **48**, 528—532; cf. A., 1924, i, 1243).—The influence of sulphur in *meta* substituents on the colour of azo dyes has been examined by methods similar to those applied for the *ortho* and *para* analogues (*loc. cit.*). Series of *m*-aminophenyl alkyl sulphides and sulphones have been prepared and coupled with sodium β-naphthol-3 : 6-disulphonate, and the resulting dyes compared with each other and with analogous derivatives in which the place of the sulphur-containing substituent is taken by methyl and methoxyl. The bathochromic effect of these groups is in the same order as that observed among the *para* analogues, *viz.*, ·SO_2Me < ·Me < ·OMe < ·SMe, but is not so distinct or so intense in the *meta* series as in the *para*.

Treatment of alcoholic sodium *m*-acetamidophenyl sulphide (cf. Zincke and Müller, A., 1913, i, 355) with methyl sulphate, ethyl iodide, butyl bromide, and benzyl chloride affords, respectively, the *methyl*, m. p. 75°; *ethyl*, liquid, d_{25}^{25} 1·0360; n-*butyl*, liquid, d_{25}^{25} 1·0101; and *benzyl*, m. p. 74·1°, m-*acetamidophenyl sulphides*, which on hydrolysis with boiling concentrated hydrochloric acid afford the *hydrochlorides* of the corresponding m-*aminothiophenyl alkyl sulphides*. *m*-Acetamidophenyl methylsulphone, m. p. 137°; *ethylsulphone*, m. p. 96°; n-*butylsulphone*, liquid, d_{25}^{25} 1·3727; and *benzylsulphone*, m. p. 134·2°, prepared by the method of Zincke and Müller (*loc. cit.*) are described, and from these, by hydrolysis with hydrochloric acid and alcohol, the corresponding m-*aminophenylalkylsulphone hydrochlorides* were prepared. F. G. WILLSON.

Manufacture of azo dyes. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 233.

Intermediate compounds [derivatives of benzenesulphone] and azo dyes. BRITISH DYESTUFFS CORPN. LTD. and K. H. SAUNDERS.—See B., 1926, 233.

Azo dyes containing chromium. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 233.

***o*-Hydroxyazo dyes.** SOC. CHEM. IND. IN BASLE.—See B., 1926, 234.

Azo dyes. CHEM. FABR. ROHNER A.-G. PRATTELN.—See B., 1926, 234.

Azo dyes. SOC. CHEM. IND. IN BASLE.—See B., 1926, 265.

Action of chlorosulphonic acid on phenols. I. Derivatives of the three cresols and phenol. J. POLLAK, E. GEBAUER-FÜLNEGG, and E. RIESZ (Monatsh., 1926, **46**, 383—397).—When submitted to prolonged treatment with excess of chlorosulphonic acid at the ordinary temperature, phenol and the cresols yield disulphonyl chlorides. The substitution is *o*- and *p*-relative to the hydroxy-group and when the disulphonyl chloride has a vacant *o*- or *p*-position, further reaction takes place at 130—140° with formation of a trisulphonyl chloride. Phenol yields the -2 : 4-*disulphonyl chloride*, m. p. 89°, and -2 : 4 : 6-*trisulphonyl chloride*, m. p. 193°; *o*-cresol yields -3 : 5-*disulphonyl chloride*, m. p. 85—86°; *m*-cresol yields -4 : 6-disulphonyl chloride, m. p. 84—89° (cf. Claus and Krauss, A., 1888, 280), and -2 : 4 : 6-*trisulphonyl chloride*, m. p. 151° [-*trisulphonamide*, m. p. 290° (decomp.)]; and *p*-cresol yields -3 : 5-disulphonyl chloride. When the reaction is carried out at 110°, condensation takes place between two molecules of the cresoldisulphonyl chloride with elimination of hydrogen chloride and formation of sulphonylides, $SO_2Cl{\cdot}C_7H_5<^{O{\cdot}SO_2}_{SO_2{\cdot}O}>C_7H_5{\cdot}SO_2Cl$ (cf. Anschütz, A., 1918, i, 424). In this way, *o*-cresol yields *tolylene*-2 : 3-*sulphonylide*-5 : 5′-*disulphonyl chloride*, m. p. 280° (decomp.), and *m*-cresol yields *tolylene*-3 : 4-*sulphonylide*-6 : 6′-*disulphonyl chloride*, m. p. 290° (decomp.). The fact that phenol cannot be converted into a sulphonylide by the action of chlorosulphonic acid suggests that the formation of these compounds is determined by the presence of alkyl groups in the nucleus. R. W. WEST.

Constitution of tribromophenol bromide and its congeners. W. M. LAUER (J. Amer. Chem. Soc., 1926, **48**, 442—451).—Treatment of 2 : 6-dichloro-4-bromophenol with chlorine in aqueous

suspension affords a *compound*, $C_6H_2OCl_3Br$, (I), decomp. about 114°. The action of bromine on 4-chloro-2 : 6-dibromophenol yields similarly a *compound*, $C_6H_2OClBr_3$, (II), decomp. about 115°, depending on the rate of heating, whilst chlorination of tribromophenol yields the isomeric *compound*, $C_6H_2OClBr_3$, (III), decomp. about 131°. When heated with alcohol, all the above compounds lose 1 atom of halogen per molecule. In the case of (I), 40% of the substance loses 1 atom of bromine, the remainder losing 1 atom of chlorine; with (II), 96% of the substance loses bromine, the remainder losing chlorine; with (III), 43·5% loses bromine, the remainder losing chlorine; whilst when Benedikt's trichlorophenol bromide (cf. A., 1880, 246) is treated similarly, 96% of the substance loses bromine, the remainder losing chlorine. Thus (II) and (III) are not identical, and (I) is not identical with Benedikt's trichlorophenol bromide. Thiele and Eichwede's *cyclo*hexadienone structure is thus rendered improbable, whilst the results can be explained on the basis of Benedikt's "hypobromite" structure if, in the case of those trihalogenated phenol chlorides which contain bromine in the *para* position, a partial rearrangement to the isomeric trihalogenated phenol bromides be postulated. F. G. Willson.

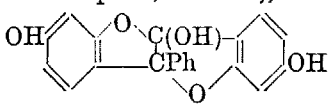
Action of alcoholic potassium hydroxide on chloronitrobenzene. D. H. Richardson (J.C.S., 1926, 522—529; cf. Heumann, A., 1873, 167; Willgerodt, *ibid.*, 1882, 953; Blom, *ibid.*, 1921, i, 413).—By heating *p*-chloronitrobenzene at 60° for 140 hrs. with a 0·5*N*-solution of potassium hydroxide in 95% ethyl alcohol, there is obtained, in the absence of acetaldehyde, a 92% yield of pure *p*-nitrophenetole; similarly, *o*-nitrophenetole may be prepared in 90% yield and *p*-nitroanisole (using methyl alcohol) in 96% yield, and under these conditions nitrophenol is the only by-product. Increase in temperature and in concentration of the alkali favours the formation of nitrophenol and the reduction of *p*-chloronitrobenzene to *pp'*-dichloroazoxybenzene; when much of the latter is produced, *p*-chloroaniline accompanies it. But the production of *pp'*-dichloroazoxybenzene is especially favoured by the presence of acetaldehyde, even if so little as 0·1% is present. Dilution of the alcohol with water decreases the reducing action, but also diminishes the rate of formation of nitrophenetole. F. M. Hamer.

Identification of phenols by means of the spectroscope. II. H. Wales and S. Palkin (J. Amer. Chem. Soc., 1926, **48**, 810—813; cf. A., 1924, ii, 630).—Absorption spectra maxima are listed for the azo dyes derived from forty-five phenols by coupling with *p*-nitrobenzenediazonium chloride, in aqueous, alcoholic, and acetone solution. Examination in more than one solvent is preferable, as dyes which, in a given solvent, have nearly coincident maxima, generally have these shifted by different amounts when the solvent is changed. F. G. Willson.

Syntheses of phenolic ketones by Hoesch's method. I. "Hydroxybenzils." W. Borsche and C. Walter (Ber., 1926, **59**, [*B*], 461—466).—According to Marsh and Stephen (A., 1925, i, 1158), the action of benzoyl cyanide on resorcinol in anhydrous ether in the presence of zinc chloride and hydrogen chloride yields a compound, $C_{14}H_{10}O_4$, which is regarded as 2 : 4-dihydroxybenzil with superoxide structure (cf. Schönberg, A., 1922, i, 663). The formula $C_{20}H_{14}O_5$, by analyses and determination of mol. wt., is indicated, however, and is supported by the isolation of a *bromo*-derivative,

$$C_{20}H_{10}O_5Br_4,2C_2H_4O_2,$$

m. p. 246—247° after softening and loss of acetic acid at 125°. Failure of the compound to react with hydroxylamine, semicarbazide, or phenylhydrazine and its derivatives, its inability to undergo the benzilic acid transformation, and its stability towards hydrogen in the presence of colloidal palladium preclude the possibility that it is a benzil derivative. The presence of three hydroxyl groups is established by the isolation of a triacetate, m. p. 159° (cf. Marsh and Stephen, *loc. cit.*), *tribenzoate*, m. p. 204°, and



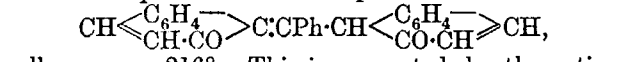
trimethyl ether, m. p. 177—178°. The annexed constitution is therefore ascribed to it. Similarly, resorcinol and *p*-methoxybenzoyl cyanide (prepared from *ω-oximinoacetophenone*, m. p. 120°) give the corresponding p-*methoxyphenyl* derivative, m. p. 229—230°. With resorcinol, cinnamoyl chloride does not give a crystalline product, whereas with phloroglucinol a *compound*, m. p. 142—143°, is obtained which has not been investigated completely. H. Wren.

Preparation of 2 : 4-dihydroxydiphenylmethane and of 2 : 4-dihydroxydiphenylethane. E. Klarmann (J. Amer. Chem. Soc., 1926, **48**, 791—794).—2 : 4-*Dihydroxydiphenylmethane*, m. p. 76—77°, b. p. 210—215°/12 mm., is obtained by the condensation of benzyl chloride with resorcinol in nitrobenzene solution in presence of aluminium chloride at 50—70°. It can also be prepared by the reduction of 2 : 4-dihydroxybenzophenone (cf. Hoesch, A., 1915, i, 820) with amalgamated zinc and boiling hydrochloric acid (1 : 3). It has a phenol coefficient of about 22, and 0·5 g. is non-toxic to guinea-pigs. 2 : 4-*Dihydroxydiphenylethane*, m. p. 131°, is obtained by reduction, as above, of 2 : 4-dihydroxydeoxybenzoin. The latter, prepared by condensation of phenylacetonitrile with resorcinol in ethereal solution in presence of zinc chloride and hydrogen chloride, with subsequent hydrolysis of the resulting imido-hydrochloride, has m. p. 121°, and gives a dark red coloration with ferric chloride (cf. Finzi, Monatsh., 1915, **28**, 1128; Chapman and Stephen, J.C.S., 1923, **123**, 404). 2 : 4-Dihydroxydiphenylethane has a phenol coefficient of about 40, and 0·5 g. is non-toxic to guinea-pigs. 4-Hydroxydiphenylmethane, m. p. 82—83° (cf. Liebmann, A., 1882, 171), has a phenol coefficient of 4·6, and 9·5 g. is non-toxic to guinea-pigs. F. G. Willson.

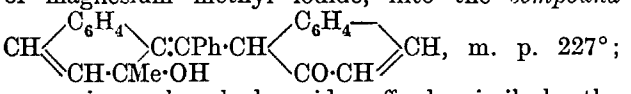
Colour and constitution. I. Influence of the methylthiol group, alone and in conjunction with the methoxyl group. H. H. Hodgson and F. W. Handley (J.C.S., 1926, 542—546).—When the 3-chloro-2-, -4-, and -6-nitrophenols, and 3-chloro-2-nitroanisole are treated with sodium disulphide, no

replacement of chlorine takes place, but the methyl ethers of 3-chloro-4- and -6-nitrophenols have been converted into 2 : 2′-*dinitro*-5 : 5′-*dimethoxydiphenyl disulphide*, m. p. 152°, and 4 : 4′-*dinitro*-5 : 5′-*dimethoxydiphenyl disulphide*, m. p. 194°, respectively. By heating with sodium sulphide and sodium hydroxide in presence of aqueous alcohol, followed by methylation with methyl sulphate, these disulphides yield 2-*nitro*-5-*methoxythioanisole*, m. p. 112—113°, and 4-*nitro*-5-*methoxythioanisole*, m. p. 79—80°, which are reduced by tin and hydrochloric acid to 5-*methylthiol*-o-*anisidine*, m. p. 44° (*hydrochloride*, m. p. about 235°), and 3-*methylthiol*-p-*anisidine*, which is an oil (*hydrochloride*, m. p. 210—211°). With Schäffer salt, R-salt, and H-acid as second components, *azo dyes* have been prepared from these amines, and from *o*- and *p*-anisidines, *o*- and *p*-thioanisidines, and 5-chloro-*o*- and 3-chloro-*p*-anisidines. The bathochromic effects of the groups in different positions are compared, and it is found that the influence of the methylthiol group is most marked in the *p*-position, whilst the methoxyl group exerts the optimum effect in the *o*-position; the maximum effect is obtained with the *p*-methylthiol group in conjunction with an *o*-methoxyl group. Chlorine shows the same influence as the methylthiol group, but less strongly. F. M. HAMER.

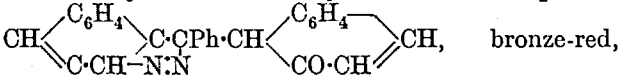
Quinonoid oxidation product of benzylidene-di-β-naphthol [phenyldi-2-hydroxy-α-naphthylmethane]. M. KOHN and L. SCHWARZ (Monatsh., 1926, **46**, 273—279; cf. A., 1918, i, 501).—Phenyldi-2-hydroxy-α-naphthylmethane (cf. Hewitt and Turner, A., 1901, i, 207) is oxidised by bromine in cold alkaline suspension to the *compound*



yellow, m. p. 216°. This is converted, by the action of magnesium methyl iodide, into the *compound*



m. p. 227°; magnesium phenyl bromide affords similarly the analogous *phenyl* derivative, m. p. 278°, whilst alcoholic hydrazine acetate yields the *azo* compound,



bronze-red, m. p. 182°, the quoted formulation of which is supported by its deep colour and by its complete passivity towards boiling acetic anhydride.

F. G. WILLSON.

Synthesis of hydroxydivarinol. F. MAUTHNER (J. pr. Chem., 1926, [ii], **112**, 268—272).—Hydroxydivarinol (3 : 4 : 5-trihydroxy-*n*-propylbenzene) occurs in *Ramalina diracerata*, which is the main constituent of the Chinese drug "Shi-Hoa." The method used for the synthesis of divarinol (Mauthner, A., 1925, i, 25) is now applied to that of hydroxydivarinol. 3 : 4 : 5-Trimethoxybenzoic acid ("Organic Syntheses," VI, 1926) is converted into the methyl ester, b. p. 297—298° (Will, A., 1888, 1089, gives 277—278°), which is condensed by an improved method with ethyl acetate and sodium to give ethyl trimethoxybenzoylacetate. This is methylated with methyl iodide and sodium ethoxide, and the product after acid hydrolysis yields 3 : 4 : 5-*trimethoxypropiophenone*, m. p. 51—52° (p-*nitrophenylhydrazone*, m. p. 182—183°). This is reduced by Clemmensen's method to 3 : 4 : 5-trimethoxypropylbenzene, b. p. 143—144°/11 mm., which by demethylation with hydriodic acid is converted into 3 : 4 : 5-trihydroxypropylbenzene, m. p. 78°, identical with hydroxydivarinol.

C. HOLLINS.

Orientation in the benzene ring. Bromination of pyrogallol 2 : 6-dimethyl ether. A. A. LEVINE (J. Amer. Chem. Soc., 1926, **48**, 797—800).—Bromination of pyrogallol 2 : 6-dimethyl ether in carbon disulphide yields 3-*bromopyrogallol* 2 : 6-*dimethyl ether*, b. p. 185—190°/40 mm., which, on treatment with excess of chlorine in the same solvent, affords 4 : 5-*dichloro*-3-*bromopyrogallol* 2 : 6-*dimethyl ether*, m. p. 127—128° (*benzoate*, m. p. 114—115°; *acetate*, m. p. 97—98°). Bromination of syringic acid (4-hydroxy-3 : 5-dimethoxybenzoic acid) in chloroform affords 2-*bromosyringic acid*, m. p. 155°. Oxidation of the latter, and of the above 3-bromopyrogallol 2 : 6-dimethyl ether, with chromium trioxide in 10% sulphuric acid and 50% acetic acid, respectively, yields 3-*bromo*-2 : 6-*dimethoxy*-p-*benzoquinone*, reddish-yellow, m. p. 148°, together with, in the latter case, a large proportion of 3 : 3′-*dibromo*-2 : 6 : 2′ : 6′-*tetramethoxydiphenoquinone* (3 : 3′-*dibromocœrulignone*), grey, m. p. 254°. Reduction of the last-named compound with sulphur dioxide in acetone affords 3 : 3′-dibromo-4 : 4′-dihydroxy-2 : 6 : 2′ : 6′-tetramethoxydiphenyl (cf. Hayduck, A., 1876, ii, 516). Similar oxidation of 4 : 5-dichloro-3-bromopyrogallol 2 : 6-dimethyl ether in glacial acetic acid yields 5-*chloro*-3-*bromo*-2 : 6-*dimethoxy*-p-*benzoquinone*, red, m. p. 164—165°. F. G. WILLSON.

Alkyl and aryl derivatives of phloroglucinol. E. KLARMANN and W. FIGDOR (J. Amer. Chem. Soc., 1926, **48**, 803—805).—*Phloro*-n-*hexophenone*, m. p. (air-dried) 95°, or m. p. 118° after drying in a vacuum, prepared by the method of Karrer and Rosenfeld (A., 1921, i, 793), yields, when reduced with amalgamated zinc and boiling 5% hydrochloric acid, n-*hexylphloroglucinol*, m. p. 108°. 2 : 4 : 6-*Trihydroxydiphenylethane*, m. p. 159—160°, is obtained similarly from 2 : 4 : 6-trihydroxydeoxybenzoin (cf. Chapman and Stephen, J.C.S., 1923, **123**, 404). The *diacetate*, m. p. 135—136°, and *triacetate*, liquid, are described. The above substituted phloroglucinols, as well as 2 : 4 : 6-trihydroxydiphenylmethane (cf. Hoesch, A., 1915, i, 820), are antiseptic, with phenol coefficients of about 8, the enhancement of the antiseptic properties of phloroglucinol by the introduction of substituents being thus analogous to that observed in the case of resorcinol.

F. G. WILLSON.

Amidines of the holocaine type. A. J. HILL and I. RABINOWITZ (J. Amer. Chem. Soc., 1926, **48**, 732—737).—Condensation of *p*-phenetidine with acetimidoethyl, *valerimidomethyl*, and phenylacetimidoethyl ether hydrochloride, respectively, in ethereal solution at the ordinary temperature, affords *bis*-p-*phenetyl-acetamidine*, m. p. 117—118°, -*valeramidine*, m. p. 96°, and -*phenylacetamidine*, m. p.

111°. Similar condensation of *p*-phenetidine with the free imido-ethers, obtained by the action of aqueous potassium carbonate on ethereal suspensions of the above hydrochlorides, yields p-*phenetylacetamidine*, $CMe(NH_2):N\cdot C_6H_4\cdot OEt$, m. p. 111—113°, *-valeramidine*, m. p. 86°, and *-phenylacetamidine*, m. p. 88—89°, respectively. The following *p*-phenetidides, prepared by boiling *p*-phenetidine with 2 mols. of the appropriate acid for 6 hrs., are described: *propionyl-*, m. p. 120°; n-*butyryl-*, m. p. 108—110°; and iso*valeryl*-p-*phenetidide*, m. p. 122°. *Bis*-p-*phenetylpropionamidine*, m. p. 84°; *-butyramidine*, m. p. 106°; and -iso*valeramidine*, m. p. 108°, are obtained from the above respective phenetidides by treating the phenetidide with phosphorus trichloride (1 mol.) in benzene at 0°, and then warming the mixture with a further mol. of the phenetidide. p-*Phenetyldiethylacetamidine*, $NEt_2\cdot CMe:N\cdot C_6H_4\cdot OEt$, m. p. 119—120°, is obtained similarly from acet-*p*-phenetidide and diethylamine. The following phenylureides,

$OEt\cdot C_6H_4\cdot N:C(R)\cdot N(C_6H_4\cdot OEt)\cdot CO\cdot NHPh$,

obtained by the action of phenylcarbimide on the amidines in ethereal solution, are described: *phenylureide* of *bis*-p-*phenetyl-acetamidine*, m. p. 164—165°; *-propionamidine*, m. p. 101°; *-butyramidine*, m. p. 105°; -n-*valeramidine*, m. p. 102—103°; and *-phenylacetamidine*, m. p. 118°; and of p-*phenetyl-acetamidine*, m. p. 164°; and -n-*valeramidine*, m. p. 158°.

F. G. Willson.

Behaviour of mixed *O*-acyl-*N*-acyl derivatives in which the reacting groups are not on adjacent carbon atoms. L. C. Raiford and E. P. Clarke (J. Amer. Chem. Soc., 1926, **48**, 483—489; cf. A., 1925, i, 809).—Benzoylation of 3 : 5-dibromo-2-hydroxybenzylacetanilide (cf. Auwers, Anselmino, and Richter, A., 1904, i, 736) affords the corresponding O-*benzoyl* derivative, m. p. 150°, which yields the original hydroxy-compound on hydrolysis, no rearrangement taking place. Migration of acyl radicals was also not observed in the case of derivatives of *o*-aminobenzyl alcohol and of 4′-amino-4-hydroxydiphenyl, the latter observation being contrary to Kaufler's (A., 1907, i, 307, 794) and Cain's (J.C.S., 1914, **105**, 1437) formulation of benzidine. Successive acetylation and benzoylation, in either order, of 8-amino-α-naphthol affords only one acetyl–benzoyl derivative, indicating that rearrangement occurs in one case, and that positions 1 and 8 of the naphthalene nucleus have a relationship approaching that of an *ortho* compound. The following compounds are described: o-*acetamidobenzyl alcohol*, m. p. 116° (*acetate*, m. p. 95°; *benzoate*, m. p. 110°); o-*benzamidobenzyl alcohol*, m. p. 95° (*acetate*, m. p. 115°; *benzoate*, m. p. 131—132°); 4-*benzamido-4′-hydroxydiphenyl*, m. p. 284° (*acetate*, m. p. 227°; *benzoate*, m. p. 273—274°); 4-*acetamido-4′-hydroxydiphenyl*, m. p. 224—225° (*acetate*, m. p. 219—220°; *benzoate*, m. p. 254—255°); 8-*benzamido-α-naphthol*, m. p. 216° (*acetate*, m. p. 180°; *benzoate*, m. p. 207—208°); and 8-acetamido-α-naphthol, m. p. 181° (acetate, m. p. 118°).

F. G. Willson.

α-Naphthylcarbimide as a reagent for alcohols. V. T. Bickel and H. E. French (J. Amer. Chem. Soc., 1926, **48**, 747—751).—α-Naphthylcarbimide reacts readily with primary and secondary, but less readily with tertiary alcohols, with formation of the corresponding urethanes. The reaction is not disturbed by the presence of water in those cases where the application of heat is unnecessary, generally with alcohols of low mol. wt. The urethane is separated from accompanying dinaphthylcarbamide by extraction with boiling light petroleum (b. p. 100—120°), in which the latter is insoluble. Naphthylurethanes prepared from the following alcohols are listed: *methyl*, m. p. 124°; *benzyl*, m. p. 134·5°; *cinnamyl*, m. p. 114°; *phenylethyl*, m. p. 119°; *lauryl*, m. p. 80°; n-*amyl*, m. p. 68°; *furfuryl*, m. p. 129—130°; m-*methylbenzyl*, m. p. 116°; o-*methoxybenzyl*, m. p. 135—136°; *ethylene glycol* (*diurethane*), m. p. 176°; *trimethylene glycol* (*diurethane*), m. p. 164°; *glycerol* (*triurethane*), m. p. 191—192°; *ethylene bromohydrin*, m. p. 86—87°; *trimethylene bromohydrin*, m. p. 73—74°; *ethylene chlorohydrin*, m. p. 101°; *trimethylene chlorohydrin*, m. p. 76°; *phenylmethylcarbinol*, m. p. 106°; *phenylethylcarbinol*, m. p. 102°; *menthol*, m. p. 119°; *borneol*, m. p. 127°; iso*borneol*, m. p. 130°; *cholesterol*, m. p. 160°; *benzoin*, m. p. 140°; *diphenylcarbinol*, m. p. 135—136°; cyclo*hexanol*, m. p. 128—129°; 2-*methyl*cyclo*hexanol*, m. p. 154—155°; 3-*methyl*cyclo*hexanol*, m. p. 122°; 4-*methyl*cyclo*hexanol*, m. p. 159—160°; *methylhexylcarbinol*, m. p. 63—64°; and *diethylcarbinol*, m. p. 71—72°. No reaction was obtained with triphenylcarbinol, diethylmethylcarbinol, or citronellol. Conversion of alcohols into chlorides and condensing these with sodium tribromophenoxide is not a satisfactory method for identification of alcohols, but *triphenylcarbinyl tribromophenyl ether*, m. p. 74—75°, was obtained in good yield by this method.

F. G. Willson.

Preparation of ethers from aromatic alcohols. J. B. Senderens (Compt. rend., 1926, **182**, 612—615; cf. A., 1924, i, 638; 1925, i, 113).—Benzyl ether is obtained in 70% of the theoretical yield by treating benzyl alcohol with sulphuric acid trihydrate in the cold. When heated with sulphuric acid trihydrate at 150—160° for 4 hrs., β-phenylethyl alcohol yields 80% of the theoretical quantity of *β-phenylethyl ether*, b. p. 317—320°, *d* 1·014. The preparation of the last-named ether is effected in 1 hr. by using concentrated sulphuric acid at 160°, but hydrocarbons are formed, and if stronger acid is employed, hydrocarbons alone are formed. α-Phenylethyl alcohol is readily dehydrated by treatment with 2% of sulphuric acid in the cold, yielding *α-phenylethyl ether*, b. p. 280—282°, *d* 1·005, but on heating the reaction mixture to 110° hydrocarbons are obtained. Cinnamyl ether is obtained by treating cinnamyl alcohol with one-tenth or even one-fifteenth of its volume of sulphuric acid trihydrate in the cold.

L. F. Hewitt.

[Triphenylcarbinol hydrochloride.] B. Helferich and H. Sieber (Ber., 1926, **59**, [*B*], 600).—The compound, m. p. 174°, described previously (A., 1925, i, 1269) as triphenylcarbinol hydrochloride is an additive compound of triphenylcarbinol and pyridine hydrochloride, $C_{19}H_{16}O,C_5H_5N,HCl$.

H. Wren.

Substitution in vicinal trisubstituted benzene derivatives. IV. L. RUBENSTEIN (J.C.S., 1926, 648—653).—Substitution processes have been studied in compounds of the type $C_6H_3(OR)(OR')X$ (1 : 2 : 3), in which X is a weakly *op*-orienting group. Nitration of 2 : 3-dimethoxybenzyl alcohol, *3-methoxy-2-ethoxybenzyl alcohol*, b. p. 148°/13 mm. (prepared by the action of methyl-alcoholic potassium hydroxide on 3-methoxy-2-ethoxybenzaldehyde), and 2 : 3-*diethoxybenzyl alcohol*, b. p. 163°/11 mm., 167°/19 mm., m. p. 35°, gives, respectively, 5-*nitro*-2 : 3-*dimethoxybenzyl alcohol*, m. p. 67°; 5-*nitro*-3-*methoxy*-2-*ethoxybenzyl alcohol*, m. p. 132°, and 5-*nitro*-2 : 3-*diethoxybenzyl alcohol*, m. p. 75°. Bromination of the three alcohols gives 5-*bromo*-2 : 3-*dimethoxybenzyl alcohol*, m. p. 82°; 5-*bromo*-3-*methoxy*-2-*ethoxybenzyl alcohol*, m. p. 55—56°; and 5-*bromo*-2 : 3-*diethoxybenzyl alcohol*, m. p. 60°, respectively. Nitration of 3-*methoxy*-2-*ethoxycinnamic acid*, m. p. 151° (prepared by heating 3-methoxy-2-ethoxybenzaldehyde and malonic acid with pyridine and piperidine), and of 2 : 3-*diethoxycinnamic acid*, m. p. 161°, yields exclusively 5-*nitro*-3-*methoxy*-2-*ethoxycinnamic acid*, m. p. 200—201°, and 5-*nitro*-2 : 3-*diethoxycinnamic acid*, m. p. 199°, respectively; nitration of 2 : 3-dimethoxycinnamic acid gives 5-*nitro*-2 : 3-*dimethoxycinnamic acid*, m. p. 229° (*ethyl* ester, m. p. 111°), together with 6-*nitro*-2 : 3-*dimethoxycinnamic acid*, m. p. 210—215° (decomp.) (*ethyl* ester, m. p. 86°), which is oxidised to a substance, m. p. above 280° (probably 6-nitro-3-hydroxy-2-methoxybenzoic acid). All the nitro- and bromo-derivatives have been oxidised in order to determine the positions of the substituents. 5-Bromo-2 : 3-dimethoxybenzoic acid has been prepared from 5-amino-2 : 3-dimethoxybenzoic acid, obtained by reduction of 5-nitro-2 : 3-dimethoxybenzoic acid.

F. M. HAMER.

Hydrolysis of *o*-benzoicsulphinide ("saccharin"). K. TÄUFEL and J. NÁTON (Z. angew. Chem., 1926, **39**, 225—229).—*o*-Benzoicsulphinide is gradually hydrolysed, in neutral or slightly acid aqueous solution, to ammonium hydrogen *o*-sulphobenzoate, hydrolysis being accelerated by raising the temperature, and being negligible after 2 hrs. at 100°. Under the same conditions, sodium *o*-benzoicsulphinide is more slowly hydrolysed to sodium ammonium *o*-sulphobenzoate. Three methods of following the course of hydrolysis are described: (i) by observing the ultra-violet absorption spectrum of the reaction mixture and comparing it with that of pure saccharin and pure ammonium hydrogen *o*-sulphobenzoate; (ii) by heating the mixture with magnesia and determining the ammonia liberated; (iii) by comparing the degree of sweetness at various times with that of pure sugar solutions. *m*-Sulphonamidobenzoic acid is obtained in 55—60% yield by oxidising *m*-toluenesulphonamide with potassium permanganate; pure ammonium hydrogen *o*-sulphobenzoate is prepared by heating saccharin with water in a sealed tube at 200°; and pure sodium ammonium *o*-sulphobenzoate by exactly neutralising the last-named acid salt with 0·1*N*-sodium hydroxide.

W. T. K. BRAUNHOLTZ.

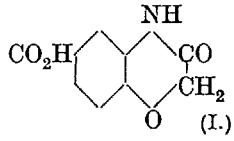
Hydrated ketonic ether. J. BOUGAULT (Compt. rend., 1926, **182**, 582—584; cf. this vol., 167).—The lactone (I), m. p. 82°, prepared by treating the sodium salt of a monoamide with more acetic acid than in the case of the isomeride of higher m. p. (cf. this vol., 404), gives the corresponding acid (II) when treated with alkalis. It was not found possible

(I.) $CH_2Ph\cdot CH_2\cdot C(=O)\cdot O\cdot C(=O)\cdot CH_2\cdot CH_2Ph$ $\qquad$ $CH_2Ph\cdot CH_2\cdot C(OH)(O\cdot C(=O)\cdot CH_2\cdot CH_2Ph)\cdot CO_2H$ (II.)

to transform the lactone, m. p. 82°, into the lactone, m. p. 120°, by the action of hydrochloric acid in acetic acid solution, hence it is probable that the isomerides are formed independently.

L. F. HEWITT.

Derivatives of *p*-carboxyphenoxyacetic acid. W. G. CHRISTIANSEN (J. Amer. Chem. Soc., 1926, **48**, 460—468; cf. A., 1925, i, 817).—Treatment of *p*-carboxyphenoxyacetic acid with methyl alcohol and hydrogen chloride affords *methyl* p-*carbomethoxyphenoxyacetate*, m. p. 92—92·7°. When warmed with concentrated aqueous ammonia, the latter yields p-*carbomethoxyphenoxyacetamide*, m. p. 164°, which is also obtained by methylating p-*carboxyphenoxyacetamide*, m. p. 282—282·5°, the latter being produced by the action of chloroacetamide on *p*-hydroxybenzoic acid in presence of alkali, together with O-p-*hydroxybenzoylglycollamide*, m. p. 257—258°. When heated with concentrated aqueous ammonia under pressure at 60—65°, *p*-carbomethoxyphenoxyacetamide is converted into p-*carboxyamidophenoxyacetamide*, m. p. 261—264·5°. Treatment of methyl *p*-carbomethoxyphenoxyacetate with nitric acid (1 mol.) in concentrated sulphuric acid affords *methyl* 2-*nitro*-4-*carbomethoxyphenoxyacetate*, pale yellow, m. p. 125·5—127°, together with *methyl* 2 : 6-*dinitro*-4-*carbomethoxyphenoxyacetate*, m. p. 118·5—119°, a *monomethyl* 2-*nitro*-4-*carboxyphenoxyacetate*, m. p. 204—205°, and methyl 2 : 4-dinitrophenoxyacetate, m. p. 70—73° (cf. Pratesi, A., 1892, 1333). Reduction of 2-nitro-4-carboxyphenoxyacetic acid with ferrous sulphate and ammonia yields 3-*keto*-3 : 4-*dihydro*-1 : 4-*benzoxazine*-6-*carboxylic acid* (I), m. p. 310—314° after softening at 306—307°, whilst reduction of the methyl ester with iron and hydrochloric acid yields the corresponding 6-*carbomethoxy*-derivative, m. p. 188—190·5°. An isomeric *monomethyl* ester of 2-*nitro*-4-*carboxyphenoxyacetic acid*, m. p. 151—154°, is obtained as a by-product as the *sodium* salt, m. p. 149—152°, decomp. at 153—154°. Treatment of (I) with methyl sulphate and alkali affords *methyl* 3-*keto*-4-*methyl*-3 : 4-*dihydro*-1 : 4-*benzoxazine*-6-*carboxylate*, m. p. 165—166°, together with the corresponding 6-*carboxylic acid*, m. p. 287—290°.


(I.)

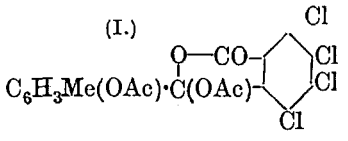
F. G. WILLSON.

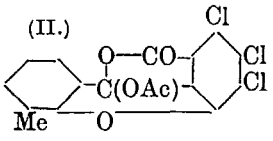
Molecular configurations of polynuclear aromatic compounds. VI. β-Dinitrodiphenic acid; its constitution and resolution into optically active components. G. H. CHRISTIE, A. HOLDERNESS, and J. KENNER (J.C.S., 1926, 671—676).—β-Dinitrodiphenic acid (*chloride*, m. p. 120°,

ethyl ester, m. p. 114—115°, *amide*, m. p. 247·5°) is regarded as 4 : 6′-dinitrodiphenic acid instead of the 6 : 6′-isomeride as previously supposed (cf. Schmidt and Kämpf, A., 1904, i, 71), giving on distillation 2 : 4′-dinitrodiphenyl. Nitration of 2-nitrophenanthraquinone yields 2 : 7-dinitrophenanthraquinone only. The "*hydrazide*," m. p. 294—295° (decomp.), of the β-acid and that of 6 : 6′-dinitrodiphenic acid (cf. Kenner and Stubbings, J.C.S., 1921, **119**, 593) are reconverted by the action of fuming nitric acid into the respective acids. β-Dinitrodiphenic acid gives a uniform *brucine* salt, but has been resolved by means of quinine. The less soluble *quinine* salt, m. p. 178—179° (decomp.), $[\alpha]_D^{16}$ −218·1° in chloroform, gives d-β-*dinitrodiphenic acid*, m. p. 296°, $[\alpha]_D^{14}$ +26·90° in ether (*sodium* salt, $[\alpha]_D^{15}$ −186·4° in water), whilst the more soluble *salt*, m. p. 93°, but after drying 162—163°, $[\alpha]_D^{16}$ −62·10° in chloroform, gives l-β-*dinitrodiphenic acid*, m. p. 296°, $[\alpha]_D^{15}$ −26·46° in ether (*sodium* salt, $[\alpha]_D^{15}$ +179·4° in water).

F. M. Hamer.

3 : 4 : 5 : 6-Tetrachloro-2′-hydroxy-3′-methylbenzoylbenzoic acid, *iso-o*-cresoltetrachlorophthalein, and some of their derivatives. W. R. Orndorff and C. Schade (J. Amer. Chem. Soc., 1926, **48**, 769—773; cf. A., 1925, i, 672).—3 : 4 : 5 : 6-Tetrachloro-2′-hydroxy-3′-methylbenzoylbenzoic acid, m. p. 219—220°, obtained from *o*-cresol and tetrachlorophthalic anhydride by the method of Ullmann and Schmidt (A., 1920, i, 53), affords a colourless *diacetate*, m. p. 182°, to which the structure (I) is ascribed, but occasionally an *anhydride*, m. p. 242·5°,

(I.) 

(II.) 

was obtained when the acid was boiled with acetic anhydride and sulphuric acid. The *zinc* salt (+3H$_2$O) and *barium* salt (+9½H$_2$O) are described. When boiled with aqueous 10% sodium carbonate, the acid is converted into the sodium salt of 5 : 6 : 7-trichloro-4-methylxanthone-8-carboxylic acid (cf. Ullmann and Schmidt, *loc. cit.*). The free acid has m. p. 286—289°, and yields an *acetate* (II), m. p. 275—280° (decomp.), whilst the methyl ester could not be prepared by the catalytic method. The *disodium* salt (+2NaOEt), dark blue, the *diacetate*, colourless, m. p. 224—227°, and the *dimethyl ether*, m. p. 261—264° (decomp.), of *iso-o*-cresoltetrachlorophthalein are described.

F. G. Willson.

Oxidation of benzaldehyde and the activation of oxygen by benzaldehyde. W. P. Jorissen and P. A. A. van der Beek (Rec. trav. chim., 1926, **45**, 245—247; cf. A., 1923, ii, 629; 1924, i, 1318).—In the oxidation of benzaldehyde by atmospheric oxygen previously described (A., 1897, i, 282; ii, 253), other solvents than acetic anhydride, which cannot act as "acceptors," can be used. With acetone and carbon tetrachloride considerable amounts of peroxide (65% in the former case) are formed, and smaller amounts with benzene, light petroleum, and chloroform. In the presence of pyridine, no peroxide was detected. In the case of acetone, Baeyer and Villiger's benzoyl hydroperoxide (perbenzoic acid) (A., 1900, i, 437) has been isolated.

R. Brightman.

Derivatives of some halogeno- and halogeno-nitro-benzaldehydes. J. van der Lee (Rec. trav. chim., 1926, **45**, 278—283).—The *phenylhydrazone*, m. p. 127—127·5°, of *p*-chlorobenzaldehyde is decomposed by light in the presence of air, apparently owing to oxidation (cf. Stobbe and Nowak, A., 1913, i, 1200). The corresponding p-*nitrophenylhydrazone* has m. p. 218—220°. The *semicarbazone*, m. p. 227—228°, and p-*nitrophenylhydrazone*, m. p. 207—208°, of *p*-bromobenzaldehyde, the *aldoxime*, m. p. 141·5—142·5°, *semicarbazone*, m. p. 244—245° (decomp.), and *azine*, m. p. 248·5—249°, of 4-chloro-3-nitrobenzaldehyde, and the *semicarbazone*, m. p. 254—255° (decomp.), and *azine*, m. p. 245—246°, of 4-bromo-3-nitrobenzaldehyde are also described. The *phenylhydrazones* of 4-chloro-3-nitro- and 4-bromo-3-nitro-benzaldehydes exist in yellow and red modifications, the yellow form rapidly changing to the red above 120°. The yellow phenylhydrazone of 4-chloro-3-nitrobenzaldehyde has m. p. 147·5—148° (after reddening at 120°), the orange form (a mixture of red and yellow), m. p. 148·5—149·5°; for the corresponding phenylhydrazone of 4-bromo-3-nitrobenzaldehyde the m. p. are 146—146·5° and 148—148·5° (cf. Chattaway and Clemo, J.C.S., 1923, **123**, 3041).

R. Brightman.

Pyrogenic decomposition of cinnamaldehyde by sudden heating to a high temperature. E. Peytral (Bull. Soc. chim., 1926, [iv], **39**, 214—216).—High-temperature decomposition of cinnamaldehyde takes place with formation of carbon monoxide and styrene, a portion of the latter decomposing into acetylene and benzene. At the same time, a more profound breaking-up of the aldehyde molecule occurs, resulting in the formation of hydrogen, methane, and ethylene, together with carbon and tarry matter.

H. J. Evans.

Isomerisation of aldehydes to ketones and its relation to the dehydration of α-secondary-tertiary hydrobenzoin glycols. S. Danilov and E. Venus-Danilova (Ber., 1926, **59**, [*B*], 377—387; cf. Danilov, A., 1923, i, 580).—Triphenylacetaldehyde is partly isomerised to phenyl benzhydryl ketone by warm 45% sulphuric acid, whereas the cold, concentrated acid causes quantitative formation of the ketone. With phosphorus pentachloride at a low temperature, the aldehyde gives a mixture of unchanged material and ketone, whilst at a higher temperature triphenylchloroethylene is produced. Triphenylacetaldehydeoxime and warm 40% sulphuric acid afford a mixture of aldehyde and ketone, whereas the semicarbazone and 50% acid yield a similar mixture in addition to a little triphenylacetic acid. Analogously, diphenyl*cyclo*hexylacetaldehyde is converted into benzhydryl *cyclo*hexyl ketone, and trimethylacetaldehyde into methyl *iso*propyl ketone. With the latter substance isomerisation is caused by hot, dilute sulphuric acid, a mixture of acetic and hydrochloric acids or cold, concentrated sulphuric

acid. Trimethylacetaldehydesemicarbazone is transformed by dilute acids into methyl *iso*propyl ketone.

The very marked influence of the concentration of the reactants and experimental conditions on the course of the dehydration of α-glycols is particularly noticeable in the case of *cyclo*hexylhydrobenzoin, which is converted by oxalic or dilute sulphuric acid into a mixture of diphenyl*cyclo*hexylacetaldehyde, αβ-diphenyl-α-*cyclo*hexylethan-β-one, and αα-diphenyl-β-*cyclo*hexylethan-β-one, and by concentrated sulphuric acid exclusively into the last ketone. If, therefore, the final product of the dehydration of a hydrobenzoin glycol is a mixture of aldehyde and ketones, it appears possible to alter the relative amounts of the ketones by modifying the conditions of the experiment; the alteration is due to the conversion of the aldehyde into one of the ketones. If, however, only ketones result from the dehydration, the relative quantities are not influenced by alteration of the usual conditions of the reaction, under which ketones are not interconvertible. The predominance of one or other ketone in the presence of dilute or concentrated acid shows that the mechanism of dehydration differs in the differing circumstances.

cyclo*Hexylhydrobenzoin*, m. p. 159·5° (*monoacetate*, m. p. 174°), is prepared by the action of magnesium *cyclo*hexyl bromide on benzoin. *Diphenyl*cyclo*hexylacetaldehyde*, m. p. 124°, yields an *oxime*, m. p. 161°, and a *semicarbazone*, m. p. 183° (also +1EtOH or $1C_6H_6$); its constitution is established by its transformation by alcoholic potassium hydroxide into formic acid and diphenyl*cyclo*hexylmethane. *αα-Diphenyl-β-*cyclo*hexylethan-β-one*, m. p. 56°, is converted by the same reagent into diphenylmethane and hexahydrobenzoic acid.

Attempts to convert triphenylacetyl chloride into triphenylacetaldehyde by catalytic hydrogenation in the presence of palladised barium sulphate (cf. Rosenmund, A., 1918, i, 300) afforded only triphenylmethane.

Attempts to cause isomerisation of ketones by cold concentrated, or boiling dilute sulphuric acid, zinc chloride, or hydrobromic acid yielded negative results. H. WREN.

Reversible interchange between aldehydes or ketones and primary or secondary alcohols of their degree of oxidation. W. PONNDORF (Z. angew. Chem., 1926, **39**, 138—143).—Aldehydes or ketones and primary or secondary alcohols can be made to interchange their functional groupings by heating them together either alone or in the presence of a catalyst. The reaction proceeds most smoothly and completely in the presence of a metallic alkoxide (*e.g.*, aluminium ethoxide), but proceeds also in the presence of sodium acetate or even through the influence of heat alone. The following preparations are detailed: cinnamyl alcohol and benzaldehyde from cinnamaldehyde and benzyl alcohol; anisyl alcohol and benzaldehyde from anisaldehyde and benzyl alcohol; geraniol, nerol, and acetone from citral and *iso*propyl alcohol; menthol, valeraldehyde, and valeric acid from menthone and amyl alcohol; carveol and acetone from carvone and *iso*propyl alcohol; menthone and cinnamic alcohol from menthol and cinnamaldehyde. The reaction is supposed to proceed, not by wandering of the $\cdot OM(OR)_2$ grouping, but according to the general scheme: $CHR_1X(OM)+R_2\cdot CO\cdot X \rightarrow CR_1X(OM)\cdot O\cdot CHR_2X \rightarrow CHR_2X(OM)+R_1\cdot CO\cdot X \rightarrow CHR_1X\cdot O\cdot CR_2X(OM) \rightarrow CHR_1X(OM)+R_2\cdot CO\cdot X$, where M=metal, and X=H or R.

W. T. K. BRAUNHOLTZ.

Catalytic action of reduced copper on oximes. (Beckmann's rearrangement. XV.) S. YAMAGUCHI (Bull. Chem. Soc. Japan, 1926, **1**, 35—40; cf. A., 1925, i, 1278).—Several oximes have been passed over reduced copper at 200° in an atmosphere of hydrogen and the products examined. From furfuraldoxime pyromucic amide was obtained. Benzamidoxime yielded benzamide, benzoic acid, and benzonitrile. Cinnamic acid was obtained from cinnamaldoxime. From dibenzylketoxime, phenylacetic acid was produced together with its amide and nitrile. Benzophenoneoxime yielded tetraphenylethane, diphenylmethane, and diphenylketimine. The products from acetoxime were acetone and *iso*propylamine. G. M. BENNETT.

Catalytic hydrogenation of the carbonyl group in aromatic compounds under pressure in presence of copper. I. B. KUBOTA and T. HAYASHI (Bull. Chem. Soc. Japan, 1926, **1**, 14—19).—The results of Sabatier and his collaborators (A., 1914, i, 548; 1921, i, 347) show that, under ordinary pressure, copper is a suitable catalyst for the dehydrogenation of the carbinol group, rather than for the hydrogenation of the carbonyl group. It was therefore expected that the reverse would be true under high pressure. This has been confirmed by heating various mono- and di-ketones, mixed with copper powder, in an autoclave under 60—90 atm. Acetophenone at 140° yielded phenylmethylcarbinol, and at 160° ethylbenzene. Benzophenone at 120° gave diphenylcarbinol and diphenylmethane, at 190° diphenylmethane and tetraphenylethane. Camphor at 120—150° gave borneol and *iso*borneol. From benzil at 100°, benzoin (43%), hydrobenzoin, and *iso*hydrobenzoin were formed, whilst at 130° hydrobenzoin (74%) and *iso*hydrobenzoin (14%) were the chief products. Benzoylacetone at 83° yielded, besides much unchanged starting material, 30% of *methyl β-hydroxy-β-phenylethyl ketone*, $CHPh(OH)\cdot CH_2\cdot COMe$, b. p. 134—136°/10 mm.; *hydrazone*, m. p. 120—122° (decomp.). At 105°, benzoylacetone was reduced mainly to γ-phenyl-α-methyltrimethylene glycol. Phthalic anhydride at 120° formed 70% of *o*-carboxybenzylphthalide (hydrodiphthalyl-lactonic acid, Wislicenus, A., 1885, 57), together with 12% of *dihydroxyphthalan*, $C_6H_4<^{CH(OH)}_{CH(OH)}>O$, giving a *dibenzoyl* derivative. A. DAVIDSON.

Polycyclic structures in relation to their homocyclic unsaturated isomerides. VI. Reactions of *iso*phorone. J. W. BAKER (J.C.S., 1926, 663—670).—From the reactions of *iso*phorone it is concluded that three types of tautomerism are superimposed: (*a*) three-carbon, αβ–βγ change, (*b*) intra-annular, (*c*) keto-cyclol. Treatment of

*iso*phorone [semicarbazone, m. p. 199·5° (decomp.), oxime, m. p. 79·5°, *monopiperonylidene* derivative, m. p. 145—146°] with bromine in carbon tetrachloride solution gives a dibromide, m. p. about 40° (probably by addition at the double linking in the three-carbon system), which liberates hydrogen bromide, forming monobromo*iso*phorone. Further bromination of *iso*phorone yields 1 : 3 : 4 : 5(?)-*tetrabromo*-3 : 3 : 5-*trimethyl*cyclo*hexan*-1-*one*, m. p. 135°. Reduction of *iso*phorone by the Clemmensen method yields a saturated hydrocarbon, $C_{18}H_{28}$, which is oxidised to *trans*-caronic acid, whence the existence of the bridged structure in *iso*phorone is deduced. Reduction by other methods gives the α- and β-forms of 1 : 1′ : 3 : 3 : 3′ : 3′-*trimethyl*dicyclo*hexyl*-5 : 5′-*dione*, m. p. 162° [*disemicarbazone*, m. p. 259—260° (decomp.)], and m. p. 126° [*disemicarbazone*, m. p. 220° (decomp.)], respectively.

F. M. HAMER.

Thiosemicarbazones and semicarbazidesemicarbazones of *cyclo*hexanones. I. MAZUREVITSCH (Mitt. wissensch.-techn. Arbeit. Republ. (Russ.), 1924, **13**, 97—101; from Chem. Zentr., 1925, II, 398).—The following compounds are mentioned: *semicarbazone* of 1-*methyl*-3-*furyl*-Δ^6-cyclo*hexen*-5-*one*, m. p. 175·5—177°; *semicarbazidesemicarbazone* of the latter compound, $C_{13}H_{20}O_3N_6$, decomp. 197—198·5°; 3-*phenyl*-1-*methyl*-Δ^6-cyclo*hexen*-5-*onesemicarbazide*-*semicarbazone*, $C_{15}H_{22}O_2N_6$, decomp. 201—202°; 1-*methyl*-Δ^1-cyclo*hexen*-3-*onethiosemicarbazone*, $C_8H_{13}N_3S$, m. p. 136—138°; 1 : 3-*dimethyl*-Δ^3-cyclo*hexen*-5-*one*-*thiosemicarbazone*, $C_9H_{15}N_3S$, sintering at 187°, decomp. at 194·5—195·5°; 1-*methyl*-3-*ethyl*-Δ^6-cyclo*hexen*-5-*onethiosemicarbazone*, $C_{10}H_{17}N_3S$, m. p. 150—151°; 1-*methyl*-3-iso*propyl*-Δ^2-cyclo*hexen*-?-*onethio*-*semicarbazone*, $C_{11}H_{19}N_3S$, m. p. 160—161°; 1-*methyl*-3-iso*butyl*-Δ^6-cyclo*hexen*-5-*onethiosemicarbazone*, $C_{12}H_{21}N_3S$, m. p. 128—129° (decomp.); 1-*methyl*-3-*furyl*-Δ^6-cyclo*hexen*-5-*onethiosemicarbazone*, $C_{12}H_{15}ON_3S$, m. p. 186—187·5° (decomp.); 3-*phenyl*-1-*methyl*-Δ^6-cyclo*hexen*-5-*onethiosemicarbazone*, $C_{14}H_{17}N_3S$, m. p. 201—203° (decomp.). The formation of semicarbazide-semicarbazones is not hindered by the occurrence of alicyclic and heterocyclic rings in juxtaposition, but is prevented in the case of fatty-aromatic ketones with double linkings in the αβ-position. The semicarbazidesemicarbazones form hydrochlorides.

G. W. ROBINSON.

Bromophenols. XVII. Preparation of brominated α-naphthaquinones. M. KOHN and L. SCHWARZ (Monatsh., 1926, **46**, 347—353; cf. this vol., 395).—Methylation of 2 : 4-dibromo-α-naphthol by means of methyl sulphate and alkali cannot be effected on account of the formation of a blue dye by the action of the alkali on the naphthol. 2 : 4-*Dibromo*-α-*naphthyl methyl ether*, m. p. 54—55°, is obtained by the action of bromine in carbon tetrachloride on α-naphthyl methyl ether. When treated with nitric acid (*d* 1·5), this yields 2-bromo-1 : 4-naphthaquinone, m. p. 132° (cf. Zincke and Schmidt, A., 1895, i, 56), and this, when treated with excess of bromine, affords 2 : 3-dibromo-1 : 4-naphthaquinone (cf. Miller, A., 1885, 667). Treatment of α-naphthol with excess of bromine in presence of iron powder affords 2 : 3 : 4 : 6 : 7-pentabromo-α-naphthol, which, on oxidation with nitric acid (*d* 1·5), affords 2 : 3 : 6 : 7-tetrabromo-1 : 4-naphthaquinone, m. p. 290°, in 40% yield (cf. Blümlein, A., 1885, 162). When treated with aqueous-alcoholic 20% potassium hydroxide, the last is converted into 3 : 6 : 7-*tribromo*-2-*hydroxy*-1 : 4-*naphthaquinone*, deep yellow, m. p. 253—254° (*potassium* salt, red; *aniline* salt, dark red, m. p. 188—189°). 3 : 6 : 7-*Tribromo*-2-*anilino*-1 : 4-*naphthaquinone*, dark red, m. p. 120°, is obtained by the action of aniline on the above tetrabromo-α-naphthaquinone.

F. G. WILLSON.

Preparation of quinizarin. H. H. REYNOLDS and L. A. BIGELOW (J. Amer. Chem. Soc., 1926, **48**, 420—422).—The influences of varying reaction period, concentration of boric acid, and temperature on the yield of quinizarin (1 : 4-dihydroxyanthraquinone) in the reaction between *p*-chlorophenol, phthalic anhydride, boric acid, and sulphuric acid (D.R.-P. 255031) have been studied, and optimum reaction conditions established. The optimum temperature for the reaction is 200°, and about 3½ hrs. at this temperature are sufficient. The best proportions of the reactants to use are *p*-chlorophenol, 115 g. (0·9 mol.); phthalic anhydride, 300 g. (2·0 mol.); boric acid, 50 g.; and 96% sulphuric acid, 2000 g. Directions are given for working up and purifiying the product, the yield of which is 74% of the theoretical, calculated on the *p*-chlorophenol, m. p. 199—200° after sintering at about 190°.

F. G. WILLSON.

Hydroxy-compounds [dyes] of the dibenzanthrone series. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 234.

[Derivatives of leuco-compounds of vat dyes.] J. I. M. JONES, B. WYLAM, J. MORTON, and MORTON SUNDOUR FABRICS, LTD.—See B., 1926, 235.

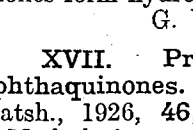
Perylene vat dye. A. ZINKE and H. SHOEPFER.—See B., 1926, 265.

Vat dyes of the perylene series. COMP. NAT. DE MATIÈRES COLORANTES.—See B., 1926, 265.

Nopinene as a technical raw material. G. AUSTERWEIL.—See B., 1926, 253.

Occurrence of sylvestrene. B. S. RAO and J. L. SIMONSEN (J. Ind. Inst. Sci., 1925, **8 A**, 287—294).—A fuller account of work already published (this vol., 72).

True α-camphenone. S. NAMETKIN and A. ZABRODIN (Ber., 1926, **59**, [*B*], 368—369).—α-*Camphenone* (I), m. p. 77—78°, is prepared in poor yield by the addition of a solution of *sec.*-α-nitrocamphene in dilute aqueous potassium hydroxide to a solution of stannous chloride in fuming hydrochloric acid (cf. Nametkin and Zabrodin, A., 1925, i, 416); the *semicarbazone*, m. p. 205° (decomp.), and *oxime*, m. p. 117—118°, are described. It is suggested that the use of the name "camphenone" for the product



(I).

obtained by Angeli (A., 1895, i, 61, 382) should be discontinued, since the compound has been shown by Bredt and Holz (A., 1917, i, 655) to be β-*pericyclo*-camphanone. H. WREN.

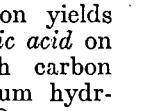
Scymnolsulphuric acid. I. S. OIKAWA (J. Biochem. [Japan], 1925, **5**, 63—70).—Sodium salts are obtained from shark bile free from lipins by extraction with alcohol, precipitation of lead salts, heating with sodium carbonate, extraction with alcohol, and precipitation with ether. At 0° with potassium hydroxide, the aqueous solution yields a precipitate which affords *scymnolsulphuric acid* on saturation of its aqueous solution with carbon dioxide. On hydrolysis with boiling barium hydroxide solution, *α-scymnol*, $C_{27}H_{48}O_5,2H_2O$, m. p. 108°, [α] +38·2°, is obtained; the substance gives a violet solution in 25% hydrochloric acid, and appears to contain five hydroxyl groups. Its oxidation *product*, $C_{27}H_{38}O_6$, m. p. 208°, has [α] 51·7°.

CHEMICAL ABSTRACTS.

α- and β-Amyrin. O. DISCHENDORFER [with O. RENDI] (Monatsh., 1926, **46**, 399—408).—In order to find the most convenient method of separating α- and β-amyrin, the mixed m.-p. curves of some of the esters have been plotted. The curves for the benzoates and *formates* (*α-ester*, m. p. 190°, $[\alpha]_D^{20}$ in benzene +80·4°, in chloroform +73·87°; *β-ester*, m. p. 240°, $[\alpha]_D^{20}$ in benzene +49·76°, in chloroform +52·36°) show the formation of eutectic mixtures. The small difference between the m. p. of the *m-nitrobenzoates* (*α-ester*, m. p. 233°, $[\alpha]_D^{20}$ +97·62° to +98·79°; *β-ester*, m. p. 236°, $[\alpha]_D^{20}$ +95·52° to +96·74°) makes the m.-p. curve difficult to follow. The curve for the *anisates* (*α-ester*, m. p. 193°, $[\alpha]_D^{20}$ +102·2° to +101·5°; *β-ester*, m. p. 250°, $[\alpha]_D^{20}$ +97·36° to +98·29°) is approximately a straight line. A description is given of the crystallographic examination of the anisate of β-amyrin. R. W. WEST.

Saponins and related substances. XV. Æscigenin. A. W. VAN DER HAAR (Rec. trav. chim., 1926, **45**, 271—277).—The total saponin from chestnut seeds (for which the name "æscin" is proposed) is an amorphous mixture of saponins which is only hydrolysed with difficulty, and it is probable that Masson (A., 1918, i, 518), Blau (Diss., Zürich, 1911), and Bosshard (*ibid.*, 1916) dealt with an incompletely hydrolysed product. Acid hydrolysis converts the æscin into *æscigenin*, a trihydric alcohol, $C_{21}H_{33}O(OH)_3$, m. p. 310—311°, $[\alpha]_D^{15}$ +35·28°, crystallising with 1EtOH or $2H_2O$ (cf. Winterstein, *ibid.*, 1923). It yields no oxime, semicarbazone, or phenylcarbamate, and no acetyl compound could be obtained, but bromine yields a crystalline *derivative*, m. p. 167—175°. It gives Liebermann's cholesterol reaction, the Salkowsky–Hess reaction, and the usual saponin and sapogenin reaction with sulphuric acid. Distillation with zinc dust in hydrogen converts æscigenin, without carbon dioxide formation, into a volatile oil with a terpene-like odour, b. p. 240—250°, *M* 191·8 (in phenol); this gives a violet sapogenin reaction in acetic acid and a hydrocarbon, non-volatile in steam, which gives Liebermann's cholesterol reaction.

R. BRIGHTMAN.

"Polymethine" dyes and a general dye formula as basis of a new generalisation of colour chemistry. W. KÖNIG (J. pr. Chem., 1926, [ii], **112**, 1—36).—A lengthy discussion of the relationship between colour and chemical constitution. It is argued that all coloured organic substances may be considered to be closed conjugated chains, and that acceptance of this conjugation theory enables the consideration of these compounds to be placed on a systematic basis. It is suggested that the essential characteristics of any dye may be represented by the common formula:  , where Pe and Pe' are "perichromes," *i.e.*, groups possessing latent affinity such as RR'N·, RS·, RO·, or RR'C:CR''·, Ms is a "mesochrome" or continuously conjugated system, and K is a "conjugator," *i.e.*, either a cation, an anion, a bipolar solvent, or an electron. The nature of the colouring matter will depend on the constitution of the mesochrome system.

R. W. WEST.

Vat dyes of the thioindigo series. A. W. JOYCE, and CHEMICAL FOUNDATION, INC.—See B., 1926, 265.

Piperidine derivatives by interaction of methylamine, formaldehyde, and acetone. C. MANNICH and G. BALL (Arch. Pharm., 1926, **264**, 65—67; cf. A., 1922, i, 351; 1917, i, 634).—When a solution of acetone (5 mols.), 30% formaldehyde (2·4 mols.), and methylamine hydrochloride (1 mol.) is boiled for 8 hrs., the product is not a single compound, as originally supposed (*loc. cit.*, 1917), but a mixture of two stereoisomerides. The two (α- and β-) compounds are both racemic; they are readily separated by fractional crystallisation from chloroform and ether. The α-form of *4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine* (this was the product originally supposed to be methyldi-γ-ketobutylamine), $\begin{matrix}NMe\cdot CH_2\cdot CHAc\\ |\\ CH_2-CH_2\cdot CMe\cdot OH\end{matrix}$, has m. p. 130°. It yields a *hydrochloride* (m. p. 173°, possesses strong anæsthetic properties), a *methochloride* (m. p. 179°), and a *methiodide* (m. p. 217°). It also affords a *monoxime* (m. p. 149°; *hydrochloride*, $+H_2O$, m. p. 140°; anhydrous, m. p. 205°) and a *benzoate* (*hydrochloride*, m. p. 176°, by interaction of the base and benzoyl chloride in cold chloroform), the functions of the two oxygen atoms being thus demonstrated. When the methiodide is subjected to Hofmann's reaction, a tarry product is obtained; when it is distilled in steam, it yields dimethylamine and methyl vinyl ketone, identified as the *phenylhydrazone* (or pyrazoline ?), m. p. 76°. The base is disrupted by alkali hydroxide, and also when subjected to oxidation, but when treated with cold alcoholic hydrogen chloride for 10 hrs. it suffers dehydration, and so affords *3-acetyl-1 : 4-dimethyltetrahydropyridine* (the unsaturated linking is not yet located), an oil (b. p. 108°/15 mm.; *hydrochloride*, m. p. 118°; *chloroplatinate*, m. p. 155°; *methiodide*, m. p. 173°; *oxime*, m. p. 120°). The same compound is obtained when either the β-form of the parent substance (see below) or

the crude mixture of bases is treated with alcoholic hydrogen chloride. It is reduced in acid solution by hydrogen in presence of palladised animal charcoal and so affords 3-*acetyl*-1 : 4-*dimethylpiperidine*, an oil (b. p. 91°/15 mm.; *hydrochloride*, m. p. 161°; *oxime*, m. p. 127°; *methiodide*, m. p. 217°), and this is further reduced by sodium amalgam and dilute acetic acid to 1 : 4-*dimethyl*-3-α-*hydroxyethylpiperidine* (m. p. 87°; *benzoate*, as *hydrochloride*, m. p. 194°, decomp.), together with much unidentified oily substance. The α-base itself is not readily reduced, but it also succumbs to the action of sodium amalgam and dilute acetic acid, yielding the α-form (see below) of 4-*hydroxy*-1 : 4-*dimethyl*-3-α-*hydroxyethylpiperidine* (m. p. 114°), together with much oily by-product.

The β-form of 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine, m. p. 85°, yields a *hydrochloride* (+H_2O, m. p. 92°; anhydrous, m. p. 149°), a *methochloride* (m. p. 68°), and a *methiodide* (m. p. 205°, decomp.), which decomposes, like its α-analogue, when subjected to steam distillation, but when boiled with dilute sodium carbonate it breaks down into methyl vinyl ketone and methyl β-dimethylaminoethyl ketone, identified as its picrate, m. p. 108°. The β-base also affords an *oxime* (m. p. 182°) and a *benzoate* (*hydrochloride*, m. p. 140°, weakly anæsthetic). When reduced with sodium amalgam and dilute acetic acid, it yields a mixture of the β- and γ-forms of 4-hydroxy-1 : 4-dimethyl-3-α-hydroxyethylpiperidine (cf. above), which are separated by fractional extraction with ether. The β-form has m. p. 140° (*methiodide*, m. p. 173°), whilst the γ-form has m. p. 80—83° (*methiodide*, m. p. 240°).

W. A. SILVESTER.

Diastereomeric 4-hydroxy-1 : 4-dimethylpiperidine-3-carboxylic acids. C. MANNICH and L. STEIN (Arch. Pharm., 1926, **264**, 77—88).—The α-form of 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine (see preceding abstract) is oxidised with barium hypobromite in cold dilute aqueous solution. The barium having been removed as sulphate and the hydrogen bromide as silver bromide, the solution obtained is evaporated to very small volume, whereupon the α-form of 4-*hydroxy*-1 : 4-*dimethylpiperidine*-3-*carboxylic acid*, $\begin{matrix}NMe\cdot CH_2\cdot CH\cdot CO_2H\\ |\\ CH_2-CH_2\cdot CMe\cdot OH\end{matrix}$ (+H_2O, decomp. 240°; *chloroaurate*, decomp. 162°), crystallises. As the formula shows, this (except for the methyl group) can be looked upon as a "half-ecgonine." The *methyl* ester (m. p. 109°; *hydrochloride*, decomp. 203°; *methiodide*, decomp. 200°) is readily benzoylated in cold chloroform solution and so gives the *benzoate* (an oil; *hydrochloride*, decomp. 199°; *methiodide*, m. p. 182°). This may be termed a "half-cocaine," and, in fact, the hydrochloride is as powerful an anæsthetic as cocaine. The *ethyl* ester (m. p. 100°; *methiodide*, m. p. 195°) similarly yields the *hydrochloride* (decomp. 219°) of its *benzoate*, which also has potent anæsthetic properties.

When the 4-hydroxy-1 : 4-dimethylpiperidine-3-carboxylic acid is boiled with phosphorus oxychloride, dehydration takes place, and 1 : 4-*dimethyltetrahydropyridine*-3-*carboxylic acid* (m. p. 184°, ethylenic linking not yet located) is produced. The *hydrochloride* (decomp. 236—238°), *hydrobromide* (decomp. 225°), and *chloroaurate* (decomp. 198—199°) are described. The *methyl* ester (b. p. 111—112°/15 mm.; *hydrobromide*, m. p. 158—159°; *methiodide*, m. p. 172°) does not resemble arecoline in physiological properties, although if the ethylenic linking is between carbon atoms 3 and 4, the compound is 4-methylarecoline. 1 : 4-Dimethyltetrahydropyridine-3-carboxylic acid is also produced when the β-form of the hydroxy-acid (see below) is treated as described above, and is, moreover, more readily obtained by oxidising (with barium hypobromite) the 3-acetyl-1 : 4-dimethyltetrahydropyridine described in the preceding abstract. It readily forms a *dibromide* (*hydrobromide*, m. p. 177—178°), and when reduced with hydrogen and palladised animal charcoal yields 1 : 4-*dimethylpiperidine*-3-*carboxylic acid* (m. p. 188°; *chloroaurate*, m. p. 159°). The *methyl* ester of this acid is an oil (*hydrochloride*, m. p. 166°; *methiodide*, m. p. 222°).

The β-form of the "half-ecgonine," obtained by oxidising the β-isomeride (m. p. 85°) of 4-hydroxy-3-acetyl-1 : 4-dimethylpiperidine as described above, decomposes at 280° (*chloroaurate*, m. p. 180—181°). *Methyl* 4-*hydroxy*-1 : 4-*dimethylpiperidine*-3-*carboxylate* (β-form) (b. p. 120—121°/15 mm.; *picrate*, m. p. 166—167°; *chloroaurate*, m. p. 115—116°; *methiodide*, m. p. 184°) yields a *benzoate* (*picrate*, m. p. 205—206°; *nitrate*, decomp. 133—134°), which is not as potent an anæsthetic as cocaine. The *ethyl* ester (an oil; *hydrochloride*, m. p. 170—171°) yields on benzoylation no crystalline product.

W. A. SILVESTER.

[Naphthacridone dyes.] J. I. M. JONES, B. WYLAM, J. MORTON, and MORTON SUNDOUR FABRICS, LTD.—See B., 1926, 235.

Synthesis of 3-arylsulphonyl-2-arylsulphonylmethylquinolines, their fission by reduction and by acids, and the determination of their constitution. J. TRÖGER and G. PAHLE (J. pr. Chem., 1926, [ii], **112**, 221—242; cf. following abstract, and Tröger and von Seelen, A., 1923, i, 1127; Tröger and Brohm, *ibid.*, 1925, i, 1452; Tröger and Dimitroff, this vol., 78).—The bromine in α-bromo-γ-arylsulphonylacetones, prepared by bromination in cold acetic acid or benzene, is readily replaced by chlorine or iodine by the action of silver chloride or iodide. With silver oxide or acetate, sodium hydroxide, carbonate, acetate, thiosulphate, or arylthiosulphonate, or lead acetate, either no reaction occurs or the products are arylmethylsulphones. Arylsulphinates react with the mono- or di-bromo-γ-arylsulphonylacetones to give 50% yields of αγ-diarylsulphonylacetones, the second bromine atom being replaced by hydrogen. α-*Chloro*-γ-p-*toluenesulphonylacetone* and the corresponding *iodo*-compound, m. p. 102°, are prepared from the bromine derivative. By the condensation of *o*-aminobenzaldehyde with α-bromo-γ-*p*-toluenesulphonylacetone, a bromine-free *compound*, m. p. 187°, was obtained once, but could not again be prepared.

α-*Bromo*-γ-o-*anisolesulphonylacetone*, m. p. 115°,

reacts with sodium *p*-toluenesulphinate in alcohol to give α-p-*toluenesulphonyl*-γ-o-*anisolesulphonylacetone*, m. p. 177° (*phenylhydrazone*, m. p. 113°), from which by condensation with *o*-aminobenzaldehyde at 160° is obtained 3-o-*anisolesulphonyl*-2-p-*toluenesulphonylmethylquinoline*,

$C_9H_5N(CH_2{\cdot}SO_2{\cdot}C_6H_4Me){\cdot}SO_2{\cdot}C_6H_3{\cdot}OMe$,

m. p. 208°. The position of the two sulphone groupings is proved by hydrolysis with fuming hydrochloric acid in a sealed tube at 210—220°, by which 3-*o*-anisolesulphonyl-2-methylquinoline (Tröger and Brohm, *loc. cit.*) is produced. Reduction with tin and hydrochloric acid gives *o*-methoxythiophenol, *p*-thiocresol, and tetrahydro-2-methylquinoline; step-wise reduction is not observed under any conditions.

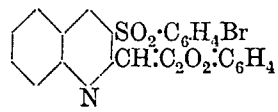
By similar reactions the following series of compounds is prepared (m. p. of α-bromo-γ-arylsulphonylacetones, α-*p*-toluenesulphonyl-γ-arylsulphonylacetones, and 3-arylsulphonyl-2-*p*-toluenesulphonylmethylquinolines are given in this order): p-*anisole* (m. p. 104°, 140°, 187°), o-*phenetole* (m. p. 125°, 144°, 194°), p-*phenetole* (m. p. 108°, 116°, 182°), p-*bromobenzene* (m. p. 150°, 163°, 193°). α-p-*Toluenesulphonyl*-γ-o-*phenetolesulphonylacetonephenylhydrazone* has m. p. 80°.

αα-*Dibromo*-γ-o-*anisolesulphonylacetone*, m. p. 160°, is prepared by bromination of *o*-anisolesulphonylacetone or the monobromo-compound in glacial acetic acid at 15°. From the mono- or the dibromo-derivative is obtained αγ-*di*-o-*anisolesulphonylacetone*, m. p. 165°, which with *o*-aminobenzaldehyde gives 3-o-*anisolesulphonyl*-2-o-*anisolesulphonylmethylquinoline*, m. p. 188°. p-*Bromobenzenesulphonylacetone*, m. p. 103°, is prepared from chloroacetone and sodium *p*-bromobenzenesulphinate. *Bis*-p-*bromobenzenesulphonylacetone*, m. p. 195°, reacts with *o*-aminobenzaldehyde to give 3-p-*bromobenzenesulphonyl*-2-p-*bromobenzenesulphonylmethylquinoline*, m. p. 132°. The following α-*p*-bromobenzenesulphonyl-γ-arylsulphonylacetones and their conversion into 3-*p*-bromosulphonyl-2-arylsulphonylmethylquinolines are described (m. p. of the ketone and the quinoline in this order): o-*anisole* (m. p. 160°, 191°); p-*toluene* (m. p. 163°, 193°); β-*naphthalene* (m. p. 165°, 195°). From the last-mentioned quinoline, by treatment with fuming hydrochloric acid in a sealed tube at 220°, there is obtained 3-*p*-bromobenzenesulphonyl-2-methylquinoline, m. p. 165°, the naphthalenesulphonyl group being lost.

In the fission of the quinoline derivatives during reduction with tin and hydrochloric acid the 1 : 2 : 3 : 4-tetrahydro-2-methylquinoline produced is accompanied by a small amount of the 5 : 6 : 7 : 8-isomeride (cf. von Braun, Gmelin, and Schultheiss, A., 1923, i, 835, and following abstract). C. Hollins.

Reduction of β-arylsulphonylquinoline derivatives. J. Tröger and A. Ungar (J. pr. Chem., 1926, [ii], **112**, 243—267; cf. Tröger and Pahle, preceding abstract; Tröger and Brohm, A., 1925, i, 1452).—By reduction with hydrochloric acid and tin in a suitable form, the β-arylsulphonyl groups in 3-benzenesulphonyl-, 3-*p*-toluenesulphonyl-, 3-*p*-chlorobenzenesulphonyl-, and 3-*p*-bromobenzenesulphonyl-2-methylquinoline are eliminated as thiophenols (isolated as disulphides, m. p. 60—61°, 56—57°, 71°, and 93·5°, respectively). The other reduction product is a mixture of *Py*- and *Bz*-tetrahydro-2-methylquinolines, separable by benzoylation of the former (cf. von Braun, Gmelin, and Schultheiss, A., 1923, i, 835). The hydrochloride of the mixture melts at 195—196° (cf. Pope and Peachey, J.C.S., 1899, **75**, 1066); that of 1 : 2 : 3 : 4-tetrahydro-2-methylquinoline at 190° (von Braun, Gmelin, and Schultheiss give 128—130°), and that of the 4 : 5 : 6 : 7-isomeride at 164°.

p-*Bromobenzenesulphonylacetone*, m. p. 100°, prepared from chloroacetone and sodium *p*-bromobenzenesulphinate, condenses with *o*-aminobenzaldehyde to give, in 80% yield, 3-p-*bromobenzenesulphonyl*-2-*methylquinoline*, m. p. 168°. 3-p-*Bromobenzenesulphonylquinophthalone* (annexed formula), obtained from the quinoline, phthalic anhydride, and zinc chloride at 150—160°, is reduced by tin and hydrochloric acid to tetrahydro-2-methylquinolines, the arylsulphonyl and the phthalyl groups being both eliminated.



3-p-*Bromobenzenesulphonyl*-2-*propenylquinoline*, m. p. 173° (*hydrochloride*, m. p. 132°), prepared from the quinoline, paraldehyde, and zinc chloride at 160°, and the corresponding 3-*p*-toluenesulphonyl compound (Tröger and Menzel, A., 1922, i, 269) both give by reduction a mixture of 2-*n*-propyltetrahydroquinolines. The 1 : 2 : 3 : 4-tetrahydro-compound is separated as benzoyl derivative, m. p. 97°, and the 5 : 6 : 7 : 8-isomeride (hydrochloride, decomp. 100°) is distilled in steam from the alkaline filtrate. 3-p-*Toluenesulphonyl*-2-n-*propylquinoline*, obtained by hydrogenation of the 2-propenyl compound in the presence of palladium, is further reduced by tin and hydrochloric acid to 2-*n*-propyltetrahydroquinolines and thio-*p*-cresol.

Reduction of 3-p-*bromobenzenesulphonyl*-2-*methylquinoline methiodide*, m. p. 157°, gives *p*-bromothiophenol and 1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline (picrate, m. p. 178°), no hydrogenation of the benzene ring being observed. In one experiment, which could not be repeated, there was obtained from the steam distillate an unidentified *base*, $C_{10}H_{19}N$(?), m. p. 58°.

By reduction of 2-amino-3-arylsulphonylquinolines (aryl being *p*-tolyl, *p*-chlorophenyl, *p*-bromophenyl, and β-naphthyl) both the arylsulphonyl- and the amino-groups are eliminated, with the production of a thiophenol, ammonia, and 1 : 2 : 3 : 4-tetrahydroquinoline (no 5 : 6 : 7 : 8-isomeride). Attempts to obtain 2-aminotetrahydroquinoline by elimination of the sulphonyl group alone by reduction were unsuccessful. Reduction of the methiodides or ethiodides gives 1-alkyl-1 : 2 : 3 : 4-tetrahydroquinolines. 2-*Amino*-3-p-*toluenesulphonylquinoline methiodide*, m. p. 185°, and 2-*amino*-3-p-*bromobenzenesulphonylquinoline methiodide*, m. p. 192°, are obtained by warming the respective bases with methyl iodide in methyl alcohol. The *ethiodides* melt at 194° and 204°, respectively. 2-*Dimethylamino*-3-p-*toluenesulphonylquinoline*, m. p. 132°, and the corresponding 2-*dibenzylamino*-compound, m. p. 164°, both give

1 : 2 : 3 : 4-tetrahydroquinoline by reduction, the dialkylamino-group being eliminated.

3-*p*-Toluenesulphonyl- and 3-*p*-bromobenzenesulphonyl-carbostyril (Tröger and Köppen-Kastrop, A., 1923, i, 368; Tröger and Meinecke, A., 1924, i, 556), on account of their sparing solubility in hydrochloric acid, are best reduced with zinc dust and hydrochloric–acetic acid. The arylsulphonyl group is completely eliminated, but the α-hydroxyl group remains, the products being a thiophenol and dihydrocarbostyril, m. p. 161°. This result is remarkable, since carbostyril itself is not reducible in acid media.

C. HOLLINS.

Isolation of homogeneous pyridine through the perchlorate. Pyridine, ammonia, and indicators. Pyridinium perchlorate as acidimetric standard. F. ARNDT and P. NACHTWEY (Ber., 1926, **59**, [*B*], 448—455).—Pyridinium perchlorate, m. p. 288° after slight softening, crystallises readily, dissolves sparingly in cold water and to a smaller extent in 20% perchloric acid, whereas the methylated homologues of pyridine do not afford precipitates even with 70% perchloric acid. For the preparation of pure pyridine, the technical product is submitted to desiccation with potassium hydroxide and fractional distillation. The portion, b. p. below 130°, is treated with so much 6*N*-hydrochloric acid that the basic odour disappears, and then with a volume of 6*N*-sodium perchlorate solution equal to that of the acid used. After some hours the precipitate is filtered off, washed with a little ice-cold water or 20% perchloric acid, and dried at 110°. The pyridinium perchlorate is decomposed with 50% sodium hydroxide solution, and the solution is distilled under diminished pressure, whereby the mixture of pyridine and water of constant b. p. is obtained; the method suffers from the drawback that complete dehydration of this mixture can only be effected by repeated use of solid potassium hydroxide. Alternatively, the solid ammonium perchlorate is treated with gaseous ammonia until a nearly homogeneous mixture is obtained, which is warmed slowly to about 60° and then subjected to a current of dry air at this temperature. The residue is distilled under diminished pressure and the distillate is freed from a small proportion of water by potassium hydroxide or barium oxide. Pure pyridine has b. p. 114·2°/739·5 mm., 115·0°/755 mm., d_4^{20} 0·9819, d_4^{25} 0·9765, m. p. −39° to −40°.

The presence of ammonia in pyridine free from its homologues is established by treatment of the specimen with aqueous cadmium chloride solution, removal of the precipitated additive compound, addition of sodium carbonate to the filtrate, removal of cadmium carbonate, and application of Nessler's reagent to the filtrate. In the absence of ammonia, the solution remains clear initially, but slowly develops a pale yellow opalescence. With 0·01—0·02% of ammonia, the usual brownish-yellow turbidity is immediately produced. Contrary to the observations of Barthe (A., 1905, i, 546), pyridine can be freed from ammonia by distillation; if water also is present, almost the whole of the ammonia passes over in the first aqueous distillates. Aqueous solutions of pyridine in the complete absence of ammonia give a blue colour with litmus tincture. Comparison of the behaviour of buffer solutions of borax and hydrochloric acid with that of 0·1*N*-aqueous pyridine towards litmus indicates the value $p_H > 8·7$, whereas from the basic constant of pyridine at 15° the value p_H 9·33 is deduced. It is therefore remarkable that 0·1*N*-aqueous pyridine gives only a pale pink colour with phenolphthalein, showing that a "basic error" is introduced by the action of the base on the indicator. Pyridinium perchlorate may be used as an acidimetric standard; the substance is dissolved in water and titrated with the alkali hydroxide under investigation at the b. p. in the presence of phenolphthalein.

H. WREN.

Nitration of 2 : 4 : 6-trimethylpyridine (collidine). P. J. VAN RIJN (Rec. trav. chim., 1926, **45**, 267—270).—The carboxyl groups in potassium collidine-3 : 5-dicarboxylate are not replaced by nitro-groups on heating with nitric acid at temperatures up to 200°. Nitration of collidine itself with nitric acid and fuming sulphuric acid (7·5% SO_3) yielded only 3-*nitro*-2 : 4 : 6-*trimethylpyridine*, m. p. 35·5° [*picrate*, m. p. 176°; *chloroplatinate*, $+2H_2O$, m. p. 216° (decomp.); *chloroaurate*, m. p. 128°]. The *methiodide*, yellow, m. p. 210—211°, is not readily obtained, and loses iodine on heating with 10% potassium hydroxide. Careful reduction of 3-nitrocollidine yields 3-aminocollidine. R. BRIGHTMAN.

[**Quinoline derivatives. II.**] C. ZÖLLNER (Ber., 1926, **59**, [*B*], 509).—The compounds from 2-phenyl-4-methylquinoline described by John (A., 1925, i, 1317) have been obtained previously by the author (D.R.-P. 421087).

H. WREN.

Quinoline derivatives. III. Oxidation of *Py*-alkylated quinolines. H. JOHN and V. FISCHL (Ber., 1926, **59**, [*B*], 387—390; cf. A., 1925, i, 1317, 1451).—The photochemical oxidation of quinolines in benzene solution in the presence of anthraquinone (cf. Eckert, A., 1925, i, 413) has been examined. Quinoline and 2-methylquinoline afford 83% of unchanged material and some resinous products. 4-Methylquinoline behaves similarly, but yields also a small amount of a product soluble in alkali hydroxide which gives crystalline precipitates with mercuric chloride and picric acid. 2-Phenyl-4-methylquinoline affords 2-phenylquinoline-4-carboxylic acid in 27% yield, whilst the rest of the base is recovered unchanged; resin is not produced. β-Phenyl-β-4′-quinolylpropane-αγ-diol behaves similarly to 4-methylquinoline, but in this case also the amount of product soluble in alkali is too small for extended examination.

H. WREN.

Condensation of 4-methoxy-2-methylquinoline with aromatic aldehydes. J. TRÖGER and E. DUNKER (J. pr. Chem., 1926, [ii], **112**, 196—220; cf. A., 1925, i, 432, 975).—In the condensation of 4-methoxy-2-methylquinoline with aldehydes, especially under increased pressure, wandering of the methyl group from oxygen to nitrogen occurs. The reaction is now further investigated and an attempt is made to synthesise cuspareine, the third alkaloid of angostura peel.

4-Methoxy-2-methylquinoline condenses with anisaldehyde in the presence or absence of zinc chloride or potassium hydrogen sulphate at 125° in the vacuum apparatus previously described (*loc. cit.*) to give 4-*methoxy*-2-p-*methoxystyrylquinoline*, m. p. 144° [*hydrochloride*, m. p. 105° (+2H_2O)]. The isomeric 1-methyl-2-*p*-methoxystyryl-4-quinolone, m. p. 283°, is obtained when the reaction takes place in a sealed tube at 185—190°. In the earlier paper (*loc. cit.*), this compound was erroneously supposed to be the *O*-ether. The *O*-ether, m. p. 144°, is converted into the quinolone, m. p. 283°, by the action of methyl iodide vapour on the molten base. Methoxyl determinations by the Zeisel method indicate 1MeO in each case, and by the Herzig–Meyer method 2Me in each case. Since *cis*- and *trans*-isomerism is excluded (see below), and the mol. wt. is normal, it is concluded that isomerisation of the *O*-ether occurs during the Zeisel determination, and that the *N*-methyl is included in the Herzig–Meyer result (cf. Decker and von Solonina, A., 1902, i, 767). The methiodides of the two bases are identical, m. p. 168° (decomp.), but with ethyl iodide the low-melting base gives 4-*methoxy*-1-*ethyl*-2-p-*methoxystyrylquinolinium iodide*, m. p. 246°, whilst the base of high m. p. yields 4-*ethoxy*-1-*methyl*-2-p-*methoxystyrylquinolinium iodide*, m. p. 246°. The bases are not *cis*- and *trans*-isomerides, since on hydrogenation in dilute acetic acid in the presence of palladised animal charcoal they give different products, namely, 4-*methoxy*-2-β-*anisylethylquinoline*, m. p. 92° (*hydrochloride* described), and 1-*methyl*-2-β-*anisylethyl*-4-*quinolone*, m. p. 214° (*hydrochloride*, m. p. 197°), respectively.

The condensation of 4-methoxy-2-methylquinoline with benzaldehyde leads to similar results, the products being 4-*methoxy*-2-*styrylquinoline*, m. p. 142°, and 1-methyl-2-styryl-4-quinolone, m. p. 297° (*loc. cit.*), neither of which shows the presence of methoxyl by the Zeisel method. Piperonal, on the other hand, gives only a single product, m. p. 186° (Späth and Brunner, A., 1924, i, 1226), whether under pressure or in a vacuum, from which cusparine, m. p. 91·5°, is obtained by hydrogenation. In this case, migration of methyl from oxygen to nitrogen seems to be inhibited, and Zeisel determinations are normal.

o-Methoxybenzaldehyde yields two products, 4-*methoxy*-2-o-*methoxystyrylquinoline*, m. p. 130° (*hydrochloride*, m. p. 191°; *picrate*, m. p. 208°), and 1-*methyl*-2-o-*methoxystyryl*-4-*quinolone*, m. p. 268°, either being obtained under the same conditions in a vacuum. The lower-melting isomeride yields a *dihydro*-derivative, m. p. 108° (*picrate*, m. p. 176°). *m*-Methoxybenzaldehyde also yields two products, 4-methoxy-2-*m*-methoxystyrylquinoline, m. p. 134·5° (*hydrochloride*, m. p. 207°), in the presence of zinc chloride (cf. Tröger and Dunker, *loc. cit.*), and 1-*methyl*-2-m-*methoxystyryl*-4-*quinolone*, m. p. 231°, in the presence of potassium hydrogen sulphate. The *dihydro*-derivative of the lower-melting base has m. p. 49° (*chloroplatinate* and *picrate*, m. p. 154°, described).

2-mp-*Dimethoxystyrylquinoline*, m. p. 109—110° (*hydrochloride* described), is prepared from 2-methylquinoline and veratraldehyde best in the presence of potassium hydrogen sulphate under reduced pressure at 130°. Its *dihydro*-derivative has m. p. 52° (*hydrochloride* and *chloroplatinate* described).

Cuspareine is much less basic than any of the dihydro-compounds here mentioned, and differs from them also in m. p. C. Hollins.

Preparation and properties of methyl*iso*propylquinoline-yellow. M. Phillips and M. J. Goss (J. Amer. Chem. Soc., 1926, **48**, 823—826).—2 : 8-*Dimethyl*-5-iso*propylquinoline*, m. p. 78·2° (*chloroaurate*, yellow), was prepared from 2-amino-*p*-cymene and paraldehyde by the Doebner–Miller method (A., 1882, 868) and converted, by treatment with phthalic anhydride and zinc chloride at 180—190°, into *methyl*isopropylquinophthalone (*methyl*isopropylquinoline-*yellow*), yellow, m. p. 220·4° (cf. Jacobsen and Reimer, A., 1883, 922). When heated with fuming sulphuric acid (23% SO_3) at 150°, the latter yields a *disulphonic acid*, isolated as the yellow *sodium* salt. The absorption spectra and light-fastness of the above compounds are not appreciably different from those of quinoline-yellow. F. G. Willson.

Carbocyanine dyes. G. O. Gutenkunst.—See B., 1926, 265.

Condensation of 9-methylacridine with formaldehyde and preparation of acridine-9-carboxylic acid. A. W. Homberger and H. Jensen (J. Amer. Chem. Soc., 1926, **48**, 800—802).—9-Methylacridine, warmed with aqueous 20% formaldehyde, gave 9-β-*hydroxyethylacridine* (β-9-*acridylethyl alcohol*), yellow, m. p. 155—156° [*hydrochloride*, yellow, m. p. 240—260° (decomp.); *picrate*, golden-brown, m. p. 186°; *benzoate*, m. p. 159°] (cf. Koenigs, A., 1900, i, 189). On oxidation with chromium trioxide in dilute sulphuric acid, the alcohol yields acridine-9-carboxylic acid (cf. Bernthsen, A., 1887, 849). When 9-methylacridine is condensed similarly with aqueous 40% formaldehyde, 9-acridyldimethylol (αγ-dihydroxy-β-9-acridylpropane), sulphur-yellow, m. p. 194°, is obtained in good yield (cf. Koenigs, *loc. cit.*). The *hydrochloride*, m. p. 250—265° (decomp.), and *picrate*, m. p. 195°, are described.

F. G. Willson.

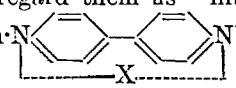
Carbazones. VI. Coloured derivatives of tetraphenylmethane. F. Kehrmann and F. Brunner (Helv. Chim. Acta, 1926, **9**, 216—220).—7-Amino-5 : 5-diphenyl-3-carbazone (*acetyl* derivative, m. p. 245—246°) begins to decompose at 240° without melting (cf. A., 1925, i, 430). The following compounds are prepared by analogous reactions (*loc. cit.*) from the corresponding imino-bases (A., 1919, i, 554): 9-*amino*-5 : 5-*diphenyl*-3-*carbazone* (*acetyl* derivative, m. p. 230°, decomposing on hydrolysis); 1 : 7 : 9-*triamino*-5 : 5-*diphenyl*-3-*carbazone*, m. p. 190—230° [*triacetyl* derivative, m. p. 310° (decomp.)]; 1 : 7 : 9-*triamino*-5 : 5-*di*(*aminophenyl*)-3-*carbazone*. The last-named compound contains 1H_2O of crystallisation, which is not removed at 110°. M. Clark.

Derivatives of diphenylcarbazine. IX. Coloured derivatives of tetraphenylmethane. F. Kehrmann, P. Tschudi, and J. Tschui (Helv. Chim. Acta, 1926, **9**, 227—230).—A series of nitro-aminodiphenylcarbazine derivatives was prepared by

reduction of the appropriate nitro-compounds (A., 1919, i, 551) with ammonium sulphide or with insufficient stannous chloride for complete reduction. *7-Nitro-3-amino-5 : 5-diphenylcarbazine* decomposes at 270° without melting. It gives an orange-red solution in alcoholic sodium hydroxide. *3 : 7-Dinitro-9-amino-5 : 5-diphenylcarbazine* gives an intense bluish-green solution in this solvent, resembling in colour that of 3 : 7-dinitrocarbazine. Reduction of the 9-nitro-group is therefore inferred. Further reduction with sodium sulphide gives the *nitrodiamino*-derivative. *3 : 7-Dinitro-1 : 9-diamino-5 : 5-diphenylcarbazine* begins to decompose at 250°. The structure is again inferred from the intense bluish-green solution in alcoholic sodium hydroxide.

Acetylation of 1 : 7-diamino-5 : 5-diphenyl-3-carbazime hydrochloride with acetic anhydride at the ordinary temperature gives a series of three derivatives. A transient crystalline precipitate, presumably the *monoacetyl* derivative, rapidly redissolves and is replaced by *1 : 7-diacetamido-5 : 5-diphenyl-3-carbazime*, isolated as *hydrochloride*. Further acetylation in presence of zinc chloride converts this compound into *1 : 7-diacetamido-3-acetimido-5 : 5-diphenylcarbazine*. M. CLARK.

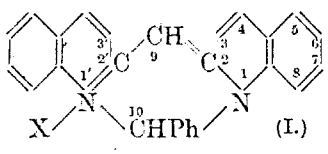
Free ammonium radicals. VI. Radicals and *meri*quinonoid compounds. I. Dipyridinium subhalides. E. WEITZ and R. FISCHER (Ber., 1926, **59**, [*B*], 432—445).—The question whether the dipyridinium subhalides are to be regarded as unimolecular monohalides of the bivalent dipyridinium radical (cf. Weitz, König, and von Wistinghausen, A., 1924, i, 425) or dimeric quinhydrones formed from 1 mol. of dipyridinium dihalide and 1 mol. of dihydrodipyridyl (cf. Emmert and Varenkamp, A., 1922, i, 1064; Dimroth and Frister, *ibid.*, 1923, i, 149) is decided in favour of the first alternative by a series of determinations of mol. wt. of 1 : 1′-dibenzyl-4 : 4′-dipyridinium subchloride and 1 : 1′-diphenyl-4 : 4′-dipyridinium subchloride in boiling methyl alcohol (the special type of apparatus is figured and described). The mean value for the benzyl compound is 197 and for the phenyl compound 174, whereas the bimolecular quinhydrone formulæ require 747 and 691, respectively, for the undissociated compounds. The observed values are lower than those theoretically possible on the assumption that the bimolecular quinhydrone is completely dissociated into three ions, whilst formation of four ions is incompatible with retention of the quinhydrone colour of the solution (solutions of dibenzyldipyridinium subchloride obey Beer's law and also do not diminish in intensity of colour when heated); they agree, however, with the values required for a heteropolar, monomeric subhalide which suffers dissociation into two ions, naturally without alteration of its properties. The somewhat higher values observed for dibenzyldipyridinium monochloride in boiling methyl alcohol by Emmert, Jungck, and Häffner (A., 1925, i, 72) are to some extent confirmed, but the concentrations used were greater than those employed in the present experiments, and Emmert's assumption of complete ionisation into three ions is not supported by evidence that the apparent mol. wt. does not decrease when the solutions are further diluted. The chemical and electrochemical behaviour of the subhalides shows them to be distinct chemical individuals (cf. Weitz, König, and von Wistinghausen, *loc. cit.*), and not loose, complex compounds of radical and dihalide, and this view is confirmed by their solubility without decomposition in glacial acetic acid at the atmospheric temperature, whereas the free radical is soluble only with decomposition.

The composition of the dipyridinium subhalides suggests that they are univalent ammonium radicals, and this conception is in agreement with their ready oxidisability. On the other hand, it has not been found possible previously to isolate a free radical of the perfect ammonium type, and it therefore appears preferable to regard them as "intramolecular quinhydrones,"  , in which each nitrogen atom is equally involved in the union of the anion and the free affinity of the univalent ammonium radical is distributed over the two halves of the molecule.

The univalent dipyridinium cation must contain an uneven number of electrons, and the "odd" electron is considered to oscillate between the carbon atoms in positions 4 and 4′. The alternation in the state of oxidation brought about by the oscillating electron is obviously responsible for the pronounced colour of the subhalides. The conception may be extended to a large class of dyes, such as those of the triphenylmethane series and to the quinhydrones, in which case the electron is assumed to vibrate between atoms of the different components which are not united by main valencies. The "bridged" linking of an atom or residue between two distant parts of a molecule is possible only with heteropolar compounds; the quinhydrone from dihydrodipyridyl and dipyridyl is therefore not comparable with the subhalides.

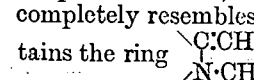
The action of 1 : 1′-dibenzyl-4 : 4′-dipyridinium on the corresponding di-iodide in methyl-alcoholic solution leads occasionally to the production of the *compound*, $[C_{72}H_{66}N_6]I_2$, analogous to the hexamethyldipyridyl-blue iodide described by Emmert, Jungck, and Häffner (*loc. cit.*). The existence of such compounds is not in contradiction to the established, unimolecular formation of the subhalides, in which sufficient unsaturated points are present at which addition of other molecules can occur. H. WREN.

Quinoline-red and related dyes of the di-quinolylmethane series. G. SCHEIBE and W. FISCHER (Ber., 1926, **59**, [*B*], 502—508).—Previous investigation (A., 1921, i, 451) has rendered probable the constitution (I) for quinoline-red. Subsequently (A., 1923, i, 250), by comparison with *ψ-iso*cyanine, the presence of the chromophore, $NR{:}C{\cdot}C{:}C{\cdot}NR_2$, in quinoline-red has been established. Further evidence with regard to the constitution of quinoline-red is obtained by examination of tri-2-quinolylmethane, which is converted by


(I.)

successive treatment with methyl iodide and sodium hydroxide into *di-2′:2″-quinolyl-2:1-methylquinolylenemethane*, m. p. 228° (*dipicrate*, decomp. 242°; additive *compound*, $2C_{29}H_{21}N_3,3HgCl_2$), which does not differ appreciably in colour from the corresponding compound of diquinolylmethane. Methylation of triquinolylmethane could not be effected with methyl sulphate, whilst ethyl iodide gave the corresponding *ethiodide*, m. p. 168°, with great difficulty. The additive *compounds* of mercuric chloride and tri- or di-quinolylmethane are incidentally described.

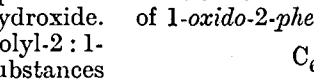
Benzyl chloride and triquinolylmethane yield the *compound* $C_{35}H_{27}N_3Cl_2$, m. p. 252°, which completely resembles the additive compound obtained with methyl iodide; attempts to remove hydrogen chloride from the product result in removal of the benzyl residue and regeneration of triquinolylmethane. Simultaneously, colourless *benzyltri-2-quinolylmethane*, m. p. 202° (*perchlorate*, decomp. about 236° after darkening at 200°), is invariably produced; *benzyltri-2-quinolylmethane hydriodide* is obtained by the use of benzyl iodide at 40°. On the other hand, the introduction of the methyl group at the central carbon atom has not been effected, whereas the amyl radical may be introduced. Other possible constitutions are excluded for quinoline-red by the observation of the absence of tinctorial properties in benzyltriquinolylmethane and by the preparation of true quinoline-red dyes substituted in position 9. Also they do not explain the stability of quinoline-red and the cyanine dyes towards alkali hydroxide. Thus, methyl iodide adds to di-2′:2″-quinolyl-2:1-methylquinolylenemethane, giving the substances $C_{30}H_{24}N_3I$, m. p. 213°, and $C_{31}H_{27}N_3I_2$, m. p. 208° (corresponding *picrate*, $C_{41}H_{31}O_4N_9$, decomp. 253°), which resemble closely quinoline-red in colour, but are not fluorescent. The characteristic fluorescence depends on the presence of the pyrimidine ring, and hence appears in the *products* $C_{35}H_{26}N_3Cl_3$ and $C_{35}H_{24}N_3I$, m. p. above 330°, obtained from triquinolylmethane and benzylidene chloride (followed by treatment with potassium iodide in the case of the iodide). Hence the constitution (I) may be regarded as established for all quinoline-red dyes.

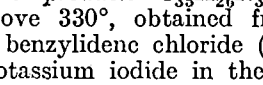
It is to be expected that substitution in position 10 would not affect the character of the dye; in confirmation, it is found that di-2-quinolylmethane and methylene iodide afford a *compound*, $C_{20}H_{15}N_2I$, m. p. above 330°, which in colour and fluorescence completely resembles quinoline-red and probably contains the ring  . Similarity to quinoline-red is also observed in the *compound* $C_{21}H_{17}N_2I$, m. p. above 330°, obtained by treating di-2-quinolylmethane successively with ethylene dibromide and potassium iodide. Tri-2-quinolylmethane and ethylene bromide give the *substance* $C_{30}H_{24}ON_3Br$, m. p. above 330°.

H. WREN.

α-Anilino-*o*-nitrophenylacetonitrile and its transformations. A. REISSERT and F. LEMMER (Ber., 1926, **59**, [*B*], 351—359).—α-Anilino-*o*-nitrophenylacetonitrile, m. p. 140° [von Walther and Hübner (A., 1916, i, 559) record m. p. 132—133°], is conveniently prepared by warming *o*-nitrobenzaldehyde with aniline and treating the products successively with concentrated sodium hydrogen sulphite solution and sodium cyanide. The cyano-group is unusually resistant towards hydrolysis. The compound is extensively decomposed by mineral acids, whereas alkalis cause a partial reduction of the nitro-group with production of *3-cyano-2-phenylindazole-1-oxide*, m. p. 190°. The latter substance is reduced by iron and hydrochloric acid, phosphorus trichloride, or alcoholic hydrogen chloride to *3-cyano-2-phenylindazole*, m. p. 106—107°, which is converted successively into *2-phenylindazole-3-carboxylamide*, m. p. 243—244°, and *2-phenylindazole-3-carboxylic acid*, m. p. 199° (decomp.) (*methyl* ester, m. p. 169—170°). Decarboxylation of the acid affords 2-phenylindazole, m. p. 81—82°. Oxidation of 3-cyano-2-phenylindazole-1-oxide with chromic acid mixture leads to the production of azoxybenzene-*o*-carboxylic acid, m. p. 105—106° (cf. Freundler, A., 1910, i, 445), which is reduced by zinc dust and sodium hydroxide to hydrazobenzene-*o*-carboxylic acid, m. p. 162—163°, and by zinc dust and hot, dilute acetic acid to benzidine-2-carboxylic acid, m. p. 211° (decomp.) (*diacetyl* derivative, m. p. 266—267°). 2-Phenylindazole-3-carboxylic acid is oxidised by potassium dichromate and glacial acetic acid to azobenzene-*o*-carboxylic acid, m. p. 91—92°.

α-Anilino-*o*-nitrophenylacetonitrile or 3-cyano-2-phenylindazole-1-oxide is converted by a hot, aqueous solution of normal sodium sulphite into a mixture of *1-oxido-2-phenyl-3-indazyl sulphite*,



m. p. 94—95°, and 3-hydroxy-2-phenylindazole, m. p. 201° after darkening at 190° (cf. Heller, A., 1917, i, 220). The ester is reduced by iron and hydrochloric acid to *anthranilanilide*, m. p. 131—132°, and is hydrolysed to sulphuric acid and a *substance*, $C_{13}H_{10}ON_2$, m. p. 250—251°, to which the constitution  is ascribed, since, unlike 2-arylated indazoles, it is stable towards oxidising agents and suffers fission of the ring to anthranilanilide when reduced with iron and hydrochloric acid.

H. WREN.

Indazole derivatives. K. VON AUWERS and P. STRÖDTER (Ber., 1926, **59**, [*B*], 529—538).—2-Amino-4′-methylbenzophenone is converted by diazotisation and treatment of the diazonium compound with sodium sulphite into *2-hydroxy-3-p-tolylindazole*, m. p. 119° (decomp.), which loses nitrogen and forms 4-methylbenzophenone when heated above its m. p., and is converted by boiling, dilute sodium hydroxide solution into *3-hydroxy-2-p-tolylindazole*, m. p. 215° (decomp.) after darkening at 190° (*acetyl* derivative, m. p. 98°; *benzoyl* compound, m. p. 154—155°). Reduction of 2-hydroxy-3-*p*-tolylindazole by stannous chloride and hydrochloric acid in alcoholic solution affords *3-p-tolylindazole*, m. p. 97—98° after softening at 91° (*picrate*, m. p. 147—148°; *acetyl* derivative, m. p. 79·5—80·5°). Starting from 2-amino-4′-methoxybenzophenone, the following series of substances is similarly obtained: *2-hydroxy-3-p-anisylindazole*,

m. p. 132° (decomp.); 3-*hydroxy*-2-p-*anisylindazole*, m. p. about 163° (decomp.) after darkening at 153° (*acetyl* derivative, m. p. 110°; *benzoyl* derivative, m. p. 139·5—140°); 3-p-*anisylindazole*, m. p. 110—111° (*picrate*, m. p. 147—148°; *acetyl* derivative, m. p. 105—106°). The compounds are thus completely analogous with those derived from *o*-aminobenzophenone, excepting that *p*-tolyl- and *p*-anisylindazole have not been isolated in two forms; their indefinite m. p. indicate, however, that the products isolated may be mixtures of isomerides.

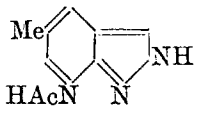
Reduction of 2-phenylindazole by sodium and alcohol appears to afford initially 2-phenyl-1 : 3-dihydroindazole, m. p. about 153° (the homogeneity of which is not established); more drastic action of these reagents leads to unexpected fission of the pyrazole ring, with production of *o*-aminobenzylaniline.

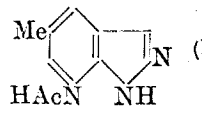
Methyl indazole-1 : 3-*dicarboxylate*, m. p. 174—175° (decomp.), is readily prepared from methyl indazole-3-carboxylate and methyl chloroformate. It is readily hydrolysed to methyl indazole-3-carboxylate, and passes into methyl 1-methylindazole-3-carboxylate when distilled under diminished pressure. Similarly, 3-*carbomethoxy*-1-*carbethoxyindazole*, m. p. 116°, b. p. 218°/13 mm., passes when strongly heated into methyl 1-ethylindazole-3-carboxylate. The presence of the carbomethoxyl group in position 3 appears therefore to prevent the wandering of the alkyl group from position 1 to 2; this observation is in contrast with those made with 3-phenylindazole-1-carboxylic esters.

Methyl indazole-3-carboxylate is converted by allyl bromide at 120—130° and hydrolysis of the product into 1-*allylindazole*-3-*carboxylic acid*, m. p. about 147°; the isomeric 2-allyl derivative does not appear to be formed.

o-Nitrobenzoyl chloride and ethyl indazole-3-carboxylate afford *ethyl* 1-*o*-*nitrobenzoylindazole*-3-*carboxylate*, m. p. 182—183°. Attempts to prepare an isomeric ester from *o*-nitrobenzoyl chloride and the silver salt of ethyl indazole-3-carboxylate gave a substance, m. p. 132·5—133·5°, the constitution of which has not been elucidated. H. WREN.

7-Amino-5-methylindazole and 7(4)-amino-2-methylbenziminazole. K. VON AUWERS and E. FRESE (Ber., 1926, **59**, [*B*], 539—555).—*o*-Nitro-*as*-*m*-xylidine is converted by diazotisation and treatment of the diazonium compound with boiling water into 7-nitro-5-methylindazole, m. p. 192·5°, which is conveniently reduced by ammonium sulphide in alcoholic solution to 7-amino-5-methylindazole, m. p. 166°. The base is converted by protracted treatment with boiling acetic anhydride into a *triacetyl* derivative, m. p. 148°, instead of the expected anhydro-compound. At 100°, 7-*acetamido*-2-*acetyl*-5-*methylindazole*, m. p. 151°, is produced, which can also be obtained in pyridine solution or from acetyl chloride and the silver salt of 7-amino-5-methylindazole. When distilled under diminished pressure, it passes into the stable 7-*acetamido*-1-*acetyl*-5-*methylindazole*, m. p. 127°, which, in contrast to the labile isomeride, is stable towards ethereal hydrogen chloride. The structure of the compounds is interpreted from the isomeric relationships of the two series of acylindazoles (A., 1925, i, 1460). lab.-7-*Acetamido*-5-*methylindazole* (I), m. p. 135°, is prepared by the cautious treatment of the diacetyl derivative, m. p. 151°, with acid or alkali or from 7-amino-5-methylindazole and cold acetic anhydride; the absence of a free amino-group in the benzene nucleus is established by the inability of the compound to condense with *p*-nitrobenzaldehyde. From the labile derivative, a stable 7-*acetamido*-5-*methylindazole*, (II), m. p. 199°, was obtained incidentally during crystallisation, and subsequent attempts to obtain the isomeride of lower m. p. uniformly gave the derivative, m. p. 199°. The constitutions (I) and (II) are assigned to the compounds. Partial

(I.) 



(II.)

hydrolysis of the diacetate, m. p. 127°, affords the compound, m. p. 199°. Contrary to expectation, the monoacetate does not yield an anhydro-base when distilled or treated with dehydrating agents. Protracted treatment of 7-amino-5-methylindazole with boiling glacial acetic acid affords only the monoacetyl derivative, m. p. 199°. 7-Amino-5-methylindazole condenses with *p*-nitrobenzaldehyde to 7-p-*nitrobenzylideneamino*-5-*methylindazole*, m. p. 247—248° after softening, which with boiling acetic anhydride or acetyl chloride and pyridine affords a *monoacetyl* derivative, m. p. 231—232°; attempts to remove the *p*-nitrobenzylidene group were unsuccessful.

Analogous results are obtained with the benzoyl derivatives. 7-Benzamido-2-benzoyl-5-methylindazole, m. p. 186—187°, is most conveniently prepared by the pyridine method. It is readily hydrolysed to 7-*benzamido*-5-*methylindazole*, m. p. 164—165° (*hydrochloride*, m. p. 199—202°; *picrate*, m. p. 189°); formation of a labile isomeride could not be detected. The monobenzoyl derivative is partly largely decomposed, partly unchanged by distillation under diminished pressure, whereas, under similar conditions, the 2 : 7-dibenzoyl compound is isomerised to 7-*benzamido*-1-*benzoyl*-5-*methylindazole*, m. p. 139—140°. Attempts to prepare an aminoindazole benzoylated only in the pyrazole ring were unsuccessful. 7-Nitro-5-methylindazole is converted by benzoyl chloride and pyridine under certain conditions into 7-*nitro*-2-*benzoyl*-5-*methylindazole*, m. p. 200—201° when introduced into a bath pre-heated almost to this temperature, which is isomerised when boiled with nitrobenzene to 7-*nitro*-1-*benzoyl*-5-*methylindazole*, m. p. 151—152°; the compounds could not be reduced successfully.

7-Amino-5-methylindazole and carbamide at 145° afford ammonia and 7-*carbamido*-5-*methylindazole*, m. p. 216—218° (decomp.); *ethyl* 7-*amino*-5-*methylindazole*-1-*carboxylate* melts indefinitely.

The difficulty of forming anhydro-bases does not appear to be peculiar to 7-amino-5-methylindazole. Thus the somewhat similarly constituted 7(4)-amino-2-methylbenziminazole, prepared by reduction of the corresponding nitro-compound or from *vic*-triaminobenzene, gives a monoacetyl derivative which can be distilled unchanged and is unaffected by heat. A

tricyclic compound could not be produced by protracted treatment of *vic*-triaminobenzene with boiling glacial acetic acid or acetic anhydride or mixtures of these substances. The view that *o*-diamines are converted into anhydro-bases by boiling glacial acetic acid and into diacetyl derivatives by acetic anhydride appears too general, since time appears to be a more important factor than the reagent. Thus *o*-phenylenediamine and acetic anhydride after protracted ebullition yield exclusively the anhydro-base, whereas *vic*-triaminobenzene under similar conditions affords a mixture of anhydro-base and triacetyl derivative, but, with glacial acetic acid, gives exclusively the anhydro-base.

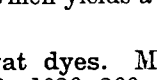
The difficulties attendant on the production of a five-membered ring from 7-amino-5-methylindazole are also encountered in attempts to form a six-membered ring. Thus the base is converted by chloroacetyl chloride in pyridine or, preferably, in anhydrous ether in the presence of potassium carbonate into a mixture of *7-chloroacetamido-5-methylindazole*, m. p. 168°, and *7-chloroacetamido-N-chloroacetyl-5-methylindazole*, m. p. 146—147°, which is essentially hydrolysed by treatment with cold, dilute alkali hydroxide solution. On the other hand, phenmorpholones are readily obtained by a similar process from the chloroacetyl derivatives of α-aminophenols. Thus *o-chloroacetamidophenol*, needles, m. p. 113·5—114·5°, or leaflets, m. p. 137—138°, is smoothly converted into phenmorpholone, m. p. 169°, and *o-chloroacetamido-s-m-xylenol*, m. p. 145—146°, gives *5 : 7-dimethylphenmorpholone*, m. p. 203—204°.

The preparation of 2 : 6-dinitroaniline by passing ammonia through a boiling alcoholic solution of 1-chloro-2 : 6-dinitrobenzene, of *vic*-triaminobenzene by reduction of 2 : 6-dinitroaniline by stannous chloride and hydrochloric acid, and of *ethyl 7-nitro-5-methylindazole-1-carboxylate*, m. p. 143—145°, from 7-nitro-5-methylindazole and ethyl chloroformate, is incidentally recorded. H. WREN.

Synthesis of phenylrosinduline. R. LANTZ and A. WAHL (Compt. rend., 1926, **182**, 705—708).—2-Hydroxy-*NN*-diphenyl-1 : 4-naphthaquinonediimine (A., 1925, i, 820) is treated with excess of aniline at 160—180° in presence of benzoic acid or zinc chloride, and air is bubbled through, phenylrosinduline being obtained, which yields a very pure azocarmine on sulphonation. L. F. HEWITT.

[Phenazine] vat dyes. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 266.

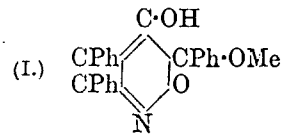
Conversion of a β-amino-acid into a metoxazine derivative. P. KARRER and E. MIYAMICHI (Helv. Chim. Acta, 1926, **9**, 336—339; cf. A., 1924, i, 1118).—β-Benzamidopropionic acid, m. p. 133° (cf. Holm, A., 1905, i, 29, m. p. 120°), gives an *ethyl* ester, b. p. 184—186°/3 mm., which with phosphorus pentoxide yields *2-phenyl-6-ethoxymetoxazine*,

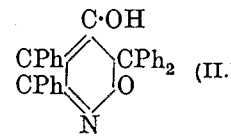


m. p. 74° (*picrate*, m. p. 103°), decomposed by warm dilute hydrochloric acid into β-benzamidopropionic acid and a trace of β-aminopropionic acid.

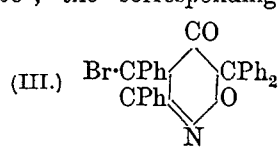
M. CLARK.

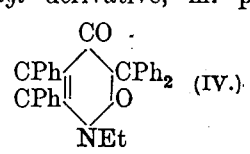
Orthoxazine [1 : 2(6)-oxazine] derivatives. E. P. KOHLER (J. Amer. Chem. Soc., 1926, **48**, 754—763; cf. this vol., 309).—When pure αγδ-triphenylbutanetrione oxime is boiled in absolute methyl-alcoholic solution it yields, together with 5-hydroxy-5-benzoyl-3 : 4-diphenyl*iso*oxazoline (*loc. cit.*), *5-hydroxy-6-methoxy-3 : 4 : 6-triphenyl-1 : 2(6)-oxazine* (I), decomp. about 173° after turning red at about 160° (*sodium* salt; *benzoate*, m. p. 163°). This gives a yellow solution in chloroform, changing to purple owing to the formation of the anhydride previously reported, whilst the solution in ether gradually deposits the original oxime, and the methyl-alcoholic solution affords similarly the above *iso*oxazoline. When exposed to light, it undergoes autoxidation, turning yellow. Treatment with methyl iodide in methyl-alcoholic sodium methoxide solution affords a *methyl* derivative, m. p. 147° (decomp.), which yields a slightly explosive *ozonide*, whilst the action of magnesium phenyl bromide in boiling ethereal solution affords *5-hydroxy-3 : 4 : 6 : 6-tetraphenyl-1 : 2(6)-oxazine*, (II), lemon-yellow, m. p. about 220°





(decomp.) [*benzoate*, m. p. 217°; *4-bromo*-derivative, (III), (*4-bromo-3 : 4 : 6 : 6-tetraphenyl-1 : 2(6)-oxaz-5-one*), m. p. 160°; *4-chloro*-derivative, m. p. 165°; *4-nitro*-derivative, m. p. 150° (decomp.)]. When treated with ethyl iodide in alcoholic sodium ethoxide solution, (II) yields *3 : 4 : 6 : 6-tetraphenyl-2-ethyl-5-keto-2 : 5-dihydro-1 : 2(6)-oxazine* (IV), m. p. 167—168°, the corresponding *methyl* derivative, m. p.





189—190°, being obtained similarly. The latter yields an *ozonide*, which, on decomposition with steam, affords methylamine and the diketone, $Bz{\cdot}CO{\cdot}CPh_2{\cdot}OH$. Oxidation of (II) in acetone solution, either with atmospheric oxygen or permanganate, affords a *solid*, decomp. about 165°, insoluble in alkalis, which could not be purified. When boiled with alcoholic acids or bases, (II) is converted into 2 : 2 : 4 : 5-tetraphenyl-3-keto-2 : 3-dihydrofuran. F. G. WILLSON.

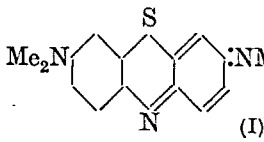
Reactions of the formamidines. XI. 2-Thion-4-thiazolidones. F. B. DAINS and S. I. DAVIS (Kansas Univ. Sci. Bull., 1924, **15**, 265—270; cf. A., 1922, i, 1185).—The 2-thion-4-thiazolidones react with substituted formamidines to give substances of the type $S{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}C{:}CH{\cdot}NHR$ and with aldehydes to form compounds of the type $S{\cdot}CS{\cdot}NH{\cdot}CO{\cdot}C{:}CHR$.

2-Thio-4-thiazolidone and diphenylformamidine yield *2-thion-5-anilinomethylene-4-thiazolidone*, m. p. 248°. *2-Thion-3-phenyl-4-thiazolidone* (from ammonium phenyldithiocarbonate and sodium chloroacetate),

affords 2-*thion*-3-*phenyl*-5-*anilinomethylene*-4-*thiazolidone*, m. p. 247° (? *hydrazone*, m. p. 215°). 2-*Thion*-3-*phenyl*-5-*α*-*naphthylaminomethylene*-4-*thiazolidone* has m. p. 279°; 2-*thion*-3-p-*tolyl*-5-*anilino*-4-*thiazolidone*, m. p. 235°, 2-*thion*-3-*phenyl*-5-p-*methoxyanilinomethylene*-4-*thiazolidone* m. p. 158—160°, 2-*benzylthiol*-5-*benzylidene*-4-*thiazolidone* m. p. 123°, 2-*benzylthiol*-5-*cinnamylidene*-4-*thiazolidone* m. p. 143°, 2-*ethylthiol*-5-*anilinomethylene*-4-*thiazolidone* m. p. 175°, and 2-*benzylthiol*-5-*anilinomethylene*-4-*thiazolidone* m. p. 221—223°. CHEMICAL ABSTRACTS.

Thiazoles. IX. Derivatives of 2-phenylbenzthiazole. M. T. BOGERT and H. B. CORBITT (J. Amer. Chem. Soc., 1926, **48**, 783—788; cf. this vol., 310).—Treatment of 2-phenylbenzthiazole with phosphorus pentachloride affords 6-*chloro*-2-*phenylbenzthiazole*, m. p. 156·7° (cf. Hofmann, A., 1880, 884), which is also obtained by treating 2-phenylbenzthiazole-6-diazonium chloride with copper bronze (cf. Morgan and Webster, J.C.S., 1921, **119**, 1070) and by fusing benzylidene-*p*-chloroaniline with sulphur. Further treatment with phosphorus pentachloride does not introduce more chlorine into the molecule, and no exchange of halogen occurs when the chloro-derivative is boiled in alcoholic solution with lithium bromide. 6-Nitro-2-phenylbenzthiazole (cf. Bogert and Abrahamson, A., 1922, i, 576) has m. p. 196°, whilst dinitrobenzthiazole (cf. D.R.-PP. 50486, 54921) has m. p. 223°. 2-m-*Nitrophenylbenzthiazole*, m. p. 186·8—187·3°, obtained from zinc *o*-aminophenylmercaptide and *m*-nitrobenzoyl chloride, is described. 2-*p*-Nitrobenzthiazole (cf. Bogert and Snell, A., 1924, i, 772) has m. p. 233°. Coupling of diazotised 6-amino-2-phenylbenzthiazole with "H" acid affords a *dye* which gives a light-fast rose-lavender shade on artificial silk. The dye also stains red blood-cells faintly in 0·1% neutral solution, and stains the plasma, but not the nucleus, of leucocytes. 2-m-*Aminophenylbenzthiazole*, m. p. 140·4—140·9°, was prepared. 2-*p*-Aminophenylbenzthiazole has m. p. 156·2—156·7° (cf. Bogert and Snell, *loc. cit.*). 6-*Hydroxy*-2-*phenylbenzthiazole*, m. p. 228—229°, obtained from the corresponding amino-derivative, is described. 2-*o*-Hydroxyphenylbenzthiazole, prepared by condensing zinc *o*-aminophenylmercaptide with salicylaldehyde, has m. p. 131·1—131·7° (cf. Hofmann, *loc. cit.*). 2-p-*Hydroxyphenylbenzthiazole*, m. p. 228·6—229·1°, obtained both from the corresponding amino-derivative and from *p*-hydroxybenzaldehyde, yields, when treated with nitric and sulphuric acids, a *mononitro*-derivative, bright yellow, m. p. 199·2—199·7°, and a *dinitro*-derivative, slightly darker in colour, m. p. 252—256·8°. Reduction of the former yields the corresponding *amino*-derivative, m. p. 234·5—235·5°. F. G. WILLSON.

Polychrome methylene-blue. W. J. MACNEAL and J. A. KILLIAN (J. Amer. Chem. Soc., 1926, **48**, 740—747).—Methylene-blue and potassium dichromate give the *chromate*, $(C_{16}H_{18}N_2S)_2CrO_4,6H_2O$. When washed with alcohol, a portion of the dye is removed. Methylene-azure-B (trimethylthionine; cf. Kehrmann, A., 1906, i, 460) has been obtained, under special conditions, as the bromide, from the above chromate. The bromide decomposes when heated to 100°. The preparation of the chloride, zinc chloride double salt, and iodide is also described. The iodide is stable at 100°. The structure (I) is ascribed to the iodide. When treated with aqueous alkalis, the colour changes to a brown or bluish-lavender, and the free base can be extracted from the aqueous solution with ether etc. Methylene-azure-A (chromate described) is the chief oxidation product when methylene-blue is boiled with hydrochloric acid and potassium dichromate, but is obtained in a purer condition by warming the zinc chloride double salt of methylene-azure-B with potassium dichromate, and boiling the crystalline precipitate, which separates on cooling, with hydrochloric acid. When boiled in dilute alkaline solution with zinc (or silver) ammonium hydroxide, methylene-azure-B affords crystalline methylene-violet. Better yields of methylene-violet are obtained by boiling methylene-blue with aqueous ammoniacal silver nitrate, filtering, boiling the filtrate with sodium carbonate for several hours, cooling, and recrystallising the precipitated dye from ethylene dichloride. The above reactions support Hantzsch and Bernthsen's *p*-quinonoid structure for methylene-blue. F. G. WILLSON.



(I).

Reduction of caffeine and theobromine to the deoxy-compounds. F. FICHTER and W. KERN (Helv. Chim. Acta, 1926, **9**, 380—383).—Deoxycaffeine and deoxytheobromine, previously obtained by electrolytic reduction of caffeine and theobromine, are readily obtained from these substances by reduction with pure zinc dust in concentrated hydrochloric or hydrobromic acid solution. M. CLARK.

Microchemical reactions of tutocaine. L. ROSENTHALER (Pharm. Zentr., 1926, **67**, 177—179).—An illustrated, non-crystallographic description of the crystals formed by the action of platinic chloride, auric chloride, potassium tetranitritocobaltidiammine, potassium iodide, and mercuric chloride on tutocaine, novocaine, and cocaine. Crystalline derivatives were not obtained from tutocaine and cocaine by the action of mercuric chloride. J. S. H. DAVIES.

Dyes from the alkaloids of ipecacuanha. F. L. PYMAN (J. Amer. Chem. Soc., 1926, **48**, 836; cf. A., 1925, i, 1087).—Emetine, *O*-methylpsychotrine, and emetamine do not couple with *p*-nitrodiazobenzene. Psychotrine does so, the dye giving a purple solution in aqueous sodium hydroxide, similar to that given by the dye from cephæline. A misquotation from the present author's paper (J.C.S., 1917, **111**, 419) with regard to the constitution of emetamine (*loc. cit.*) is corrected. F. G. WILLSON.

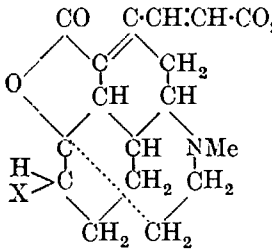
Dyes from the alkaloids of ipecacuanha. S. PALKIN and H. WALES (J. Amer. Chem. Soc., 1926, **48**, 836—837; cf. preceding abstract).—An acknowledgment of Pyman's correction (*loc. cit.*).
F. G. WILLSON.

Oxidation of harmaline and bromoharmaline. V. HASENFRATZ and R. SUTRA (Compt. rend., 1926, **182**, 703—705).—Harmaline hydrochloride is oxidised

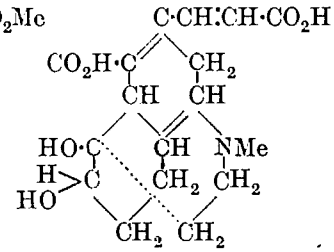
by chromic acid, giving an 86% yield of harmine hydrochloride. Bromoharmaline when heated with chromic acid for 1 hr., and then treated with alcoholic potassium hydroxide, yields *iso*bromoharmine, which is precipitated by addition of water.

L. F. HEWITT.

Action of ozone on dihydrocodeine and ethyldihydromorphine. Fission of the morphine molecule. E. SPEYER and A. POPP (Ber., 1926, **59**, [*B*], 390—406).—Ozonisation of codeine in neutral or formic acid solution causes profound change in the molecule, but does not lead to crystalline products. Dihydrocodeine, dissolved in formic acid, is transformed into a *compound* (I) which could not be caused to crystallise and for which the name "ozodihydrocodeine" is provisionally proposed. Absence of aldehydic or ketonic groups is established by the



(I.) X=OH. (II.) X=Cl.

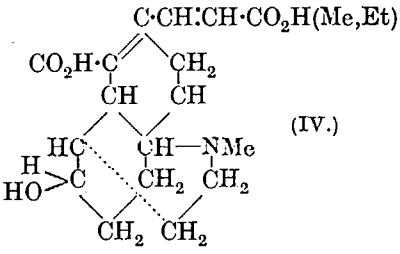


(III.)

indifference of the substance towards hydroxylamine, phenylhydrazine, semicarbazide, Fehling's solution, or Schiff's reagent. It contains one methoxyl group. Its insolubility in cold alkali hydroxide establishes the persistence of the oxygen bridge of dihydrocodeine. It yields a *hydrochloride*, $C_{18}H_{23}O_5N,HCl$, decomp. 242°, $[\alpha]_D^{18}$ +77·6 in aqueous solution; *hydrobromide*, decomp. 238°; *hydriodide*, decomp. 248—250°; *picrate*, decomp. 238—239° after softening at 230°, and *methiodide*, decomp. 155° after softening at 152°. The presence of a secondary alcoholic group is established by the formation of an *acetate* (isolated as the *picrate*, decomp. 208—209°) and by the formation, by means of phosphorus pentachloride in the presence of chloroform, of *chloro-ozodihydrocodeine* (II), m. p. 157—158° after softening at 152° (*picrate*, decomp. 249—250°). Hydrolysis of ozodihydrocodeine with potassium hydroxide affords *dihydromorphinic acid* (III), decomp. 227° after softening at 195°, $[\alpha]_D^{16}$ +30·9° in water. The acid is very closely related to the "morphinic acid" of Wieland and Kappelmeier (A., 1911, i, 743), but in consideration of its ketonic properties it is suggested that the name "morphinonic acid" is more appropriate to the latter compound.

It appears, therefore, that under the influence of ozone the morphine ring suffers rupture at the $\Delta^{3:4}$-position in the benzene nucleus, whereas the nitrogen ring remains intact. In support of this view, it is observed that ethyldihydromorphine is converted by ozone in the presence of dilute formic acid into the non-crystalline *ozoethyldihydromorphine* [(I) with $\cdot CO_2Me$ replaced by $\cdot CO_2Et$], characterised as the *hydriodide*, decomp. 255—256°, $[\alpha]_D^{17}$ +70·4° in water, which is hydrolysed to dihydromorphinic acid identical with the acid described above.

Ozodihydrocodeine is reduced by zinc dust and dilute acetic acid to a non-crystalline substance which yields a *hydrochloride*, $C_{18}H_{27}O_5N,HCl$, m. p. 232—233°, in small amount, so that full investigation is impossible. Electrolytic reduction, according to Tafel, converts ozodihydrocodeine into *deoxydihydromorphinic acid*



(IV.)

(IV), m. p. 248° (decomp.) after softening at 245°, $[\alpha]_D^{17}$ +28·7° in aqueous solution (*picrate*, decomp. 222—223°). The conception that reduction causes fission and addition of hydrogen at the lactone ring accompanied by hydrolysis of the ester is established by the production of the same acid from ozoethyldihydromorphine. Addition of hydrogen at the lactone ring instead of at one of the double linkings appears remarkable, but a similar result is attained when hydrogenation is effected in neutral solution in the presence of palladium. Thus, ozodihydrocodeine hydrochloride affords *methyl deoxydihydromorphinate* [cf. (IV)], m. p. 150—151° (*hydrochloride*, m. p. 247—248°, $[\alpha]_D^{18}$ +13·3° in aqueous solution; *hydriodide*, decomp. 195°; *picrate*, decomp. 228—229°; *methiodide*, m. p. 183—184°). The presence of the secondary alcoholic group is established by the isolation of the *acetyl* derivative, which could not be caused to crystallise (corresponding *methiodide*, decomp. 225°), and of *methyl chlorodeoxydihydromorphinate*, m. p. 143° (*picrate*, decomp. 213—214°). Methyl deoxydihydromorphinate is hydrolysed to deoxydihydromorphinic acid, identical with that derived by electrolytic reduction of ozodihydrocodeine or ozoethyldihydromorphine. Analogously, ethyldihydromorphine is transformed by hydrogen in the presence of palladium into *ethyl deoxydihydromorphinate* [cf. (IV)] (characterised as the *picrate*, decomp. 234—235°), which is hydrolysed to deoxydihydromorphinic acid.

Morphinic acid is reduced by hydrogen in the presence of palladium to *tetrahydromorphinic acid*, m. p. 217—218° after softening at 202°; it has not been established whether hydrogenation takes place at the nucleus or side-chain.

H. WREN.

Importance of alkyl esters of aromatic sulphonic acids for the alkylation of organic compounds. W. RODIONOW (Bull. Soc. chim., 1926, [iv], **39**, 305—325).—Phenyltrimethylammonium *p*-toluenesulphonate may be advantageously substituted for the chloride of the same base as a methylating agent owing to the greater facility with which it may be prepared. It is obtained by heating methyl *p*-toluenesulphonate (186 g.) with dimethylaniline (121 g.) until the reaction begins. The product, m. p. 160—161°, is obtained in quantitative yield and may be used without preliminary purification if the starting materials are pure. Methyl benzenesulphonate combines quantitatively with

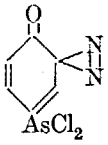
dimethylaniline to form phenyltrimethylammonium benzenesulphonate, which was used in the methylation of morphine. Phenyldimethylethylammonium *p*-toluenesulphonate is prepared from ethyl *p*-toluenesulphonate and dimethylaniline; with alcoholic sodium ethoxide this gives phenyldimethylethylammonium hydroxide, which alkylates phenol to phenetole and was also used in alkylating morphine. Codeine when boiled with methyl *p*-toluenesulphonate and water yields α-methylmorphimethine, which forms a *metho*-p-*toluenesulphonate*, m. p. 250—251°. This substance on treatment with sodium hydroxide solution is transformed into β-*methylmorphimethine metho*-p-*toluenesulphonate*, m. p. 297—300°. Methyl *p*-toluenesulphonate acts on narcotine with formation of narceine, and with hydrastine forms the *metho*-p-*toluenesulphonate*, m. p. 228—229°, which in presence of sodium hydroxide yields methylhydrastine. The *metho*-p-*toluenesulphonate* of *papaverine* has m. p. 165°, of *brucine*, m. p. above 250°, and of *phenylmethylpyrazolone*, m. p. 91—92°. The last-named on treatment with sodium hydroxide and chloroform is converted into antipyrine, from which the nitroso-derivative was obtained and reduced to the *amino*-derivative, m. p. 230—231°. Aminoantipyrine hydrochloride on treatment with methyl *p*-toluenesulphonate and sodium hydroxide is transformed into pyramidone. Theobromine with methyl *p*-toluenesulphonate yields caffeine, and with the ethyl ester ethyltheobromine is formed. Methyl *p*-toluenesulphonate with cotarnine yields a non-crystallisable oil which on treatment with potassium iodide is converted into cotarnomethine methiodide; papaverine and brucine behave similarly. Methyl *p*-toluenesulphonate and potassium iodide in aqueous solution yield methyl iodide; ethyl iodide and bromide may be similarly obtained. Aromatic halides are not formed in this manner. A similar reaction occurs with potassium cyanide, aceto- or propio-nitrile being formed. Sodium nitrite with the methyl or ethyl ester of *p*-toluenesulphonic acid yields, respectively, nitromethane and nitroethane.

H. J. Evans.

Reaction of alkaloids with furfuraldehyde and sulphuric acid. L. Ekkert (Pharm. Zentr., 1926, **67**, 179—181).—A few drops of a mixture of 1 g. of a 1% aqueous solution of furfuraldehyde and 10 g. of concentrated sulphuric acid for 0·01—0·03 g. of substance is recommended as a reagent for colour tests with the following alkaloids, especially atropine, scopolamine, and hyoscine. Veratrine and colchicine form blue to violet, and yellow to brownish-yellow colorations, respectively, at the ordinary temperature, whilst morphine, codeine, ethylmorphine, and *apo*morphine form red solutions under similar conditions. With the remainder careful heating is necessary before the characteristic colours develop: atropine, intense violet- or cherry-red; novatropine, methylhomatropine, "quinoine," bright blue to dark green; scopolamine, intense violet- or cherry-red; hyoscine, intense violet-red; veratrine, wine-red to intense dark red, yellow on dilution with water; colchicine, yellow, green, then brown; quinine, violet streaks; morphine, red to violet-red; codeine, red to violet-red, blue on dilution with water; ethylmorphine, as for codeine; *apo*morphine, dark red, grey on dilution with water, green on addition of alkali, red on shaking; antipyrine, blood-red to dark mulberry-red, violet on dilution with water, the chloroform extract of which is yellow; Tinct. and Extract. Belladonnæ and Extract. Hyoscyami, rose-red to violet-red; Tinct. Veratri, cherry- to violet-red. No distinctive colorations are given by β-eucaine, caffeine, theobromine, cocaine, strychnine, brucine, and eserine.

J. S. H. Davies.

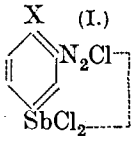
Aromatic compounds of arsenic. II. Internal complex salt of benzenediazonium chloride and arsenic chloride and its transformation into *p*-phenylenearsinic acid. H. Schmidt and F. Hoffmann (Ber., 1926, **59**, [*B*], 560—564; cf. A., 1920, i, 897).—The complex *salt* (I), decomp. about 100°, is prepared by diazotisation of *p*-aminophenylarsenic acid dissolved in 5*N*-hydrochloric acid, followed by treatment of the solution with sulphur dioxide in the presence of a trace of iodine or by direct diazotisation of *p*-aminophenyldichloroarsine in aqueous hydrochloric acid or, preferably, by use of amyl nitrite and alcoholic hydrogen chloride. It is converted by an aqueous suspension of sodium hydrogen carbonate into p-*phenylenearsinic acid* [(II), X=(:O)·OH] (the *monohydrate* is also described), the unimolecular structure of which is established by determination of the mol. wt. of p-*phenylenechloroarsine* [(II), X=Cl], into which

(I.) (II.) (III.) 

it is transformed by solution in alcoholic hydrogen chloride and reduction with sulphur dioxide in the presence of a little iodine. 3-Amino-4-hydroxyphenylarsinic acid is transformed by diazotisation in 5*N*-hydrochloric acid solution and subsequent reduction by sulphur dioxide and iodine into the *compound* $C_6H_4ON_2Cl_3As$, which when precipitated from its solution in methyl alcohol by ether loses 1 mol. of hydrogen chloride and affords the *quinonediazide* (III).

H. Wren.

Aromatic compounds of antimony. IX. Internal complex salts from benzenediazonium chloride and antimony chloride. H. Schmidt and F. Hoffmann (Ber., 1926, **59**, [*B*], 555—560).—4-Chloro-3-nitrophenylstibinic acid is reduced by stannous chloride and hydrochloric acid to 4-*chloro*-3-*aminophenyldichlorostibine hydrochloride*, m. p. 151—153°, which is converted by sodium nitrite and 5*N*-hydrochloric acid or, preferably, by acetic acid and amyl nitrite in methyl-alcoholic solution into the *salt* [(I) X=Cl], decomp. about 100°; this is immediately decomposed by cold, dilute alkali hydroxide solution into nitrogen and stibinic acids soluble in alkali. Similarly, *m*-aminoacetanilide, m. p. 86·5° (hydrochloride, m. p. 245°), is converted successively into *m*-acetylstibanilic acid, *m*-aminophenylstibinic acid, *m*-aminophenyldi-

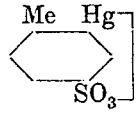
(I.) 

chlorostibine hydrochloride, and the complex *salt* [(I) X=H], decomp. 165—167°. p-*Aminophenyldichlorostibine hydrochloride*, m. p. 122—125°, gives an analogous *salt*, $ClN_2 \cdot C_6H_4 \cdot SbCl_2$, which is very unstable. H. WREN.

Organo-chromium compounds. VI. Chromium tetraphenyl. F. HEIN and W. EISSNER (Ber., 1926, **59**, [*B*], 362—366; cf. A., 1921, i, 826; 1922, i, 76, 77; 1924, i, 437, 889).—*Chromium tetraphenyl* is prepared as a smooth deposit or crystalline precipitate, which retains the colour of chromium tetraphenyl salts, by the electrolysis of a solution of chromium tetraphenyl iodide in liquid ammonia at −40° to −50°. The cathode consists of a platinum plate; the graphite anode is placed in a porous cell. The substance readily decomposes with formation of diphenyl; it is converted quantitatively by alcohol into chromium tetraphenyl hydroxide. Its mol. wt. has not been determined. H. WREN.

***p*-Chloromercuribenzoic acid and related compounds.** F. C. WHITMORE and G. E. WOODWARD (J. Amer. Chem. Soc., 1926, **48**, 533—536).—p-*Chloromercuribenzoic acid* is obtained as a white, amorphous powder which cannot be purified, by the oxidation of mercury *p*-tolyl chloride (cf. Whitmore, Hamilton, and Thurman, A., 1923, i, 501) with alkaline permanganate. When treated with iodine in alcohol, it affords *p*-iodobenzoic acid in 95% yield. The *sodium* salt, ill-defined, granular crystals, is described. When boiled with aqueous-alcoholic sodium hydroxide, the acid yields *sodium* p-*hydroxymercuribenzoate*, and this, when treated with aqueous sodium iodide or bromide, affords respectively *sodium* p-*iodomercuribenzoate* and p-*bromomercuribenzoate*. p-*Mercuribisbenzoic acid*, $Hg(C_6H_4 \cdot CO_2H)_2$, is obtained by treating *p*-chloromercuribenzoic acid with stannous chloride in aqueous sodium hydroxide. The *sodium* salt is very soluble in cold water, and when a concentrated aqueous solution is heated, a precipitate forms which redissolves on cooling, a phenomenon ascribed to hydrolysis at the higher temperature. Treatment of *p*-chloromercuribenzoic acid with phosphorus pentachloride in chloroform affords the *acid chloride*. This could not be purified, but yielded, when boiled with *n*-butyl alcohol, n-*butyl* p-*chloromercuribenzoate*, m. p. 170°. F. G. WILLSON.

Mercurisation of aromatic sulphonic acids. F. C. WHITMORE and L. EHRENFELD (J. Amer. Chem. Soc., 1926, **48**, 789—791).—Mercurisation takes place when aromatic sulphonic acids or their sodium salts are boiled in aqueous solution, under reflux, with 1 mol. of mercuric acetate and sufficient acetic acid to prevent hydrolytic precipitation of mercuric oxide. With the free acids, reaction is complete in about 1 hr., but the sodium salts require several hours' refluxing before the reaction mixture remains clear on being cooled, diluted, and basified. Of a number of sulphonic acids studied, pure products were obtained only from *p*-toluenesulphonic acid. Extraction of the crude reaction product with water afforded 2-*hydroxymercuritoluene*-4-*sulphonic acid dihydrate*, which yielded the anhydrous *acid* when dried over calcium chloride, and, when dried in a vacuum over phosphorus pentoxide, was converted into the *anhydride* (I). The position of the mercury atom was identified by treating the acid with iodine in aqueous solution, and converting the resulting 2-iodotoluene-4-sulphonic acid into the acid chloride and amide. F. G. WILLSON.



(I.)

Constitution of the cyanomercurisalicylic acids and of "hydrargyrum salicylicum." E. RUPP and H. GERSCH (Arch. Pharm., 1926, **264**, 88—92).—According to Boedecker and Wunstorf (A., 1925, i, 1107), the sparingly soluble and the readily soluble cyanomercurisalicylic acids, obtained when "hydrargyrum salicylicum" is treated with potassium cyanide, are the 3- and 5-derivatives, respectively. This is not so; the sparingly soluble acid is the 5-derivative, because it yields solely (the product is homogeneous but the yield variable, viz., 30—50%) 5-nitrosalicylic acid (m. p. 226°) when treated with hot dilute (33%) nitric acid, or with cold concentrated nitric acid, or with sodium nitrite and sulphuric acid, or in various other ways. Similarly, the readily soluble acid yields solely 3-nitrosalicylic acid (m. p. 144°, or $+H_2O$, m. p. 125°). The great difference between the m. p. of these compounds leaves no doubt as to their identity, and they are readily separated by fractional crystallisation. Thus it is that commercial samples of "hydrargyrum salicylicum" can be rapidly and simply tested. The formation of the cyanomercurisalicylic acids provides a means of carrying out a roughly quantitative test. Commercial preparations of "hydrargyrum salicylicum" are all mixtures. W. A. SILVESTER.

Physical and chemical properties of rhodoxanthin. T. LIPMAA (Compt. rend., 1926, **182**, 867—868).—Rhodoxanthin has been found in a large number of plants and may be separated from xanthophyll by means of the different solubility of these two substances in a mixture of carbon disulphide and methyl alcohol, or by means of the greater readiness with which xanthophyll is absorbed by calcium carbonate from carbon disulphide solution. Rhodoxanthin is very stable when kept in the dark, exhibits several absorption bands distributed through the spectrum, gives a dark green precipitate when treated with potassium hydroxide, and does not crystallise when treated with potassium hydroxide in 40% ethyl-alcoholic solution. Rhodoxanthin therefore has properties quite distinct from those of xanthophyll. L. F. HEWITT.

Isoelectric points of various proteins. F. A. CSONKA, J. C. MURPHY, and D. B. JONES (J. Amer. Chem. Soc., 1926, **48**, 763—768).—The isoelectric points of a large number of proteins were determined by measuring the amount of protein dissolved by shaking in a range of buffer solutions. The p_H value of the solution which gave the least precipitate with tungstic acid was taken as the isoelectric point of the protein. Proteins having greater solubility in aqueous solutions have the lower isoelectric points, and proteins of the same group have isoelectric points in close approximation to each other, those of albu-

mins ranging from p_H 4 to 5, globulins 5 to 5·5, and prolamines 6 to 6·5. Proteins requiring the greater amount of ammonium sulphate for their precipitation from saline solutions have lower isoelectric points than those requiring less. Thus β-globulins have lower isoelectric points than α-globulins. Albumins are more soluble, in the buffer solutions used, on the alkaline side of their isoelectric points, whilst globulins have greater solubility on the acid side.

F. G. WILLSON.

Determination of the Grignard reagent. H. GILMAN and C. H. MEYERS (Rec. trav. chim., 1926, **45**, 314—319).—In view of recent work by Job and Reich (A., 1924, i, 24; 1925, i, 173), the authors have repeated earlier work (A., 1923, ii, 272) and show that with magnesium ethyl bromide and iodide prepared under anhydrous conditions the acid titration method gives results less than 5% higher than the gas method. The revised iodine titration method with the same compounds appears to give results about 10% lower than those given by the gas method. The acid method gives results 10% higher than the gas method if the Grignard reagent is partly decomposed by moisture and oxygen, the basic compounds formed increasing the acid titre. The iodine titration is essentially free from this objection, but is regarded as of more limited application than the acid titration method.

R. BRIGHTMAN.

Alkalimetric determination of formaldehyde by means of sodium sulphite. K. TÄUFEL and C. WAGNER (Z. anal. Chem., 1926, **68**, 25—33).—The determination of formaldehyde by measuring the amount of alkali set free from sodium sulphite on adding an excess of this reagent to the solution under examination does not give very satisfactory results when phenolphthalein is used as indicator, unless the solution is saturated with sodium chloride before titration. The original formaldehyde solution must also be tested for acidity and due allowance made in calculating the results. For dilute formaldehyde solutions, thymolphthalein is a better indicator than phenolphthalein; no addition of sodium chloride is necessary in this case.

A. R. POWELL.

Iodometric determination of aldehyde sugars. M. E. PAUCHARD (J. Pharm. Chim., 1926, **8**, 248—255).—Solutions of the sugar, excess of standard iodine, and sodium carbonate, all cooled to 1°, are kept in a stoppered flask for at least 2½ hrs. The oxidation, $R{\cdot}CHO+I_2+H_2O=R{\cdot}COOH+2HI$, is then complete, no secondary reactions taking place. The solution is acidified with hydrochloric acid and the excess of iodine titrated with thiosulphate.

B. W. ANDERSON.

Oxidimetric determination of tartaric acid in the presence of nitrite by the method of Täufel and Wagner. M. WIKUL (Z. anal. Chem., 1926, **68**, 45—47).—On acidifying an alkaline solution containing tartrate in the presence of an excess of nitrite, the nitrogen oxides evolved oxidise part of the tartaric acid to carbon dioxide and water. This may be avoided by adding sodium sulphite to the alkaline solution, acidifying with sulphuric acid, and boiling until the excess of sulphur dioxide is expelled. The resultant solution is treated with an excess of dichromate and the excess determined iodometrically (cf. Täufel and Wagner, A., 1925, ii, 1007). The method is applicable to the determination of the tartaric acid in the complex adsorption compound, $C_4H_4O_6Co{\cdot}ONa+7NaK_2Co(NO_2)_6,H_2O$, which has been suggested by Wikul as suitable for the gravimetric determination of potassium (cf. this vol., 491).

A. R. POWELL.

"Formol" titration of certain amino-acids. S. L. JODIDI (J. Amer. Chem. Soc., 1926, **48**, 751—753).—Cystine can be accurately determined by the "formol" titration method (cf. Sörensen, A., 1910, ii, 466), whilst in the case of tryptophan the titration indicates only about 87% of this substance, which thus shows analogy with histidine and proline. Direct titration of hippuric acid with standard alkali yields results as accurate as those given by the "formol" method.

F. G. WILLSON.

Biochemistry.

Action of varying concentrations of cations on the osmotic resistance of blood-corpuscles. A. SIMON (Biochem. Z., 1926, **170**, 244—253).—In concentrations, in physiological sodium chloride, of the order of $M/6$ to $M/48$, the alkali and alkaline-earth cations increased the resistance of blood-cells to hæmolysis by hypotonic sodium chloride solutions. The order of efficiency was Li>Na>K>Mg>Ca. With cadmium, copper, iron, and bismuth ions, concentrations of $M/600$ to $M/10{,}000$ were effective. In both classes, there was, with increasing concentration, a reversal of the effect, so that the resistance of the cells became diminished. The ammonium ion showed only a diminution of the resistance of the cells. These results are discussed in relation to the changes in the corpuscular membrane and the nature of reversible hæmolysis.

R. K. CANNAN.

Barometric pressure and gaseous metabolism of erythrocytes. J. FÖRSTER (Biochem. Z., 1926, **169**, 93—99).—The oxygen consumption of defibrinated rabbit's blood is higher in those animals which have been living in a rarefied atmosphere. The erythrocyte count increases, but no nucleated cells were seen, although an increase in cell diameter was of constant occurrence in all the experimental animals.

C. RIMINGTON.

Physiology of high altitudes. I. Effect of diminished pressure on the p_H and carbon dioxide-combining power of blood. G. FRITZ (Biochem. Z., 1926, **170**, 236—243).—The p_H and carbon dioxide-combining power of the blood of rabbits and cats were lower at Davos than at Budapest. If the animals were submitted to artificial

reduction of the atmospheric pressure with constant carbon dioxide tension, the acidosis was accentuated. The carnivorous cat compensated the acidosis less readily than the herbivorous rabbit.

R. K. CANNAN.

Oxidative enzymes of the leucocytes. H. MIELKE (Klin. Woch., 1925, 4, 2201—2202).

CHEMICAL ABSTRACTS.

Proteolytic enzymes of serum. I. H. J. FUCHS (Biochem. Z., 1926, **170**, 76—101).—By determination of the increase in soluble nitrogen in incubated mixtures of serum and fibrin of the horse, ox, and sheep, it is shown that serum will only effect the digestion of fibrin of another species. The digestion is arrested by the accumulation of the products and may be accelerated by their removal, so that the fibrin may be completely dissolved. Dialysis against a salt solution comparable with the salt composition of serum still further facilitated the process. Although protein dialysed for long periods against such a salt solution suffers slight hydrolysis, the amount is insufficient to vitiate the above experiments. Serum submitted to a temperature of 56° for 30 min. loses its power to digest fibrin. Serum contains a specific enzyme for each foreign protein, but some evidence is advanced for the view that these may arise from a common non-specific zymogen.

R. K. CANNAN.

"Effective" osmotic pressure of the plasma proteins. G. F. FAHR and W. W. SWANSON (Amer. J. Physiol., 1926, **76**, 201—203).—The effective osmotic pressure is defined as the actual osmotic pressure exerted by the plasma proteins minus the pressure of the Donnan equilibrium which is set up. A sample of anasarca fluid was placed on the outside of the osmometer, as it was considered to be the nearest approach to the ultrafiltrate actually outside the blood capillaries. The mean value found for the "effective" osmotic pressure of the plasma proteins at 37° was 21·5 mm. of mercury. Comparison is made with the results of other workers.

R. K. CANNAN.

Ammonia content of, and ammonia formation in, the blood. IV. Is ammonia present in the circulating blood? J. K. PARNAS and A. KLISIECKI (Biochem. Z., 1926, **169**, 255—265; cf. A., 1925, i, 323, 454, 1484).—The circulating blood contains definite quantities of ammonia, which vary with the species, the individual, and the region from which the blood is derived. In dogs, in which the individual variation is very great, the ammonia content is of the order of 0·00001% of the arterial blood, of the venous blood somewhat higher. Ammonia formation in blood on keeping occurs in two stages. The first, occupying 3—4 hrs., is regarded as physiological. The second, commencing after 5 hrs., is probably of an autolytic nature.

E. C. SMITH.

Argon in blood. L. HACKSPILL, A. P. ROLLET, and M. NICLOUX (Compt. rend., 1926, **182**, 719—721; cf. A., 1925, i, 865, 1202).—Argon and nitrogen are present in defibrinated blood in approximately the proportions predicted by Henry's law. No argon was detected in the blood clot after it had been dried in a vacuum. The presence of argon in the blood is therefore due to physico-chemical equilibrium with the atmosphere, and not to radioactive decomposition of potassium, as suggested by Pictet, Scherrer, and Helfer.

L. F. HEWITT.

Ketonic substances of the blood. E. VON FAZEKAS (Biochem. Z., 1926, **170**, 224—229).—In ketonuria, the concentration of ketonic substances in the urine bears no direct relation to their concentration in the blood. In the blood, these substances are contained substantially in the corpuscles, except in diabetic coma, when they appear in the plasma. Injection of insulin leads to an immediate and notable fall in the concentration of β-hydroxybutyric acid in the blood before any significant fall occurs in the blood-sugar or acetone. A direct effect of insulin on fat metabolism is indicated.

R. K. CANNAN.

Evidence for the presence of an isomeride of dextrose in blood. M. B. VISSCHER (Amer. J. Physiol., 1926, **76**, 59—68).—The optical rotation of "protein-free" blood-filtrates prepared by the method used by Winter and Smith (A., 1923, i, 513) rises over a period of several days and then falls slowly. The maximum rotation does not agree with the dextrose content determined by copper reduction. Altering the method of removal of protein from the blood changes the optical behaviour of the extracts, so that the behaviour of diabetic blood reported by Winter and Smith was duplicated with normal blood. The optical changes are probably associated with protein in the blood-filtrates, and not with an isomerism of the dextrose of the blood.

R. K. CANNAN.

Partition of phosphorus between serum plasma and red blood-corpuscles. S. POSTERNAK (Compt. rend., 1926, **182**, 724—727).—The phosphorus of horse blood is present to the extent of 11·7% in the plasma and 88·3% in the red cells. Of the plasma phosphorus, 62·9% is extracted by alcohol or ether, and the remainder is in the form of inorganic phosphates. Of the phosphorus contained in the red cells, 21·7% is soluble in alcohol or ether, 11·5% is in the form of inorganic phosphates, whilst 61·1% of the phosphorus is contained in water-soluble organic compounds. In the dog also, the plasma phosphorus content is accounted for solely by alcohol- or ether-soluble compounds and inorganic phosphates, whilst 47·9% of the phosphorus content of the red cells is accounted for by soluble organic phosphorus compounds.

L. F. HEWITT.

Influence of magnesium salts on the coagulation of citrated or phosphated blood. (MISS) E. SLUITER (Arch. Néerl. Physiol., 1926, **10**, 461—467).—See this vol., 123.

Rôle of calcium in the coagulation of the blood. M. M. LOUCKS (Amer. J. Physiol., 1926, **76**, 186).—Calcium is essential, not only to the formation of thrombin, but also to its activity. The calcium content of fibrin is variable and may be removed by washing.

R. K. CANNAN.

Fractionation of serum proteins and removal of proteins from antidiphtheritic serum. P. SÉDALLIAN and J. LOISELEUR (Compt. rend., 1926, **182**, 723—724).—The euglobulin precipitated by addition of 21% of sodium chloride to antidiphtheritic serum at p_H 4·7 is devoid of antitoxic effect, whilst the globulin precipitated by concentrations of 22% and upward contains most of the antitoxic material. L. F. HEWITT.

***iso*Hæmagglutination. I. Significance of electrolytes in *iso*hæmagglutination.** P. RONA and H. A. KREBS (Biochem. Z., 1926, **169**, 266—280).—Both the insoluble (euglobulin) and the soluble fractions of serum rendered electrolyte-free by electrodialysis contain the group-specific *iso*agglutinin, but in variable proportion. The rate of agglutination at first decreases slightly with decreasing concentration of electrolyte (the osmotic pressure being maintained by addition of dextrose or lævulose), but when the electrolyte concentration is reduced to one-third of its normal value, agglutination is considerably accelerated. The agglutination is, however, not specific, and may be reversed by addition of electrolyte. *iso*Agglutination is not affected by replacement of sodium chloride by sodium sulphate or calcium chloride, but low concentrations of lanthanum chloride are slightly inhibitory. The *iso*agglutination is, within wide limits, independent of the p_H. A slight inhibition below p_H 6 is probably due to hæmolysis of the corpuscles or coagulation of the serum proteins. Above p_H 10·6, agglutination is somewhat inhibited.

Methyl-, ethyl-, and *iso*propyl-urethane in $M/5$ concentration have no effect on *iso*agglutination. Quinine hydrochloride, *iso*amylhydrocupreine, and *iso*octylhydrocupreine cause hæmolysis, with slight inhibition of agglutination, but ethylhydrocupreine in 1/1200 concentration inhibits agglutination without hæmolysis, the agglutination of corpuscles of groups 2 and 3 by serum of group 1 being affected to different, although variable, extents. E. C. SMITH.

Dextrose and colloidal equilibria of lipins. M. NECHKOVITCH (Compt rend. Soc. Biol., 1925, **93**, 651—652; from Chem. Zentr., 1925, II, 2171).—Dextrose exerts only a weak protective action on lecithin solutions *in vitro* against precipitating reagents such as ammonium sulphate, nitric acid, and phosphotungstic acid. On the other hand, it protects red blood-corpuscles against hæmolytic agents which attack the proteins of the surface (ethyl alcohol, chloral hydrate, hydrochloric acid). Hæmolysis by chloroform is attributable to its effect on lipins and is scarcely affected by the presence of dextrose. G. W. ROBINSON.

Gaseous exchange between the blood and the lumen of the stomach and intestine. M. A. MCIVOR, A. C. REDFIELD, and E. B. BENEDICT (Amer. J. Physiol., 1926, **76**, 92—111).—Studies of the movement of carbon dioxide into and out of the stomach of the anæsthetised cat led to the conclusion that it was entirely governed by the physical laws of diffusion. The rates of absorption of carbon dioxide, oxygen, nitrogen, hydrogen, methane, and hydrogen sulphide from loops of the intestine varied widely. Carbon dioxide was the most rapidly absorbed and nitrogen the least. The factors governing these differences are discussed in relation to the laws of diffusion. R. K. CANNAN.

Normal carbon-dioxide and oxygen tensions in the tissues of various animals. J. A. CAMPBELL (J. Physiol., 1926, **61**, 248—254).—Nitrogen is injected under the skin and into the abdominal cavity, and the tensions of the gases are determined after equilibrium has been attained with the carbon dioxide and oxygen of surrounding tissue spaces and body-fluids. The average carbon dioxide tension of the tissues of a group of cold-blooded animals at the ordinary temperature was 14—23 mm. of mercury, and that of a group of warm-blooded animals was 40—50 mm. The average oxygen tension of both groups was 20—30 mm. The oxygen tension in the abdominal cavity of warm-blooded animals was some 10 mm. higher than that under the skin. The results are in general agreement with those of other workers obtained by indirect methods. R. K. CANNAN.

Cytochrome, porphyratin arising from its hydrolysis, and the related porphyrin. O. SCHUMM (Z. physiol. Chem., 1926, **152**, 147—159).—Keilin's observations (A., 1925, i, 1112) are confirmed and the iron–pyrrole complex present in cytochrome is investigated. Plant cytochrome contains a porphyrin strikingly similar to hæmochromogen or α-hæmatin. A "porphyratin" is isolated from fresh fungi. "Porphyratin" is a term introduced to designate the natural and artificial metal-complex compounds of the porphyrins, which, in pyridine, especially after addition of a little hydrazine hydrate, yield a similar absorption band in the green to that of pyridine–hæmochromogen, but with differing positions of the pair of bands. Cytochrome of yeast, beans, walnuts, potatoes, and sugar-beet is investigated with the view of showing that the cytochrome of plants and animals is identical. From the plant pigment a porphyratin is obtained which, in a mixture of hydrazine hydrate and acetic acid, yields a porphyrin spectroscopically similar to that of β-phylloporphyrin (Marchlewski) and to α-porphyroidin (α-hæmatoporphyrin), but corresponding most closely with the latter. The porphyrin when treated by Zaleski's method yields a porphyratin which corresponds spectroscopically with that obtained by the same method from α-hæmatoporphyrin (A., 1925, i, 88). P. W. CLUTTERBUCK.

Muscle pigment and MacMunn's myohæmatin. II. O. SCHUMM (Z. physiol. Chem., 1926, **152**, 55—65).—Heart-muscle, examined immediately after the death of the animal, contains MacMunn's myohæmatin, which spectroscopically is almost identical with Keilin's cytochrome. The spectrum of this pigment or group of pigments does not agree with that of any hitherto described blood pigment. If the spectrum of "myochromogen" (a weak band at 550 μμ) is observed in, say, a muscle preparation, then the complete myohæmatin spectrum will appear if the concentration of the pigment or the depth through which it is observed is sufficiently increased. Myochromogen probably occurs as a component of

myohæmatin, and not as a separate pigment. MacMunn's myohæmatin is probably a mixture of several porphyratin compounds, the principal component of which is a porphyratin which is not identical with the iron compound of coproporphyrin.

H. D. KAY.

Porphyrins and hæmatins. I. Identification of coproporphyrin, and value of spectrochemical methods for investigation of porphyrins and allied pigments. II. Hæmatin in pathological sera. O. SCHUMM (Z. physiol. Chem., 1926, **152**, 1—17).—I. Coproporphyrin and Nencki's hæmatoporphyrin may be distinguished by the difference between the absorption spectra of the two substances in concentrated sulphuric acid solution. The positions of the principal absorption bands of these two porphyrins and of seven other porphyrins when dissolved in pure sulphuric acid have been determined. The method of preparation of a characteristic bromine derivative of coproporphyrin is described. A summary is given of methods used for the preparation of porphyrins and their derivatives for spectroscopic examination. Certain details of spectrophotographic technique are discussed, particularly the best length of spectrum for accurate measurement. The spectrophotographic method is particularly useful for determining the exact boundaries of absorption bands in the extreme violet.

II. The presence of α-hæmatin in the serum in hæmatoporphyria and also in cases of pernicious anæmia is confirmed. H. D. KAY.

Iron content of meats. E. B. FORBES and R. W. SWIFT (J. Biol. Chem., 1926, **67**, 517—521).—Analyses are given of numerous kinds of meat with respect to their content of iron, the results indicating that, of the meats in common use, beef is the richest in this element. C. R. HARINGTON.

Participation of pyrroles in the synthesis of melanin. P. RONDONI (Biochem. Z., 1926, **169**, 149—151).—Evidence is set forth supporting the pyrrole theory of melanogenesis. The value of the pine splinter test for pyrrole derivatives is also examined (cf. Bloch and Schaaf, this vol., 87).

C. RIMINGTON.

Structural colours in insects. I. C. W. MASON (J. Physical Chem., 1926, **30**, 383—395).—All whites of insects are regarded as structural colours. Uric acid, previously considered to serve as a pigment in butterflies (Hopkins, Phil. Trans., 1896, **186**, 661), plays a very minor and unimportant part in producing the white of butterfly scales, since extraction of this acid leaves the whiteness undiminished. The various lustres exhibited by butterflies are to be explained on the basis of the structures present; pearly and metallic lustres, for example, are due to superposed, transparent, parallel laminæ. Tyndall-blue occurs in a few insects, *e.g.*, in *Enallagmæ* and in *Libellula pulchella*. Apart from *Xylocopa cærulea*, insects do not appear to possess blue pigments. Structural conditions may modify the appearance of pigment colours very considerably.

L. S. THEOBALD.

Synthesis and elimination of certain components of bile in obstructive jaundice. J. L. BRAKEFIELD and C. L. A. SCHMIDT (J. Biol. Chem., 1926, **67**, 523—545).—Experimental obstructive jaundice, produced by ligation and subsequent resection of the common bile-duct in dogs, resulted in a preliminary increase and subsequent decrease in the excretion of bile acids and bile pigments; the excretion of nitrogen and sulphur (especially "neutral sulphur") increased for a week after onset of jaundice and then fell to the normal level. The injection of sodium taurocholate into jaundiced dogs resulted in an increased excretion of this substance in the urine; such an increase did not occur in normal dogs. Administration of benzoic acid to jaundiced dogs resulted in much less increase in the excretion of hippuric and benzoylglycuronic acids than is the case with normal animals. C. R. HARINGTON.

Excretion of phosphoric acid in the urine in psychoses. S. TSUCHIYA (Z. ges. Neurol. Psychiatr., 1924, **90**, 235—247; from Chem. Zentr., 1925, II, 2172).—The normal daily excretion of phosphoric oxide in the urine of healthy men is 2·5—3·5 g., of which two-thirds is in the form of the potassium phosphate and the remainder as sodium and calcium phosphates. In mental disorders different values may be obtained. G. W. ROBINSON.

Excretion of phosphoric acid in the urine in rabbits treated with anti-cerebral serum. S. TSUCHIYA (Z. ges. Neurol. Psychiatr., 1924, **90**, 248—254; from Chem. Zentr., 1925, II, 2172—2173).—An anti-cerebral serum was obtained by injecting guinea-pigs with a 10% emulsion of rabbits' brains. The phosphorus excretion after injection of this serum was almost invariably increased.

G. W. ROBINSON.

Enzyme content of the blood in experimental sympathicotonia. S. SOROCHOVITCH (Biochem. Z., 1926, **169**, 409—416).—The enzyme content of rabbit's blood is practically unaltered in sympathicotonia. In the depancreatised dog, the diastase, phenolase, and thrombokinase content of the blood is unchanged, but the lipase is diminished. A great part of the lipase of the blood is derived from the pancreas. E. C. SMITH.

Characteristic changes in blood chemistry in whooping cough. J. C. REGAN and A. V. TOLSTOOUHOV (J. Amer. Med. Assoc., 1926, **86**, 191—192).—The most characteristic changes in the blood in whooping cough are a lowering of the hydrogen-ion concentration and a diminution of the inorganic phosphorus content. CHEMICAL ABSTRACTS.

Old age and death from a chemical point of view. N. R. DHAR (J. Physical Chem., 1926, **30**, 378—382).—Old age is associated with a marked decrease in the catalytic activity of body enzymes.

L. S. THEOBALD.

Formation of gastric hydrochloric acid from chlorides of the blood. J. MOSONYI (Biochem. Z., 1926, **169**, 120—124).—A critique of existing theories. If the gastric hydrochloric acid is derived from chlorides of the blood, a diminished content of the

latter should occur during secretion, and any theory must reconcile this fact with the increase in hydrogen carbonate content which also occurs.

C. RIMINGTON.

Fate of acid in the body. C. H. FISKE, R. A. GOODELL, L. E. HATHAWAY, jun., and E. J. WEST (J. Biol. Chem., 1926, **67**, 385—396; cf. Fiske and Sokhey, A., 1925 i, 723).—After administration by stomach tube to cats of 100 c.c. of 0·1*N*-sulphuric acid per kg., the proportion of acid neutralised by ammonia is less than is the case with smaller doses; such large doses are followed by much increased excretion of fixed base, but whereas the excretion of ammonia remains high for several days, that of fixed base falls below normal after the first day; the changes in the excretion of fixed base consist of approximately equal changes in the sodium and potassium, and the post-acidotic retention of fixed base is accompanied by a retention of phosphate. C. R. HARINGTON.

Metabolism of aromatic acids. VIII. Acetylation of amino-compounds. J. B. MUENZEN, L. R. CERECEDO, and C. P. SHERWIN (J. Biol. Chem., 1926, **67**, 469—476).—Anthranilic acid and its acetyl derivative are excreted unchanged after administration to men, dogs, and rabbits; *m*- and *p*-aminobenzoic acids are also excreted unchanged by dogs, but appear in the urine of men and rabbits as the corresponding acetyl derivatives. An attempt to investigate the metabolism of *p*-hydrazinobenzoic acid failed owing to the toxicity of the substance, 0·5 g. of which proved fatal when injected into a dog weighing 12 kg.

p-*Aminohippuric acid*, m. p. 199°, is prepared by reduction of *p*-nitrohippuric acid with ammonium sulphide. C. R. HARINGTON.

Conjugation of benzoic acid in the dog. Determination of hippuric acid. A. J. QUICK (J. Biol. Chem., 1926, **67**, 477—490).—The increase in the excretion of hippuric acid in dogs, on a diet containing little or no glycine, following administration of benzoic acid, is fairly constant and independent of the dosage of the latter; after large doses of benzoic acid, the excretion of benzoylglycuronic acid is much increased and represents the greater part of the benzoic acid administered; a small increase only in the excretion of hippuric acid was produced by administration of glycine simultaneously with the benzoic acid. Hippuric acid can be satisfactorily determined in urine by extracting the latter with ether in a continuous extractor after acidification, hydrolysing the extracted material with hydrochloric acid, and determining the glycine in the resulting solution by "formol" titration or by the method of Van Slyke. C. R. HARINGTON.

Muscular contraction. E. GORTER and F. GRENDELL (Nature, 1926, **117**, 552—553).—It is calculated that the total surface of the fibrils and transversal discs in 1 g. of rabbit's skeletal muscle is about 6 m.², whilst it is observed that the lipins extracted therefrom when spread out on a water surface and measured with an Adam–Langmuir apparatus give results between 6·7 and 7·1 m.² Thus the lipins exist as a unimolecular layer on the surface of the fibrils and possibly of some transversal discs. With heart-muscle, where the distances between the fibrils are about one-half of the former, the lipins from 1 g. occupied 16·6—17·8 m.² The phenomenon of muscular contraction is hence regarded as due to the formation of hydrolecithin and hydrokephalin from lecithin–kephalin molecules, effecting not only a change in size from 2 to 1, but also a change in rigidity of the surface of the fibrils. Although lactic acid cannot produce this hydrogenation it has a striking effect in reducing the area of the muscle protein on water, the respective computed values being 1400×10^{-16} and 450×10^{-16} m.²/mol. Agreement exists between the amount of lactic acid required to produce this sudden change and that calculated to be produced in a single contraction. Larger quantities of acid produce the reverse effect. Since there is some evidence that hæmoglobin is oriented at some surface inside a red blood-cell, so that all the hæmochromogen and iron is at the surface, it is suggested that the cystine (or glutathione) part of each protein molecule in muscle is oriented at some external surface, probably the surface of the fibrils, and that the glutathione–lecithin is oriented in opposite places, in order to give reversible effects (cf. Garner, A., 1925, i, 607). A. A. ELDRIDGE.

Lactic acid formation in *rigor mortis* of plain muscle. II. E. MANGOLD and C. SCHMITT-KRAHMER (Biochem. Z., 1926, **169**, 186—191).—The lactic acid content of the gastric musculature of the hen increases rapidly after death, reaching a maximum about the fifth hour, but not until later in the case of the pigeon. In both instances, however, mechanical changes develop simultaneously with acid production and appear to be due to the latter. C. RIMINGTON.

Respiratory quotient of resting muscles. H. E. HIMWICH and W. B. CASTLE (Amer. J Physiol., 1926, **76**, 188).—The respiratory quotient, determined from the blood of resting muscle *in situ* with its blood supply intact, was close to that of the whole animal and was less than unity. Resting muscles do not oxidise carbohydrate exclusively. R. K. CANNAN.

Sugar metabolism of unicellular organisms. W. E. BURGE (Amer. J. Physiol., 1926, **76**, 229—230).—Chloroform and ether notably reduced the catalase content and sugar metabolism of *paramœcia*. Nitrous oxide and ethylene had little effect on either factor. Insulin greatly increased the sugar metabolism, low temperature led to a decrease, and thyroxin was without effect. R. K. CANNAN.

Carbohydrate and phosphate metabolism. J. ABELIN (Klin. Woch., 1925, **4**, 1732; from Chem. Zentr., 1925, II, 2174).—The increase in the respiratory quotient of rats after administration of carbohydrate is greater with than without phosphate. The formation of glycogen in the liver is decreased by the addition of phosphate to a carbohydrate ration.

G. W. ROBINSON.

Effect of calcium and inorganic phosphorus on milk. J. ZAYKOWSKY (Biochem. Z., 1926, **169**, 66—76).—Addition of either chalk or calcium phosphate to the normal diet of cows leads to the same

result in either case, an increase in the calcium and phosphorus content of the milk ash. Simultaneously the quantity of the milk, its specific gravity, and its fat content are raised. C. RIMINGTON.

Iron metabolism of the animal organism after splenectomy. J. IRGER (Biochem. Z., 1926, **169**, 417—426).—Determination of iron in the urine, fæces, bile, and blood of dogs before and after splenectomy gave no indication of any alteration in iron metabolism. E. C. SMITH.

Synthesis and destruction of phosphatides in the animal organism. K. KOIZUMI (J. Biochem. [Japan], 1925, **5**, 171—184).—Lymph was collected from the thoracic duct of dogs before and after feeding with emulsified liver oil. After feeding of fat there was an increase in the phosphatide content as well as a synthesis of phosphatide in the intestinal mucosa. The increase of lipin in the lymph is due to a mono-aminophosphatide similar to lecithin, but failing to form a precipitate either with cadmium chloride solution or on addition of acetone. The liver is regarded as the principal lecithin-forming organ. Injection of lecithin into a vein is followed by a definite increase of lecithin, fat, and phosphorus in the liver. The phosphorus is considered to be derived from the inorganic phosphorus of the blood-serum. There is thus a building of fat from fatty acids and glycerol after the introduction of lecithin, and evidence of an inter-conversion of fat and lecithin in the liver.

CHEMICAL ABSTRACTS.

Agglutination of spermatozoa by chemical reagents. B. E. KALVARIJSKI (Biochem. Z., 1926, **169**, 352—408).—Prolonged exposure of the frog (*Rana temporaria*) to an atmosphere of carbon dioxide is without effect on the movements of the spermatozoa. Exposure of the spermatozoa themselves results in a transitory inhibition of movement, the subsequent motility never reaching the normal. In distilled water or 0·3% magnesium chloride, agglutination of the spermatozoa takes place when the partial pressure of carbon dioxide is 2% of the normal, but in conductivity water a partial pressure of 60% is necessary. In sodium hydrogen carbonate, agglutination will not take place with an atmosphere of pure carbon dioxide. The carbon dioxide acts in virtue of its effect on hydrogen-ion concentration. Agglutination does not occur above p_H 5·5, and is independent of the vitality of the spermatozoa. Uni- and bi-valent cations inhibit agglutination, their activity increasing in the order (NH_4, K), Na, Mg, Ca, Li. In solutions of p_H 2·5, the anions Br, Cl, I, SO_4, CNS, have no action. Free acids exert a strong agglutinating action, the surface of the spermatozoa becoming charged in such a way that the direction of migration in the electric field is reversed. In this respect, the surface layer behaves as a suspensoid colloid. The spermatozoa of *R. esculenta*, *Bufo vulgaris*, and *Esox lucius* also undergo acid agglutination. E. C. SMITH.

Influence of some chemical agents on gaseous metabolism. M. KOCHMANN (Leopoldina, 1926, **1**, 34—38).—Guanidine, glycine, alanine, creatine, adrenaline, and arsenic were without effect on the respiratory quotient of the fasting animal. Opium and quinine caused a rise in the value, due to a diminished oxygen uptake, whilst, on a carbohydrate diet, adrenaline restrained the rise in respiratory quotient by repressing the normal increase in carbon dioxide output. The view that the products of protein catabolism are antagonistic to the action of insulin is supported by the observation that guanidine, and to a less extent glycine, alanine, and creatine, reduced the rise in respiratory quotient following the administration of insulin. Opium, on the other hand, magnified this effect of insulin. R. K. CANNAN.

Effects of certain heavy metals on respiration. S. F. COOK (J. Gen. Physiol., 1926, **9**, 575—601).—Addition of solutions of the chlorides of mercury and copper and of silver nitrate to cultures of *Aspergillus niger* causes the carbon dioxide production to decrease. The speed of the toxic action varies as a constant power of the concentration, and the temperature coefficient of the toxic action is from 1·5 to 2. The mechanism of the action of the metals is discussed. H. J. CHANNON.

Effect of sleep on urinary chlorides and p_H. G. E. SIMPSON (J. Biol. Chem., 1926, **67**, 505—516).—After awakening in the morning there was observed in the urine a rise in the p_H and the rate of excretion of chloride, independently of variations in urinary volume; such changes did not occur on mornings following sleepless nights. No constant changes were observed in the composition of the urine following periods of sleep during the day. C. R. HARINGTON.

Relative toxicity of the lupin alkaloids. J. F. COUCH (J. Agric. Res., 1926, **32**, 51—67).—Intraperitoneal injections into guinea-pigs of the alkaloids places them in the following decreasing order of toxicity: *d*-lupanine, sparteine, lupinine, spathulatine, hydroxylupanine. The minimum lethal dose of sparteine and hydroxylupanine by subcutaneous injection is nearly twice as great as that by intraperitoneal injection. H. J. CHANNON.

Trypanocidal action of the cinchona alkaloids *in vitro*. A. E. TSAKALOTOS (Biochem. Z., 1926, **169**, 454—470).—The trypanocidal action of quinine, hydroquinine, ethyl-, *iso*propyl- *iso*butyl-, and *iso*-amyl-hydrocupreine, quinotoxine, and hydroquinotoxine has been investigated. Hydroquinotoxine is most toxic and ethylhydrocupreine more so than the remainder. The action on infected mice of quinine and ethylhydrocupreine is practically the same as the action *in vitro*, but the action of hydroquinine is greater, that of hydroquinotoxine much less, than *in vitro*. Experiments on tadpoles show that the general toxicity is by no means parallel to the specific effect on the trypanosomes *in vitro*, ethylhydrocupreine being comparatively non-toxic, whereas *iso*-amylhydrocupreine is exceedingly so. Hydroquinotoxine is, however, highly toxic both to trypanosomes and to tadpoles. E. C. SMITH.

Hypnotics of the barbituric acid series. C. NIELSEN, J. A. HIGGINS, and H. C. SPRUTH (J. Pharm. Exp. Ther., 1925, **26**, 371—383).—The toxicities and efficiencies of sixteen members of the

barbituric acid series have been determined for the albino rat. The cat and dog have been found unsuitable for work on hypnotics. C. P. STEWART.

Effect of hydrogen-ion concentration on the antiseptic action of certain phenols and aromatic acids. T. KURODA (Biochem. Z., 1926, **169**, 281—291).—The author has investigated the antiseptic action of phenol, the three isomeric cresols and chlorophenols, thymol, benzoic acid, and salicylic acid on *Bacillus prodigiosus*, *B. coli*, and yeast at different hydrogen-ion concentrations. The antiseptic action is greatest in acid solution, least at neutrality. In strongly alkaline solution, antiseptic action can be detected. The distribution coefficient of phenol between water and olive oil is greater in acid than in neutral solution. E. C. SMITH.

Pharmacology of benzyl alcohols. A. A. CHRISTOMANOS (Biochem. Z., 1926, **169**, 344—351).—The antiseptic action of the isomeric hydroxybenzyl alcohols towards *Bacillus coli* increases in the order *ortho*, *meta*, *para*, being the reverse of the order of activity of the hydroxybenzoic acids. *o*-Hydroxybenzyl alcohol has definite local anæsthetic properties, the *m*-derivative a weak action, and the *p*-derivative none. In frogs and mice, the hydroxybenzyl alcohols cause general paralysis of central origin, followed by a period of heightened reflexes. An increase in urinary sulphate follows the administration to man of *o*- and *p*-hydroxybenzyl alcohols, the former being partly excreted as a conjugated salicylic acid. 2 : 6-Bishydroxymethyl-*p*-cresol is not excreted in combination with sulphuric acid. E. C. SMITH.

Chemotherapy of antimonial compounds in kala-azar infection. XV. Derivatives of *p*-aminobenzeneantimonic acid. U. N. BRAHMACHARI and J. DAS (Indian J. Med. Res., 1925, **13**, 17; cf. *ibid.*, 1925, **12**, 735).—Sodium *p*-acetamidophenylantimonate, when stirred in aqueous solution with sodium hypochlorite, and acetic acid added, yields a *compound* (" chlorostibacetin "),

$$C_8H_8O_4NClSbNa,$$

which is purified by precipitation from ammoniacal solution. On neutralisation with acetic acid of an ammoniacal solution of *p*-acetamidophenylantimonic acid and precipitation with absolute ethyl alcohol, a *compound* (" ammonium stibamine "), $C_{18}H_{23}O_7N_4Sb_3$, is produced. " Glucose-stibamine " and " glucose ammonium stibamine " are described.

CHEMICAL ABSTRACTS.

Origin of the blood changes in lead poisoning. P. SCHMIDT (Leopoldina, 1926, I, 98—101).—The anæmia arises secondarily from the action of lead on the bone marrow. R. K. CANNAN.

Adsorption of poisons on charcoal. III. Partition of poison between charcoal and stomach- or intestinal-wall. E. DINGEMANSE and E. LAQUEUR (Biochem. Z., 1926, **169**, 235—244).—Mercuric chloride is adsorbed by the stomach wall, but is almost entirely removed by shaking with charcoal. The intestine removes some of the salt which has been adsorbed on charcoal. Strychnine behaves in a similar manner except that it is not removed from charcoal by the intestine.

C. RIMINGTON.

Calcium assimilation. VII. Influence of sunlight on calcium equilibrium in milking cows. E. B. HART, H. STEENBOCK, C. A. ELVEHJEM, H. SCOTT, and G. C. HUMPHREY (J. Biol. Chem., 1926, **67**, 371—383).—During periods of high production of milk, a negative calcium balance was observed in cows fed on a normal winter diet supplemented with green grasses and kept indoors; when the animals were exposed to direct sunlight, the loss of calcium decreased, but the balance remained negative. The results indicate the necessity of a high intake of calcium in both summer and winter, and, in winter, of an additional supply of the antirachitic vitamin during periods when the milk production exceeds about 40 lb. per diem. C. R. HARINGTON.

Physiological action of light. VII. Blood calcium in direct irradiation of blood. C. I. REED and W. R. TWEEDY (Amer. J. Physiol., 1926, **76**, 54—58).—The blood of etherised dogs was irradiated directly by a carbon arc while flowing through a quartz tube interposed in the carotid artery. There was no immediate change in the blood calcium. R. K. CANNAN.

Biological action of *X*-rays of different wave-lengths. A. DOGNON (Compt. rend., 1926, **182**, 655—657; cf. Dauvillier, this vol., 199).—It is maintained that *X*-rays of wave-lengths 0·22, 0·70, and 1·54 Å., respectively, exert biological actions (cf. Compt. rend., 1925, **181**, 1130) in the ratio of 2 : 1 : 1·5. The principle of equal biological action of absorbed *X*-rays of different wave-lengths but of equal energy content is not accepted.

L. F. HEWITT.

Thermostability of plant amylase zymogens. J. BODNÁR and I. VILLÁNYI (Biochem. Z., 1926, **169**, 1—12).—Wheat contains a thermolabile amylase, extractable by water, and also an amylase zymogen insoluble and not destroyed by heat, but in germinating seeds all the enzyme is present in the active form. Zymogen and enzyme were also found in the leaves of several plants. C. RIMINGTON.

Catalase content of warm-blooded animals and evergreen trees. W. E. BURGE (Amer. J. Physiol., 1926, **76**, 229).—The catalase content of the needles of several species of pine increased with the summer and fell with the winter. On the other hand, the catalase content of the blood of mice kept in the open decreased with the rise in external temperature. It is pointed out that the same contrast in reaction toward temperature is shown by the oxidative processes of plants and warm-blooded animals. R. K. CANNAN.

Kinetics of ester hydrolysis by liver lipase. NOGAKI (Z. physiol. Chem., 1926, **152**, 101—118).—This enzyme combines both with substrate and with hydrolysis products. The amount of ester decomposed by the lipase is only approximately proportional to the time. After an initial rapid fall or in some cases a slight rise (depending on the nature of

the ester hydrolysed), the reaction velocity falls off toward the end of the reaction. The fall is not due to gradual destruction of enzyme, but to combination between the enzyme and the products of hydrolysis. At an acid p_H, both the acid and alcohol produced combine in this way; at an alkaline p_H, only the alcohol combines with the lipase. The extent of inhibition of lipase activity by alcohol depends on the enzyme concentration and on the reaction temperature. The slower the reaction, the more clearly marked is the inhibition effect. The form of the reaction curve is dependent not only on the affinity of lipase for the enzyme and the products of hydrolysis, but also on the velocity with which the reaction takes place, which itself depends on the enzyme concentration and on the temperature.

H. D. KAY.

Are oxygen transportases and hydrogen transportases identical? A. BACH and K. NIKOLAJEW (Biochem. Z., 1926, **169**, 105—112).—According to the hydrogen activation theory of Wieland, methylene-blue and molecular oxygen function as hydrogen acceptors in the Schardinger system, which may be regarded as a reductase or oxydase system, according to the point of view.

The preparation obtained by precipitating buttermilk with acetone will, with salicylaldehyde as substrate, produce more salicylic acid in aërobic than in anaërobic conditions; the converse holds, however, after purification of this material. The discrepancy is due to the presence in the crude material of impurities (probably lipins) which function as hydrogen acceptors and are then directly oxidisable by molecular oxygen, as is leuco-methylene-blue. Such interfering circumstances might simulate an oxydase action on the part of the enzyme. C. RIMINGTON.

Mechanism of the guaiacum reaction. E. UYS-SMITH (Biochem. Z., 1926, **168**, 448—450).—The intensity of the guaiacum reaction with various concentrations of *p*-cresol and pyrocatechol was examined and also the quantity of pyrocatechol formed from the cresol by the action of the oxydase of the potato. The results of these experiments showed that the quantity of pyrocatechol derivative formed from *p*-cresol under the influence of the oxydase is sufficient to account for the guaiacum reaction and thus support the views of Onslow and Robinson (A., 1925, i, 1010). H. I. COOMBS.

Action of oxydoreductase on methylglyoxal. A. LEBEDEV (Biochem. Z., 1926, **169**, 501; cf. this vol., 324).—Methylglyoxal is oxidised by oxydoreductase in the presence of methylene-blue, but one-thirtieth as rapidly as glyceraldehyde.

E. C. SMITH.

Tyrosinase. E. ABDERHALDEN and M. BEHRENS (Fermentforsch., 1926, **8**, 479—486).—Experiments to prove the presence of a carboxylase in tyrosinase were not successful. Biological and chemical tests applied to the product of the action of tyrosinase on tyrosine were also negative. The first point of attack of the tyrosine is probably the phenol nucleus—an oxidation taking place. In support of this, when tyrosinase was allowed to act on tyrosine a solution was obtained which reduced silver nitrate, gave characteristic colours with ferric chloride, and gave a dark colour in the presence of air, alkali, etc. This intermediate compound was not homogentisic acid.

H. I. COOMBS.

Enzymic cleavage of sinigrin. H. VON EULER and S. E. ERIKSSON (Fermentforsch., 1926, **8**, 518—523).—Sinigrinase (myrosinase) obtained from *Sinapis alba* decomposes sinigrin according to the equation $C_{10}H_{16}O_9NS_2K+H_2O \rightarrow C_3H_5{\cdot}N{:}CS+C_6H_{12}O_6+KHSO_4$. The sulphatase action, as determined by sulphate determinations, has a slight optimum near neutrality. H. I. COOMBS.

Law of mass action and the kinetics of the action of invertase. L. MICHAELIS (Z. physiol. Chem., 1926, **152**, 183—188).—A reply to Hedin (A., 1925, i, 1212). P. W. CLUTTERBUCK.

Inactivation of invertase by heat. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **152**, 254—263).—Partial heat-inactivation of invertase, either in aqueous solution at the optimal p_H or in presence of dextrose or lævulose as a protective substance, has no effect on the affinity of the residual invertase for the different forms of dextrose or lævulose. P. W. CLUTTERBUCK.

Inhibition phenomena during the enzymic hydrolysis of sucrose. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **152**, 31—55).—The hydrolysis of sucrose by invertase is inhibited to a greater or lesser extent by various concentrations of dextrose or lævulose. This is due to a combination between the invertase molecule and the two hexoses, a different grouping in the enzyme molecule being concerned in each case. If now other sugars, or related substances, are added to the reaction mixture (containing sucrose, invertase, and excess of either dextrose or lævulose) changes are produced in the amount of inhibition, whence it is possible to determine whether the added substance combines with the group in the enzyme molecule which normally displays affinity for dextrose, or that which displays affinity for lævulose. Galactose, sodium hexose-phosphate, and acetaldehyde all appear to affect the dextrose inhibition of invertase, but not the inhibition by lævulose. The aldehyde grouping in the molecule appears to be the one concerned in this effect. Yeast hexosephosphoric ester appears to be more nearly related to dextrose than to lævulose. H. D. KAY.

Enzymic production of sucrose from sucrose-phosphates. C. NEUBERG and M. BEHRENS (Biochem. Z., 1926, **170**, 254—264).—From the products of the digestion of neutral sucrosephosphates with preparations of horse kidney, crystalline sucrose was isolated in good yields. This phosphatase action is analogous to the production of sucrose in the hydrolysis of raffinose by emulsin. R. K. CANNAN.

Autolysis of animal organs at the ordinary temperature. S. KAPLANSKY (Biochem. Z., 1926, **169**, 245—248).—After keeping for 24 hrs. at the ordinary temperature under toluene, the non-protein nitrogen of an aqueous suspension of muscle increased 10%, of liver 18%, and of spleen 29%. The amino-

acid nitrogen of the suspensions increased 15, 33, and 100%, respectively. E. C. SMITH.

Action of rennin on the proteins of milk. II. J. ZAYKOVSKI. **III. The enzymes of new-born calves.** N. M. PAVLOVSKI and J. ZAYKOVSKI (Fermentforsch., 1926, **8**, 537—546, 547—552).—II. Caseinogen and the casein produced from it by the action of rennin are different chemically and not merely physically.

III. A fistula was made in the rennin stomach of a new-born calf and an enzyme able to clot milk was obtained before the first feeding. When milk was taken by the calf, the amount of rennin increased. H. I. COOMBS.

Nephelometric investigation of enzymic proteolysis. V. P. RONA and H. KLEINMANN (Biochem. Z., 1926, **169**, 320—343).—The nephelometric method of caseinogen determination (A., 1925, i, 473) has been applied to the determination of the rate of destruction of trypsin at the ordinary temperature and at different hydrogen-ion concentrations. Trypsin is most stable at p_H 1·7, the rate of destruction being 3—4% per hour. Between p_H 3 and 11, the destruction is 20—30%; at p_H 12, it is complete in 1 hr. Trypsin is not, therefore, destroyed by passage through the stomach. E. C. SMITH.

Dialysis during tryptic digestion of proteins. B. LUSTIG (Biochem. Z., 1926, **169**, 139—148).—Investigation of the dialysates obtained from consecutive samples of the digest from caseinogen, serum-albumin, and globulin indicates a rapid production of amino-acids, especially of histidine from caseinogen. Caseinogen also yields diffusible substances giving the biuret reaction more rapidly than do the other proteins, but the amount of amino-nitrogen is not considerably greater. The Molisch reaction appears only after some time, especially in the case of serum-globulin, whilst substances precipitable by phosphotungstic acid are also of late appearance. All the sulphur (loosely bound) remains in an indiffusible form. C. RIMINGTON.

Antitrypsin. M. SEREJSKI (Biochem. Z., 1926, **169**, 249—254).—The inhibitory action of the soaps of the unsaturated fatty acids on the hydrolysis of caseinogen by trypsin (Jobling and Petersen, J. Exp. Med., 1914, **19**, 239, 251, 459) is due to precipitation of trypsin by the soap. This action is not specific, since caseinogen itself is partly coagulated by treatment with soap solution. The author considers that the use of the term antitrypsin for substances of this nature is unjustified, since it is a question only of mutual precipitation of colloids. E. C. SMITH.

Plant proteases. IV. Ereptic component of some plant proteases. V. Identity of plant proteases. R. WILLSTÄTTER, W. GRASSMANN, and O. AMBROS (Z. physiol. Chem., 1926, **152**, 160—163, 164—182).—IV. The absorption methods of Willstätter and Waldschmidt-Leitz (cf. A., 1925, i, 1360; this vol., 323) are used for the separation of the supposed ereptic component of plant proteases. Papain was tested for erepsin and found to be inactive against substrates of glycylglycine, glycine anhydride, *dl*-leucylglycine, and leucylalanine at p_H 4·7—8. Freshly-prepared juice from leaves and stems also gave a negative result. Pumpkin fruit, however, gave a positive but faint result with leucylglycine as substrate. A dry preparation from pineapple also gave a negative result, although the juice of freshly-imported pineapple gave a faint positive result. It is necessary to repeat the experiment with fresh juice of unripe fruit.

V. A critical study of the methods of determination of the proteases of papain and of the juice of *Cucurbita*, by solution of fibrin and by hydrolysis of peptone, particularly in respect to Vines' results (A., 1903, ii, 321). The methods are used to follow the fractionation of the enzymes by salt solution and by fractional adsorption on alumina, kaolin, and fibrin. P. W. CLUTTERBUCK.

Hydrogen-ion concentration and alcoholic fermentation. III. E. HÄGGLUND, A. SÖDERBLOM, and B. TROBERG (Biochem. Z., 1926, **169**, 200—207).—The rate of disappearance of sugar remains unchanged between p_H 4 and 8·5; sulphite at p_H 8 causes no inhibition except in the later stages. Carbon dioxide evolution occurs most rapidly between p_H 5 and 6, and fermentation ceases above p_H 10. C. RIMINGTON.

Influence of hydrogen-ion concentration on alcoholic fermentation. E. HÄGGLUND and A. M. AUGUSTSSON (Biochem. Z., 1926, **170**, 102—125).—Fermentation of pyruvic acid was most rapid at p_H 2—3 in the case of a top yeast, at p_H 4 for a bottom yeast, and at p_H 6 for dried yeast and maceration juice. In neutral or mildly alkaline media, fermentation was appreciable only in the case of dried yeast. These differences are connected with the permeability of the cell-wall to pyruvic acid. The action of dried yeast is not simply that of free "zymase." The optimum p_H for yeast carboxylase is 6 and the activity falls rapidly on the alkaline side of this value. In the presence of hydrogen sulphite, pyruvic acid is not fermented if the reaction is more alkaline than p_H 7. These results are not yet reconciled to prevalent views of the process of alcoholic fermentation. Whereas acetaldehyde undoubtedly occupies a critical place in this process, the slow rate of fermentation of pyruvic acid offers difficulties to its acceptance as an intermediate product. It is possible that enolisation of the pyruvic acid governs its fermentation. R. K. CANNAN.

Alcoholic fermentation by dried yeast. E. ABDERHALDEN (Fermentforsch., 1926, **8**, 574—578).—Dried yeast contains cells capable of life on moistening. Alcoholic fermentation of sugar solutions depends on the presence of these cells. If a sugar solution be acted on by dried yeast, the mixture centrifuged, and the residue added to a further sample of the sugar, there is now no induction period, as in the first case (cf. Sobotka, A., 1924, i, 802; Harden, *ibid.*, 1925, i, 1010). H. I. COOMBS.

Formation of acetylmethylcarbinol during the fermentation of sucrose by yeast. L. FLION (Biochem. Z., 1926, **169**, 471—477).—In addition to

causing the formation of acetylmethylcarbinol (cf. Neuberg and Reinfurth, A., 1924, i, 248), the addition of acetaldehyde to sucrose undergoing fermentation by yeast results in an increased production of glycerol, and diminished formation of alcohol. E. C. SMITH.

Maltase. VIII. Direct fermentation of maltose by yeast rich in maltase. R. WILLSTÄTTER and E. BAMANN (Z. physiol. Chem., 1926, **152**, 202—214).—Investigation of the velocity of fermentation of maltose at varying p_H in presence of different amounts of maltase shows that the most favourable conditions for fermentation involve an acid reaction (p_H 4·5) at which the hydrolytic ferment is inactive. Optimum fermentation occurs over quite a narrow range of p_H; *e.g.*, at p_H 5 conversion was 50%, whereas at p_H 6·4 it was only 32·5%.
P. W. CLUTTERBUCK.

Synthesis and fermentation of glycogen by maltase-free yeast. A. GOTTSCHALK (Z. physiol. Chem., 1926, **152**, 132—135).—*Saccharomyces Ludwigii*, which is completely free from maltase, is capable of building up glycogen from dextrose and also of fermenting glycogen with rapid liberation of carbon dioxide. It follows—at least in this type of yeast, and probably in other types also—that maltose is not a necessary intermediate in the fermentation of glycogen. H. D. KAY.

Synthesis of coproporphyrin by yeast. H. FISCHER (Z. physiol. Chem., 1926, **152**, 144—145).—Hæmin and traces of coproporphyrin are found in cultures of *Saccharomyces anamensis* grown in beer wort. Yeast is capable of synthesising cytochrome from sugar and inorganic material. Kammerer's porphyrin appears to be present, in addition to coproporphyrin, in fresh malt. H. D. KAY.

Influence of previous treatment of the yeast on the affinity constants of invertase. I. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **152**, 66—87).—By previous growth of yeast on sucrose or dextrose, there is a marked increase in the affinity of the invertase, produced on the autolysis of the yeast, for α-glucose but not for β-glucose or lævulose. By previous growth on α-glucose, it is possible to obtain an invertase which shows a greater affinity for α- than for β-glucose. At the same time, there is an increase in the affinity between the enzyme and the sucrose. The production of invertases with differing specific affinities, by previous fermentation on different sugars, supports the view that various invertases with differing hydrolytic powers exist. They vary, for example, in the relative number of lævulose- and dextrose-binding groups in the molecule.
H. D. KAY.

Fermentation of galactose by yeast after preliminary treatment with this sugar. II. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **152**, 249—253).—The preliminary treatment gives much more favourable results with "bottom" than with "top" yeast (cf. A., 1925, i, 866, 1214).
P. W. CLUTTERBUCK.

Effect of growth of yeast on galactose on the fermentability of the latter by the former. E. ABDERHALDEN (Fermentforsch., 1926, **8**, 584).—The paper of the above title (A., 1925, i, 1362) was almost the same as that of Euler and Lövgren (*ibid.*, 1214). The work, however, was quite independent, but the latter authors have the priority.
H. I. COOMBS.

Zymase production and co-enzyme activity. A. LEBEDEV (Z. physiol. Chem., 1926, **152**, 146).—Recent work of Euler and Nilsson (A., 1925, i, 1361) has confirmed earlier work of the author that the co-enzyme of yeast activates the fermentation of sugar by zymase in stoicheiometric proportions. The statement of these authors that boiled yeast juice from top yeasts is rich in co-enzyme is not true for all yeasts. H. D. KAY.

Reductase (dehydrogenase) of yeast. III. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **152**, 264—270).—Further experiments on the decolorisation of methylene-blue by means of co-reductase of yeast in presence of washed dried yeast show that with small concentrations of co-reductase the reaction velocity is proportional to the amount of reductase, but with higher concentrations the velocity approaches a maximum. With the usual small concentrations of methylene-blue, the amount of hydrogen donator of the yeast is sufficient, and addition of succinate makes no difference, but not so with higher concentrations. An attempt is made to define the conditions under which the concentration of co-reductase can be measured (cf. this vol., 323).
P. W. CLUTTERBUCK.

Carboligase. M. BEHRENS and N. N. IVANOV (Biochem. Z., 1926, **169**, 478—481).—When *o*- or *p*-tolualdehyde is added to sucrose undergoing fermentation with yeast, reduction mainly occurs to the corresponding alcohol, but the aldehyde in part unites with acetaldehyde, forming *o*- or *p*-toluoylmethylcarbinol. E. C. SMITH.

Cleavage of polypeptides composed of amino-acids not yet found among the breakdown products of proteins. VII. E. ABDERHALDEN. Cleavage of polypeptides containing *dl*-phenylserine. S. BUADZE (Fermentforsch., 1926, **8**, 487—496).—*Chloroacetyl*-dl-*phenylserine*, m. p. 155—157°, was obtained by the action of chloroacetyl chloride on *dl*-phenylserine; dl-α-*bromoisohexoyl*-dl-*phenylserine*, m. p. 115—120°, was similarly prepared. These were converted by the action of ammonia into *glycyl*-dl-*phenylserine*, decomp. at 188°, and dl-*leucyl*-dl-*phenylserine*, m. p. 206°, respectively. Both of these dipeptides are hydrolysed by yeast maceration juice, as shown by polarimetric determinations and also in the case of the glycyl compound by isolation of the components (cf. A., 1924, i, 351).
H. I. COOMBS.

Influence of piperazines and piperazine derivatives on the fermentation of dextrose by yeast. E. ABDERHALDEN (Fermentforsch., 1926, **8**, 530—532).—The vitamins of yeast may possibly owe their activity to the presence of piperazine or the deriv-

atives of piperazine. Piperazine, dimethylpiperazine, and leucylpiperazine repeatedly relieve the convulsions in pigeons fed on polished rice. They also accelerate the alcoholic fermentation of dextrose by yeast. H. I. COOMBS.

Action of yeast maceration juice on *dl*-leucyl-γ-aminobutyric acid. E. ABDERHALDEN, H. PIEPER, and R. TATEYAMA (Fermentforsch., 1926, **8**, 579—583).—γ-Aminobutyric acid was converted by means of α-bromo*iso*hexoyl bromide into *α-bromoisohexoyl-γ-aminobutyric acid*, an oil. dl-*Leucyl-γ-aminobutyric acid*, decomp. about 215°, was obtained by treatment with ammonia. Although *dl*-leucylglycine was asymmetrically hydrolysed by yeast maceration juice, *dl*-leucyl-γ-aminobutyric acid was unchanged by it. H. I. COOMBS.

Protective action of milk yeasts on cultures of lactic acid bacteria. N. SLOBODSKA-ZAYKOVSKA (Biochem. Z., 1926, **169**, 77—92).—Certain yeasts found in milk exert a marked protective action on lactic acid bacteria, so that cultures of the latter are still thriving after 8 months. Such mixed cultures have a lower grade of acidity. Added lactic acid has an unfavourable effect on the growth of the yeast-cells, and both yeast and bacteria grow less readily in milk containing large amounts of sugar. The association cannot be regarded as symbiotic. C. RIMINGTON.

Micro-injection studies on the oxidation-reduction potential of the cell-interior. J. NEEDHAM and D. M. NEEDHAM (Proc. Roy. Soc., 1926, **B**, **99**, 383—397).—Oxidation-reduction potential indicators exhibit no anomalies when injected into *Amœba proteus* which can oxidise the leuco-form of indicators of lower oxidation-reduction potential than its own; it has an r_H which appears to be independent of external oxygen concentration. *Nyctotherus cordiformis* has internal p_H 7·1 and r_H 19—20 and 9·5—10·5 under aërobic and anaërobic conditions, respectively. H. J. CHANNON.

Biochemical synthesis of fumaric acid from pyruvic acid. A. GOTTSCHALK (Z. physiol. Chem., 1926, **152**, 136—143).—The mould *Rhizopus nigricans*, growing in an inorganic nutrient medium in presence of excess of chalk, produces fumaric acid from added pyruvic acid. Fumaric acid is also produced by the action of the same organism on hexoses. The chemical mechanism of this fermentation probably consists in the following stages: hexose → pyruvic acid → acetaldehyde + CO_2 → acetic acid → succinic acid → fumaric acid. H. D. KAY.

Acetone-ethyl alcohol fermentation. S. BAKONYI (Biochem. Z., 1926, **169**, 125—128).—Fermentation of starch and sugar by *Bacillus macerans* or *B. acetoethylicus* leads to the production of acetone and ethyl alcohol in the molecular proportion of 1 : 2. Acetaldehyde is an intermediate product and is itself fermentable. Reduction of a portion to ethyl alcohol probably occurs, but the bulk condenses to acetaldol, also fermentable, which then suffers dismutation to acetic acid and ethyl alcohol. The acid, or calcium salt when chalk is present, then yields acetone, and consequently does not accumulate in the medium. The fermentation equation is $2C_6H_{10}O_5 + 3H_2O \rightarrow 2EtOH + Me_2CO + 5CO_2 + 4H_2$. C. RIMINGTON.

Oxidation of glycerol to dihydroxyacetone by bacteria. A. I. VIRTANEN and B. BÄRLUND (Biochem. Z., 1926, **169**, 169—177).—A bacterium (*Bacillus dihydroxyacetonicum*) has been isolated from beetroot juice, which oxidises glycerol almost quantitatively to dihydroxyacetone. There is a sharp optimum at p_H 5·0, whilst that for *B. xylinum* lies between p_H 5 and 6. Dihydroxyacetone can be determined by means of Fehling's solution. C. RIMINGTON.

Effect of metallic aluminium on nitrogen-fixing bacteria. G. TRUFFAUT and N. BEZSSONOFF (Compt. rend., 1926, **182**, 663—665).—Maize can be cultivated and reach maturity in a medium deprived of nitrogenous constituents in the presence of nitrifying bacteria. The amount of nitrogen fixed by the bacteria is increased in the presence of metallic aluminium. L. F. HEWITT.

Bacterial oxidation of sulphur. G. GUITTONNEAU (Compt. rend., 1926, **182**, 661—663; cf. A., 1925, i, 766, 1218).—The formation of thiosulphates and sulphates from sulphur in culture media takes place no matter what the source of organic nutriment may be, *e.g.*, ammonium succinate, acetate, lactate, citrate, or tartrate, acetamide, alanine, asparagine, or peptone in the case of bacteria, and glycerol, dextrose, or starch in the case of *Microsiphoniæ*. This sulphur metabolism is therefore a specific property of the micro-organisms involved and is independent of secondary fermentations. L. F. HEWITT.

Soluble specific substance of a strain of Friedländer's bacillus. M. HEIDELBERGER, W. F. GOEBEL, and O. T. AVERY (J. Exp. Med., 1925, **42**, 701—707).—The *E* strain of Friedländer's bacillus yields a nitrogen-free, non-reducing polysaccharide with specific properties of the order possessed by the soluble specific substances of the three fixed types of *Pneumococcus*. It is a strong acid, equivalent about 685, [α]+100°, yielding soluble alkali salts, and on hydrolysis affords reducing sugars, including dextrose. CHEMICAL ABSTRACTS.

Chemical and immunological relationships of *Pneumococcus* type II and a strain of Friedländer's bacillus. O. T. AVERY, M. HEIDELBERGER, and W. F. GOEBEL (J. Exp. Med., 1925, **42**, 709—725).—The chemical and immunological properties of the soluble specific substances of *Pneumococcus* type II and a strain of Friedländer's bacillus are described and correlated. CHEMICAL ABSTRACTS.

Soluble specific substance of *Pneumococcus*. M. HEIDELBERGER, W. F. GOEBEL, and O. T. AVERY (J. Exp. Med., 1925, **42**, 727—745).—The soluble specific substance of *Pneumococcus* type II is a weakly acidic, nitrogen-free polysaccharide, equivalent about 1250, [α]+74°, made up chiefly of glucose units. It is precipitated by basic lead acetate and by uranium compounds. With acetic anhydride and pyridine it yields a triacetyl derivative. The soluble substance

of type III is also an acid, nitrogen-free polysaccharide, equivalent about 340°, [α]—33°, made up of glucose units and those of glycuronic acid or a derivative. It is precipitated by concentrated hydrochloric acid, barium hydroxide, or heavy metal salts. The soluble specific substance of type I is also a sugar derivative, but contains nitrogen (5%); it is a strong acid and weak base with isoelectric point about p_H 4, and is dextrorotatory. It does not give the usual protein colour tests. Half of the nitrogen is liberated by nitrous acid, which also causes the appearance of reducing sugars, whilst the substances of types II and III are unaffected by nitrous acid. Probably a nitrogenous sugar derivative is linked to galacturonic acid through the reducing group of the latter. The type I substance is precipitated by barium hydroxide, by heavy metal salts, and by phosphotungstic acid. The substances differ from the starch–glycogen group of carbohydrates in giving no colour with iodine, and in their resistance to the ordinary carbohydrate-splitting enzymes. CHEMICAL ABSTRACTS.

Preparation of the hormone of the œstrous cycle and its chemical and pharmacological properties. E. LAQUEUR, P. C. HART, S. E. DE JONGH, and I. A. WIJSENBEEK (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 890—899).—Follicular liquid is shaken with an organic solvent (*e.g.*, chloroform) and salt or acid to coagulate the proteins, the extract is evaporated to dryness, and the residue taken up with distilled water. The substance is protein-free and probably also free from cholesterol, nitrogen, phosphorus, and sulphur. It is soluble in water and volatile solvents, and appears to be non-toxic to men and animals. The name *menformon* has been suggested. Substances prepared by other investigators, which produce similar œstrous phenomena, but which act on the blood pressure and are apparently insoluble in water, are probably menformon mixed with impurities, especially lipins (cf. Dickens, Dodds, and Wright, A., 1925, i, 1513).
M. S. BURR.

Parathyroid hormone and its physiological action. J. B. COLLIP (Ann. Clin. Med., 1925, **4**, 219—230).—The administration of parathyroid hormone to normal dogs causes an increase in the calcium content of the serum; immediately before death, after repeated injections, the calcium, phosphorus, and non-protein nitrogen content of the blood increased. CHEMICAL ABSTRACTS.

Active principles of the posterior lobe of the pituitary body. W. SCHLAPP (Quart. J. Exp. Physiol., 1925, **15**, 327—347).—Treatment of depressor-free extracts of the posterior lobe of the pituitary body with *n*-butyl alcohol yields a fraction containing the greater part of the oxytocic activity, whereas the active pressor and melanophore substances may be adsorbed on lead sulphide to a much greater extent than the oxytocic principle.
CHEMICAL ABSTRACTS.

Effect of insulin on the dextrose consumption of perfused skeletal muscle. C. H. BEST (Proc. Roy. Soc., 1926, **B**, **99**, 375—382).—Insulin greatly accelerates the rate of sugar disappearance from defibrinated blood used to perfuse the isolated limbs of the cat. H. J. CHANNON.

Chemistry of the blood-sugar in insulin hypoglycæmia. Z. ERNST and J. FÖRSTER (Biochem. Z., 1926, **169**, 498—500).—Polarimetric determination of the dextrose content of the blood of rabbits in insulin hypoglycæmia showed that when the "blood-sugar" is at its lowest value 51—76% of the reduction is due to dextrose. E. C. SMITH.

Photoactivation of cholesterol, fats, and other substances by *X*-rays. S. HAMANO (Biochem. Z., 1926, **169**, 432—434).—Cholesterol, borneol, elaidic and oleic acids, and cod-liver oil, which after irradiation with ultra-violet light affect a photographic plate in the dark (this vol., 98), give a similar effect when irradiated with *X*-rays for 5 hrs. No activation occurs in an atmosphere of carbon dioxide. E. C. SMITH.

Antirachitic value of irradiated cholesterol and phytosterol. V. Chemical and biological changes. A. F. HESS, M. WEINSTOCK, and E. SHERMAN (J. Biol. Chem., 1926, **67**, 413—423).—Cholesterol, after many recrystallisations, and in the anhydrous condition, could still be endowed with antirachitic properties by ultra-violet irradiation; cholesteryl acetate could also be rendered antirachitic in the same way, which, in conjunction with the previously reported (A., 1925, i, 1020) failure to activate dihydrocholesterol, indicates that it is to its double linking and not to its hydroxyl group that cholesterol owes its capacity to be activated by irradiation. Irradiation of cholesterol, for periods up to 2 hrs., increases its power of inhibiting hæmolysis by digitonin; as is the case with the antirachitic properties, more prolonged irradiation reverses this effect. Addition of digitonin to a solution of cholesterol after irradiation precipitated 95·5% of the cholesterol originally present; the substances not precipitated by digitonin had no antirachitic activity.
C. R. HARINGTON.

Diet and reproduction. G. GRIJNS (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 942—952).—The effect on the fertility of rats of three different corn-food diets composed of maize, peanut, coconut, or meat meal, hardened fat, and a mixture of salts, has been compared with that of a normal food containing whole wheat meal, meat meal, suet, a salt mixture, and milk, all the diets having practically the same content of protein, fat, and carbohydrate. The progeny were kept on the same food as the parents. Fertility on the corn-food diets was variable, but much less than on the normal diet. The young that survived in the former cases grew as well as their parents; matings between them, however, were infertile in all cases but one. Matings between males of the second generation on the experimental food and females on normal food were infertile. The females of the second generation on corn-food, mated with males on normal food, were productive and raised their young. It is evident that the factors controlling reproduction are not the same as those controlling growth, and that the requirements of the males are different from those of the females. The discrepancies between the experimental results of different investig-

ators on the relation of diet to fertility are probably due to variations in the quality of the milk used. Milk may contain all the factors necessary for reproduction, but not in all cases in sufficient quantity. The experiments described do not allow a definite statement to be made on the existence or otherwise of vitamin-*E*. M. S. BURR.

Rapid method for demonstrating the effects of plants on a culture solution. P. L. HIBBARD (Science, 1925, **62**, 515—516).—The plants, *e.g.*, wheat seedlings, are arranged so that the roots are compressed into a small space, dilute solutions of single salts being applied on successive days, the roots being kept immersed by dilution if necessary. The change in concentration of the various ions is determined. With potassium nitrate both ions, but with the chloride, phosphate, or hydrogen carbonate only the potassium, were completely removed in 9 hrs. With calcium and sodium nitrates the nitrate was used, but most of the cation remained; much ammonium sulphate remained unabsorbed, the solution becoming acid. A. A. ELDRIDGE.

Acetaldehyde as an intermediate product in the germination of fat-containing seeds. K. PIRSCHLE (Biochem. Z., 1926, **169**, 482—489; cf. this vol., 439).—Acetaldehyde, in relatively large amounts, may be extracted by means of sodium sulphite from seeds rich in fat during germination. It is probably formed during the utilisation of the dextrose derived from the fat of the seeds, but may possibly be an intermediate in the actual conversion of fat into sugar. E. C. SMITH.

Law of photochemical equivalents in photosynthesis by chlorophyll. R. WURMSER.—See this vol., 486.

Aluminium in organic life. J. STOKLASA (Intern. Rev. Sci. Practice Agric., 1925, **3**, 654—662).—Plants which prefer dry surroundings have a low, and hygrophytes a high, aluminium content. There appears to be a specific porosity of the cells of the root system to aluminium. Plasmolysis due to excess of iron is prevented by aluminium, which is injurious to plants if sulphite or sulphate is present. The relation of aluminium to the colour of plants, animals, and minerals is considered.

CHEMICAL ABSTRACTS.

Asperuloside in plants. Extraction of the glucoside from *Galium aparine*, L. H. HÉRISSEY (Compt. rend., 1926, **182**, 865—867; cf. A., 1925, i, 1165, 1369).—The colour reactions of asperuloside are given by extracts of *Rubia tinctorum*, L., *R. Peregrina*, L., *Galium cruciata*, Scop., *G. Verum*, L., *G. Molugo*, L., *G. aparine*, L., *Asperula tinctoria*, L., and *Sherardia arvensis*, L. A small amount of asperuloside has been extracted from *G. aparine*.

L. F. HEWITT.

Application of the biochemical method of examining hydrolysable glucosides by means of rhamnodiastase to the study of fresh roots of *Polygonum cuspidatum*. Isolation of a new glucoside, polydatoside. M. BRIDEL and C. BÉGUIN (Bull. Soc. Chim. biol., 1926, **8**, 136—143).—See this vol., 440.

Ethereal oils of tobacco. A. SCHMUCK (Inst. Exp. Tobacco Cult., Krasnodar [Russia], 1924, No. 19, 1—16).—No relation was found between the content of oil and that of other organic constituents. The physico-chemical constants of the ethereal oils vary with the variety of tobacco; furfuraldehyde was isolated from Dewbek (? Dubec) oils. Fractionation yields (i) at 80° a butyl ester, (ii) at 120° probably hexyl formate, (iii) the residue, resembling diallylcarbinol. CHEMICAL ABSTRACTS.

Resins and aromatic substances of tobacco. A. SCHMUCK (Inst. Exp. Tobacco Cult., Krasnodar [Russia], 1924, No. 20, 5—13).—From 100 g. of tobacco, hot benzene extracts 6·87 g., of which 0·46 g. is an unsaturated compound, $C_9H_{16}O_2$, m. p. 86°, forming a bromo-compound, m. p. 118—120°. A further 0·41 g. is an acid, $C_{24}H_{40}O_5$, similar to kentukilic acid, $C_{23}H_{40}O_5$. Other fractions consist of an acid, $C_9H_{22}O_2$, a resin alcohol, $C_6H_{10}O$, and the phenols, these three amounting to 5·03 g. From 100 g. of tobacco, ethyl alcohol extracts 22·89 g., yielding a substance, m. p. 140°, probably a glucoside, $C_{22}H_{20}O_{24}$. Light petroleum extracted 0·10 g. from 100 g., and ethyl ether extracted 3·66 g. of an unknown substance with a pungent odour.

CHEMICAL ABSTRACTS.

Attempt to determine the character of the carbohydrate complex of tobacco. A. SCHMUCK (Inst. Exp. Tobacco Cult., Krasnodar [Russia], 1924, No. 20, 19—22).—In Dewbek (? Dubec) tobacco were found no starch, 1·68% of dextrin, and 9·58% of complex and simple sugars, of which 8·35% reduce Fehling's solution. CHEMICAL ABSTRACTS.

Incrustations of flax. F. EHRLICH and F. SCHUBERT (Biochem. Z., 1926, **169**, 13—66).—Extraction of the fibre with water at 120—135°/2 atm. removes the pectin in a water-soluble form (hydropectin) in a yield of 16% of the dried flax. As in other plants, the conversion of the pectin into a soluble form entails chemical decomposition. Hydropectin is a mixture of 55 parts of hexopentosan and 45 parts of calcium magnesium pectate. Separation is effected by means of 70% alcohol and hexopentosan, obtained by evaporating the alcoholic extract to dryness, dissolving the residue in water, and evaporating. It is a dark brown substance giving the orcinol reaction, reducing Fehling's solution, more intensely after acid hydrolysis, and having $[\alpha]_D$ −23·1°, but by repeated boiling of this material with alcohol of gradually decreasing strength, an increase in rotation occurs, as is the case with araban. The maximum value is $[\alpha]_D$ −144·1°.

When hydrolysed by acid, hexopentosan yields a syrup, $[\alpha]_D^{20}$ +32·6°, giving all the reactions of pentose and partly fermentable, indicating the presence of hexoses; it contains 55% of pentoses, 17% of *d*-galactose, and 20% of lævulose. *l*-Arabinose and *d*-galactose were identified by means of their benzylphenylhydrazones, and the Selivanov reaction was positive. The presence of *l*-xylose was inferred from the rotatory power of the hydrolytic products, and the composition of hexopentosan is therefore a galactan-lævulosan-xylan-diaraban.

Calcium magnesium pectate after purification remains as a colourless powder of constant ash content (6·3%). It has $[\alpha]_D$ +93°, contains C 40·28%, H 5·69%, MeO 3·6%, and yields furfuraldehyde corresponding with 38·80% of pentoses. The free acid obtained by precipitation with alcohol and hydrochloric acid still contains 0·8% of ash. It has *M* (cryoscopic) 1421. The aqueous solution is acid and yields precipitates with baryta and lime water. It is similar in properties to the pectic acid of turnips, but the methoxyl content is not so high, also the yield of acetic acid from acetyl groups is 8·6%, in place of 11% in the latter compound.

On acid hydrolysis galacturonic acid was isolated, corresponding with 56% of the pectic acid. The presence of *l*-arabinose, *l*-xylose, and *d*-galactose was also established in quantities suggesting the formula $C_{46}H_{68}O_{40}$ and the composition as that of a diacetyl-arabino - xylo - galacto - dimethoxy - tetragalacturonic acid. C. RIMINGTON.

[Incrustive substances of plants. VI.] E. HEUSER (Ber., 1926, **59**, [*B*], 598—600).—Objection is raised to the use of the conceptions "skeleton substance and incrustation" (cf. Schmidt, Haag, and Sperling, A., 1925, i, 1370) in the analysis of crude plant materials, since such terms are not clearly defined and indicate only a return to arbitrary conventions such as "crude fibre."

The use of chlorine dioxide is preferable to that of chlorine in the determination of cellulose, which is less attacked by the former than by the latter. It requires to be supplemented by that of sodium hydroxide in order to obtain the total carbohydrates. H. WREN.

Leaf-tissue fluids of Egyptian cottons. J. A. HARRIS, W. F. HOFFMAN, W. B. SINCLAIR, A. H. JOHNSON, and R. D. EVANS (J. Agric. Res., 1925, **31**, 1027—1033; cf. Harris and others, A., 1924, i, 815; 1925, i, 216, 450).—Although typical Egyptian varieties differ to some extent among themselves, the leaf juices from all of them have a higher osmotic concentration and specific conductivity than the upland varieties. There is no difference in the ratio of specific conductivity to f.-p. depression. A. G. POLLARD.

Leaf cytoplasmic proteins. A. C. CHIBNALL (J. Amer. Chem. Soc., 1926, **48**, 728—732).—A general discussion of the influence of the physico-chemical properties of cytoplasm on the mechanism of cell permeability. Analysis of the cytoplasm of spinach leaves gave the following results: alcohol-soluble, 12·7%; ash, 15·1%; and protein, 64·6%. Part of this material can be separated from all fatty material and carbohydrates by filtration through paper pulp, whilst the remainder appears to be in some kind of loose combination with fatty substances, which can be removed by washing with alcohol. The "free" and "combined" substances do not differ materially in their content of amino-acids, of which cystine, arginine, histidine, and lysine were identified. The following isoelectric points of leaf cytoplasmic proteins were determined, together with the corresponding p_H values of the cell contents, the figures being placed in this order: spinach, 5·0—4·0 and 6·57; hogweed, 5·0—4·3 and 6·19; broad bean, 5·1—4·3 and 5·69; cabbage, 4·7—4·0 and 5·60; rhubarb, 3·5 and 4·00; and *Vitis vinifera*, 4·8—4·4 and 3·02, respectively. The cell contents of the leaves are highly buffered, and no variation greater than p_H 0·3 has so far been observed in any variety of leaf. The cytoplasm of the living cell thus appears to be in contact, at its inner surface, with a solution sufficiently buffered to keep its reaction fairly constant, whilst its outer surface is in contact with a medium the reaction of which can vary with environment, but it is probable that any change of reaction must be such that the isoelectric point of the cytoplasmic proteins is not reached, as they are completely precipitated at this point, with probable disruption of the complex and death of the cell. F. G. WILLSON.

Alkaloids of *Ceanothus americanus*. A. H. CLARK (Amer. J. Pharm., 1926, **98**, 147—156).—The drug prepared from the root of *Ceanothus americanus* was ground, mixed with lime, moistened, and extracted with ether. The extract was washed with light petroleum, and extracted with acetic acid, addition of ammonia to the latter precipitating an amorphous mixture of alkaloids, m. p. about 190°, which may be freed from resins by precipitating their hydrochloric acid solution with silicotungstic acid. A crystalline *alkaloid*, m. p. 255°, forming a crystalline *chloroaurate* and *picrate*, and yielding a red precipitate with potassium bismuth iodide, was obtained from the mixture, which also yielded, on fractional solution in ether, amorphous *alkaloids*, m. p. 241° and 183°. B. FULLMAN.

New constituent of plants, allantoic acid. R. FOSSE (Compt. rend., 1926, **182**, 869—871).—Allantoic acid (1 mol.) condenses with xanthhydrol (2 mols.), giving *dixanthylallantoic acid*. This last-named compound has been obtained by treating extracts of *Phaseolus* with xanthhydrol. It is suggested that the carbamide, and the substance reacting with hydrazine produced by heating certain vegetable extracts (cf. this vol., 438) are formed by hydrolysis of allantoic acid in the plants. Xanthylallantoin has been obtained by treating extracts of *Phaseolus* with xanthhydrol. L. F. HEWITT.

Variation of threshold value for amylogenous condensation in different plant cells. A. MAIGE (Compt. rend., 1926, **182**, 588—590).—Plant-tissues depleted of stores of starch materials are first bathed in a sucrose solution, and then the starch supplies are again allowed to become partly exhausted. The amylogenous thresholds of the stomata, endoderm, root, parenchyma, and lacuna are lower than those of the other cells, since starch is found in them when it has disappeared from other parts of the plant. L. F. HEWITT.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1926.

BIBLIOTE POLITECNICO

General, Physical, and Inorganic Chemistry.

Spectrum of hydrogen. A. SOMMERFELD and A. UNSÖLD (Z. Physik, 1926, **36**, 259—275).—The spectrum of hydrogen is treated as being of the same type as that of the alkalis. The relativity formula for the difference of levels remains the same, but the quantum numbers assigned to them are changed. In this way, anomalies in the ratio of the intensities of the fine-structure lines are explained, and it is further suggested that the 2*s* term represents a metastable state. The discovery that a Paschen–Back effect could be obtained with H_α raised one great objection to the original scheme for the hydrogen spectrum, which allowed only for a normal Zeeman effect for all magnetic fields, whereas the lines coalesce on applying a field of 10,000 gauss, as is the case with the corresponding lithium line 6104. It is, however, necessary to assign to j values of $\frac{1}{2}$, $\frac{3}{2}$, etc. These values have previously been regarded as derived from the interaction of the electron with the rest of the atom, although for hydrogen no such interaction is possible; it must therefore be ascribed to the radiating electron itself. E. B. LUDLAM.

Hydrogen doublet. W. V. HOUSTON (Nature, 1926, **117**, 590).—The doublet separations at a pressure of 0·5 mm. and a current density of 0·25 amp./cm.^{2} are: H_α 0·316±0·002; H_β 0·329±0·005; H_γ 0·353±0·007; R=109,677·70±0·04. It is assumed that the forbidden components for which Δk=0 are present, increase in intensity with an increase in current, and are polarised with the electric vector parallel to the current. Experimental support for this view is forthcoming. The results support the suggestions of Uhlenbeck and Goudsmit (this vol., 215). A. A. ELDRIDGE.

Absorption and resonance radiation in excited helium and the structure of the 3889 line. W. H. MCCURDY (Proc. Nat. Acad. Sci., 1926, **12**, 231—233).—Eleven lines of the principal series of both the singlet and doublet systems, and also the diffuse subordinate series of both systems in the helium spectrum, have been completely reversed by an absorbing column of excited gas 80 cm. long at 4 mm. pressure. Small amounts of hydrogen greatly reduce the absorption, probably owing to a decrease in the life of the excited atoms. The excitation of helium by electron impacts is largely to the 1σ state at higher pressures and to the 1*S* state at low pressures. The absorption falls off for the higher terms of a series, owing to a decrease in the probability of a transition to the states of higher energy. Resonance radiation in weakly excited helium has been photographed, the intensity of the 3889 (1σ—2π) line being greatly increased by the action of radiation from another tube containing helium. The line consists of at least two components, a weak component 0·044 Å. on the short wave-length side of the main component having been observed. R. A. MORTON.

Excitation of the spectra of nitrogen by electron impacts. D. C. DUNCAN (Astrophys. J., 1925, **62**, 145—167).—Associated with the emission of radiation between 7000 and 2000 Å., six energy levels have been established for the neutral molecule and only one definitely for the ionised molecule. The fifth positive group lies between 2973·2 and 2825·3 Å., the sixth between 2828·1 and 2111·0 Å., and the seventh between 2338·7 and 2040·0 Å. The second negative system extends from 2638·6 to 2112·5 Å., and is related to the Deslandres negative bands. The third positive group, which did not appear, is probably due to a compound of nitrogen; the cyanogen bands are also apparently due to a carrier other than nitrogen.

A. A. ELDRIDGE.

Relative intensities of the D_1D_2 lines of sodium in comets and in low-pressure laboratory sources. H. B. LEMON and N. T. BOBROVNIKOFF (Nature, 1926, **117**, 623).—Excitation of the *D* lines in carbon monoxide at 10^{-5} cm. pressure, using a hot cathode richly coated with oxides containing very minute traces of sodium and an anode consisting of a nickel cylindrical Faraday cage, the end opposite to the cathode being of iron gauze, produced a relative intensity D_2/D_1=5—25 or more, the conditions finally suggesting those observed in a comet near perihelion. A. A. ELDRIDGE.

Enhanced lines produced by the interrupted arc in sodium and potassium vapours. F. H. NEWMAN (Phil. Mag., 1926, [vii], **1**, 721—726).—In the spectrum of the intermittent arc produced in the vapour from a sodium–potassium alloy, the principal series lines of sodium and potassium are faint, and the subordinate series lines of sodium are almost entirely absent. The corresponding potassium lines are present, but are only slightly more intense than those of sodium. The complicated enhanced line spectra of the two metals predominate. The origin of the enhanced lines in this case is discussed.

A. E. MITCHELL.

Fine structure of the *X*-ray absorption edge in the *K*-series of argon and its possible interpretation. D. COSTER and J. H. VAN DER TUUK (Nature, 1926, **117**, 586—587).—In the case of argon, with gypsum as the analysing crystal, no "fine structure" of the absorption edges could be detected, although good positive results were obtained for chlorine or potassium. Hence it is concluded that absorption processes connected with transitions of more than one electron do not appreciably contribute to the absorption of *X*-rays, and that such transitions cannot account for the fine structure of absorption edges. With calcite as the absorbing crystal, however, and a narrow slit (0·025 mm.), there were obtained for argon two different absorption edges separated by a rather sharp, black line. The difference of the observed edges, corresponding with 1·7 (±20%) volts, is of the order to be anticipated if the fine structure corresponds with transitions to the different optical orbits available for the electron removed from the inside of the atom by an absorption process. A. A. ELDRIDGE.

Method for exciting spectra of certain metals. J. K. ROBERTSON (Phil. Mag., 1926, [vii], **1**, 752—761).—The spectra of tin, zinc, cadmium, and mercury are excited by an electrodeless discharge in an evacuated quartz tube containing the metals. The results are equally good whether the tube is cold or heated at temperatures of the order of 1000°. With a cold tube traces of air, hydrogen, or water vapour are necessary to carry the discharge. The only lines appearing with any considerable intensity are the ultimate and penultimate lines of the neutral atom, together with ultimate lines of the ionised element. It is suggested that either the effect is due to vaporisation of the metals, with the result that sufficient atoms are present in the discharge region to give lines of marked intensity, or that the atoms of the metal are present as the result of a reaction between excited gas atoms and the metal or its oxide. The bulk of the evidence appears in favour of the second alternative. A. E. MITCHELL.

Absorption spectra of the vapours of zinc, cadmium, lead, tin, bismuth, and antimony. J. G. FRAYNE and A. W. SMITH (Phil. Mag., 1926, [vii], **1**, 732—737).—An examination of the applicability of the absorption cell described by Zumstein (A., 1925, ii, 453) to metals of low b. p. In accordance with theory, cadmium vapour shows strong absorption of both the $1S$— $2P$ and the $1S$—$2p_2$ lines. In zinc vapour, the $1S$—$2p_2$ line was strongly absorbed, whilst the $1S$—$2P$ line was not detected. The results for lead vapour are in accordance with those of Grotrian (A., 1923, ii, 710), whilst bismuth vapour gives the line absorption found by Foote, Rognley, and Mohler. Tin vapour gave results in agreement with those of McLennan and others (A., 1925, ii, 454). The line absorption found by Narayan and Rao (*ibid.*, 927) for antimony vapour was not detected.
A. E. MITCHELL.

Arc spectra of iodine, bromine, and chlorine in the Schumann region. L. A. TURNER (Physical Rev., 1926, [ii], **27**, 397—406).—For iodine, 66 lines between 2062·1 and 1234·2; for bromine, 47 lines between 1633·6 and 1232·5; and for chlorine, 7 lines between 1396·5 and 1335·8 Å. are tabulated. The doublet differences of 7600, 3685, and 881 wave-number units, respectively, are considered to be the separations of the two levels of normal doublet p states of the atoms. Hence, the resonance lines are 1782·9, 1540·8, and 1379·6 Å., and the radiating potentials 6·92, 8·01, and 8·95 volts for iodine, bromine, and chlorine, respectively. The heat of dissociation of the iodine molecule is computed to be 35·3 Cal./g.-mol. A. A. ELDRIDGE.

Low-voltage arc in cæsium vapour. F. H. NEWMAN (Phil. Mag., 1926, [vii], **1**, 705—711).—An extension to cæsium vapour of previous work (A., 1925, ii, 450, 1014) on the low-voltage arc spectra of sodium and potassium vapours. At 1·6 volts accelerating potential, the doublet 8493, 8521 Å. of the series 1σ—1π appears. This is followed at 2·7 volts by the 1σ—2π doublet at 4593 Å., whilst at 3·2 volts the $1\pi_1$—3σ doublet at 7944 Å. and the 1σ—3π line at 3889 Å. appear. At 3·9 volts, the ionisation potential, the complete arc spectrum appears. The voltages at which these lines appear are in fair agreement with those calculated. Other lines corresponding with the 2π orbit which, according to the Bohr selection principle, should be excited by interorbital transfer below 2·69 volts, were not obtained. The results indicate that, in common with sodium and potassium vapours, cæsium vapour gives a line-by-line spectrum corresponding with orbital changes involving less energy than the ionisation potential. A. E. MITCHELL.

Magnitudes of the terms of spectral series. A. UNSÖLD (Z. Physik, 1926, **36**, 92—100).—The radiating electron and the rest of the atom are regarded as constituting a di-pole, and the polarisation is calculated on the assumption that the atomic trunk containing p loosely-bound electrons interacts with an outer electron as a group of p isotropic harmonic oscillators of frequency equal to that of the resonance radiation. The calculation is applied to the spectra of the elements in the first three groups of the periodic system. E. B. LUDLAM.

Intensity problem of spectral lines. H. HÖNL (Ann. Physik, 1926, [iv], **79**, 273—323).—A theoretical paper in which quantum aspects of the intensity relationships exhibited of Zeeman components, multiplets, and band lines are co-ordinated in as comprehensive a manner as is yet possible. Not only are the intensities of single lines connected by rational numbers, but also the functions depending on the determinative quantum numbers are themselves rational. The range of the validity of intensity formulæ is discussed in detail, and the extension of the formulæ to term systems (cf. Kronig, A., 1925, ii, 458) in the neon spectrum is shown to be possible. The relations between the summation rules, polarisation rule, and correspondence principle and an experimental suggestion concerning resonance radiation in a magnetic field are discussed. A symmetrical representation of intensities of Zeeman components is given with respect to the quantum numbers of initial and end states. R. A. MORTON.

Nature of soft X-rays. A. DAUVILLIER (Compt. rend., 1926, **182**, 927—929).—Further experiments on soft X-rays have been conducted using anodes of molybdenum and tantalum. The discontinuity observed in earlier experiments (this vol., 330, 552), where a tungsten anode was used, was attributed to the K band of carbon in the celluloid window, but it now appears also to be partly due to the tungsten itself. It is also established that the lighter solid elements emit characteristic rays when bombarded by electrons, and that the soft X-rays so far studied are composed chiefly of the L and K carbon rays and N and O rays of the celluloid. C. J. STILL.

Problem of X-ray line intensities. F. H. LORING (Nature, 1926, **117**, 622—623).—Lines of wave-length 1·040 and 1·038 Å. appear when the substance on the copper anticathode is one that might contain an element of atomic number 87. On plates, lines of wave-length 1·038 and 0·930 Å. have been obtained under defined conditions. The bromine $K\alpha$ line has wave-length 1·0377, and it is suggested that when a weak radiation closely corresponding therewith falls on a plate, the bromine alone or in conjunction with the emulsion may be stimulated into greater photographic sensitivity. The rubidium $K\alpha_1$ line has a wave-length of 0·928 Å.

A. A. ELDRIDGE.

Effect of temperature on X-ray absorption. H. S. READ (Physical Rev., 1926, [ii], **27**, 373—380).—With aluminium, copper, iron, nickel, silver, and lead, the average atomic absorption coefficients for the total X-radiation from a tungsten target increased practically linearly by about 0·2% per 100°. Measurements were made between 20° and temperatures near the m. p. of the absorber. A. A. ELDRIDGE.

Quantitative experimental control of resonance absorption of X-rays. V. POSEJPAL (Compt. rend., 1926, **182**, 767—769).—To obtain such control, the absorbing sheet of tungsten in the apparatus previously described (this vol., 216) must be traversed at all points by homogeneous pencils of rays. By using sheets of copper along with the tungsten sheet, and measuring the densities by a photomicrometer, the thickness of copper equivalent in absorptive power to the tungsten has been determined. Using the value for the absorption coefficient of copper calculated from the formula of Bragg and Peirce, the absorption coefficients (τ/ρ) of the rays K_{α_1} and K_{α_2} of tungsten are found to be 3·92° and 3·71°, respectively. The values of the ratio $\tau/\rho : \tau_0/\rho$ corresponding with the values of τ_0/ρ given by the above formula are 1·40 and 1·25, as compared with 1·50 and 1·25 required by the author's theory. R. CUTHILL.

Production of fluorescence in the region of X-rays. P. AUGER (Compt. rend., 1926, **182**, 773—775; cf. A., 1925, ii, 175).—The results of the absorption of high-frequency radiation have been analysed by C. T. R. Wilson's condensation method. Under the influence of X-rays of 20 kilovolts, krypton emits from the K level an electron at 6 kilovolts and a tertiary ray at 11 kilovolts, whilst a secondary β-ray from the ionisation of the L level emerges at 18 kilovolts. The ratio R of the number of characteristic quanta emitted as fluorescence to the number of incident quanta absorbed is 0·51, and the ratio J of the number of incident quanta absorbed at the K and L levels is 7·58. With argon the photo-electric effects at the two levels cannot be separately distinguished, but extrapolation of Allen's curve connecting J and the atomic number (Physical Rev., 1924, [ii], **24**, 1) gives $J=8·3$, from which $R=0·072$. Qualitative experiments with neon and xenon indicate that R increases with increasing atomic number.

R. CUTHILL.

Correspondence principle in the Compton effect. G. BREIT (Physical Rev., 1926, [ii], **27**, 362—372).—It is shown that the Compton shift is a properly taken mean of the classical Döppler shift. Similarly, the amount of light scattered in various directions may be determined if it is assumed that the intensity in the quantum theory equals a proper average of the intensities scattered according to the classical theory. The author assumes that the corresponding classical electron has the same direction of motion as the scattered quantum.

A. A. ELDRIDGE.

Properties of Compton radiation. H. KALLMANN and H. MARK (Z. Physik, 1926, **36**, 120—142).—When monochromatic X-radiation acts on a free electron at rest, the electron acquires momentum from the radiation which is then scattered, but with its frequency reduced; ordinary scattered radiation is due to the bound electrons of the atom which do not acquire appreciable kinetic energy and do not reduce the frequency of the scattered radiation appreciably. The polarisation of the Compton radiation depends on that of the unscattered ray, just as does the ordinary scattered radiation; Compton radiation shows no interference maxima, hence the radiation is non-coherent, the electrons which give rise to the Compton effect not being subject to forces which hold the crystal together; the intensity of the Compton radiation from the $K\alpha$ line of zinc scattered by lithium decreases as the angle of scattering increases up to 90°, but thereafter increases again; for shorter wave-lengths this increase above 90° does not occur. E. B. LUDLAM.

Compton effect from γ-rays. G. HOFFMANN (Z. Physik, 1926, **36**, 251—258).—The γ-rays from a strong source of radium were allowed to fall on a cylinder of carbon and the secondary radiation was passed into an ionisation chamber through various thicknesses of lead. The change produced in the wave-length was calculated from the change in absorption; the angle of scattering was altered by rotating the radium round the carbon rod. Both change in wave-length and intensity relation to angle of scattering were in satisfactory agreement with the theory of the Compton effect. E. B. LUDLAM.

Duration of emission of monochromatic radiations and the mean life of the stationary states. A. PONTREMOLI (Atti R. Accad. Lincei, 1926, [vi], **3**, 149—154).—Mathematical. A procedure is indicated which appears to allow of the calculation of the duration of emission of monochromatic radiation by an atom passing between two stationary states, at

any rate in the simplest case of passage between two circular orbits. T. H. POPE.

Life-periods of the metastable s_3 and s_5 states of neon. H. B. DORGELO (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 7—14).—See this vol., 101.

Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum. E. E. WITMER (Proc. Nat. Acad. Sci., 1926, **12**, 238—244).—Lyman has found that the admixture of small amounts of hydrogen with argon may under certain conditions cause the appearance of eleven groups of lines between 1063 and 1670. The exclusion of the rest of the secondary spectrum of hydrogen in the extreme ultra-violet is due to the fact that the presence of argon limits the velocity of the free electrons to 11·6 volts (resonance potential). Electrons of greater velocity suffer inelastic impact with argon atoms. Hydrogen molecules are excited by collisions of the second kind with excited argon atoms. The Lyman bands of hydrogen constitute a one-dimensional series with a common vibrational state in the upper level.

The heat of dissociation of the hydrogen molecule is computed as 100,100 cal. (4·34 volts). The Glitscher diagram has been used to calculate the higher resonance potentials and the ionisation potential of the hydrogen molecule. The values 11·61, 13·665, 14·31, 14·64, 14·81, and $V_{ion.}$ 15·19 are obtained and are confirmed by an independent calculation, employing a Rydberg formula. The use of a Ritz formula would increase the ionisation potential, but the spectroscopic value would still be lower than that obtained from electronic impacts. The discrepancy is due to the fact that the electron impacts must produce a certain minimum vibrational energy in the act of exciting a given electronic transition. Hence the observed critical potentials will be higher than the spectroscopic data indicate. R. A. MORTON.

Resonance potentials of helium and double impacts by electrons in helium. G. GLOCKLER (Physical Rev., 1926, [ii], **27**, 423—431).—Franck's method (0·13—13·00 mm.) gave 19·87±0·06 volts for the first, and 20·62+0·06 volts for the second critical potential in helium. Lenard's method (0·96—2·85 mm.) gave 19·83±0·02 and 20·57±0·06 volts, respectively. The values agree with the transitions $1S \longrightarrow 2s$ and $1S \longrightarrow 2S$. Critical potentials due to double impact were observed at 39·62, 40·67, and 40·96±0·04 volts, corresponding with $1S \longrightarrow 2s$ and $1S \longrightarrow 2s$; $1S \longrightarrow 2s$ and $1S \longrightarrow 2S$; $1S \longrightarrow 2s$ and $1S \longrightarrow 2P$. The observed difference between the first critical potential (19·85 volts) and the most prominent double impact point (40·96 volts) corresponds with the transition $1S \longrightarrow 2P$. A. A. ELDRIDGE.

Critical potentials of *K* levels of light atoms. M. HOLWECK (Compt. rend., 1926, **182**, 779—781).—Application of the method previously described (this vol., 104) to oxygen, nitrogen, nitrous oxide, and boron trihydride shows that the observed discontinuities have a fine structure, one or more absorption lines preceding the band, and that this structure depends on the state of combination of the particular element. For nitrogen, an absorption line (397, **400**, 403 volts) precedes the band at 403 volts, whilst nitrous oxide has a single band at 397 volts. Oxygen gives two lines (528, **531**, 533; 533, **534**, 535 volts), then a band at 535 volts. Boron trihydride shows no anomaly between 150 and 210 volts, but the transparency of fused boric oxide is anomalous at 192 volts. If the potential of the K level be taken as represented by the first discontinuity, the values obtained lie accurately on a Moseley diagram. The author considers that Dauvillier's demonstration of the pressure variations caused by discharges in gases (this vol., 330) is based on insufficient and inaccurate experimental data. R. CUTHILL.

Critical voltages of radon. F. STRUWE (Z. Physik, 1926, **36**, 410—413).—A linear relationship exists between the critical voltages for argon, krypton, and xenon which by extrapolation leads to the following values for radon: first excitation voltages, 6·7 and 5·5; second excitation voltages, 8·4 and 7·2; ionisation potentials, 9·5 and 8·0 volts. E. B. LUDLAM.

Concurrent variations in the thermionic and photo-electric emission from platinum and tungsten with the state of the surfaces of these metals. T. H. HARRISON (Proc. Physical Soc., 1926, **38**, 214—233).—The thermionic and photo-electric work functions were measured for the same specimens of tungsten and platinum. The results obtained depended on the previous heat treatment of the material, and the irregularities observed are attributed to the state of the surfaces.

C. J. SMITHELLS.

Photographic effect of slow electrons. G. F. BRETT (Proc. Leeds Phil. Soc., 1925, **1**, (1), 1—5).—The methods for sensitising films for use in the ultra-violet region of the spectrum are discussed. Kodak "duplitised" X-ray films were found very satisfactory, dense markings being obtained from 100-volt electrons after the film had been suitably treated. At the lowest voltage tried, 65 volts, the sensitivity of the treated film was still maintained.

J. S. CARTER.

Secondary electrons from iron. H. E. FARNSWORTH (Physical Rev., 1926, [ii], **27**, 413—422).—Curves showing the ratio of secondary to primary electron current as a function of the accelerating potential have sharp maxima at 1·2 and 7·0 volts, and minima at 3·7 and 12·0 volts, together with a less marked maximum and minimum at 10 and 9 volts, respectively. Only in the cases of iron and copper have sharp maxima and minima been observed. A layer of iron, deposited by evaporation, is crystalline, whilst a similar layer of copper is amorphous.

A. A. ELDRIDGE.

Theory of current transference at the cathode of an arc. J. SLEPIAN (Physical Rev., 1926, [ii], **27**, 407—412).—If the adjacent gas, but not necessarily the cathode itself, is at a sufficiently high temperature (for calcium, 4000°; for copper, 6000° Abs.), thermal ionisation may account for the carriage of the current to the cathode, thermionic emission not being essential. A. A. ELDRIDGE.

Mobility of ions in gases. M. LAPORTE (Compt. rend., 1926, **182**, 781—784).—The results of experiments with the apparatus previously described (this vol., 449) show that the ions of a particular gas do not all possess the same mobility. R. CUTHILL.

Ionometric measurement of *X*-rays incident on unit surface and of *X*-rays absorbed by unit volume. M. DE LAROQUETTE (Compt. rend., 1926, **182**, 771—773).—To obtain precise results with the Salomon ionometer, the incidence of radiation on the walls and support of the ionisation chamber must be prevented by surrounding the instrument with a lead box having an aperture 1 cm.^{2} opposite the chamber. The difference between the readings at two points 1 cm. apart in a given medium represents the radiation absorbed per c.c. R. CUTHILL.

Statistical mechanics of assemblies of ionised atoms and electrons. R. H. FOWLER (Phil. Mag., 1926, [vii], **1**, 845—875).—Mathematical. Previous work on the statistical mechanics of assemblies of isolated systems has been extended to the expression of atomic dissociation in terms of atomic ions and free electrons. The energies of the various atoms in the various stationary states and in their various states of ionisation, together with the weights to be included in these calculations, are specified. Special treatment is made of the partition functions for the stationary states of excited atoms and a variation of the theory of Urey (A., 1924, ii, 434) is given. The general results are discussed in connexion with the views of Planck and others. A. E. MITCHELL.

Isotopic composition and atomic weight of chlorine from meteorites and from minerals of non-marine origin. W. D. HARKINS and S. B. STONE (J. Amer. Chem. Soc., 1926, **48**, 938—949).—A detailed account of previously published work (A., 1925, ii, 1108). The mean atomic weight of meteoric chlorine was found to be 35·458 and that of terrestrial chlorine 35·457. Terrestrial chlorine of non-marine origin has the same atomic weight as that obtained from the sea. The results support Harkins' theory that the relative abundance of isotopes is most largely conditioned by their relative stability. S. K. TWEEDY.

Efficiency of β-ray recoil of radium-*C* from radium-*B*. A. W. BARTON (Phil. Mag., 1926, [vii], **1**, 835—845).—When a specially prepared clean surface of radium-*B* is used, the efficiency of β-ray recoil of radium-*C* from radium-*B* is found to be not more than 6%. When surfaces not absolutely free from contamination were employed, the maximum efficiency obtained was 2%. The low efficiencies obtained are explainable if it be assumed that the velocities of the electrons causing the recoil may be such that more than half of the recoil atoms have not sufficient energy to escape from the surface. It is suggested that the high values of the efficiency obtained by Muszkat (*ibid.*, 1920, [vi], **39**, 690) were due to the contamination of the radium-*B* employed. A. E. MITCHELL.

Period of decay of radium-*B* and radium-*C*. P. BRACELIN (Proc. Camb. Phil. Soc., 1926, **23**, 150—154).—By means of an accurate galvanometer method, measurements have been made of the saturation current produced, between two parallel plates, by a pure sample of radium-*C*, at pressures from 20 to 40 cm. of mercury. These indicate values for the radioactive constant λ of $(3{\cdot}514\pm0{\cdot}007)\times10^{-2}$ min.$^{-1}$, and of the period of half-decay, $P=19{\cdot}72\pm0{\cdot}04$ min. The latter is approximately 1% greater than the commonly accepted value of 19·5 min. The value of λ for radium-*B*, deduced from the decay curve of a source of radium active deposit, prepared without the application of an electric field, appears to be between $2{\cdot}587\times10^{-2}$ min.$^{-1}$ and $2{\cdot}596\times10^{-2}$ min.$^{-1}$, corresponding with half-value periods for radium-*B* of 26·7 and 26·8 min., both of which values have been previously obtained. A table is given showing the percentages of radium-*C* calculated to be present in the active deposit after different periods of time; these are compared with those deduced by Lawson and Hess (Sitzungsber. Akad. Wiss. Wien, 1918, II*a*, **127**, 626). M. S. BURR.

Method for measuring ionising radiations [such as α-particles]. H. GREINACHER (Z. Physik, 1926, **36**, 364—373).—The receiving electrode in the ionisation chamber is connected to the grid of a valve and the change in potential on the electrode is amplified. Further amplification is obtained by means of low-frequency transformers, so that a loud-speaker can be used, or a galvanometer may be substituted. Various forms of ionisation chamber have been tried, as well as varying the length of path of the α-particles, and the effect in air has been compared with that in coal gas. The effect of natural disturbances can be greatly reduced, although not entirely eliminated. As the effect of an α-particle is several hundred times greater than that of a β-particle, it is possible to use the apparatus for analysing the radiation from radioactive sources and the method can be extended to give photographic registration. E. B. LUDLAM.

Collisional β-radiation (δ-rays). P. AUGER (J. Phys. Radium, 1926, [vi], **7**, 65—68).—Electrons set free by ionisation of molecules bombarded by α-particles can acquire sufficient energy to effect ionisation in their turn. Photographs of α-particle trajectories in a hydrogen–water vapour condensation chamber were obtained which showed numerous short branches from the main track, attaining lengths of 1 mm. and 2·9 mm., respectively, when polonium and thorium-*C*′ were used as sources of α-particles. The inclination of the track of the β-particle to the main track decreases as the velocity of the electrons is increased. The maximum range of the β-particles varies directly as the velocity of the α-particle which collides with the liberated electron. For unit length of α-particle trajectory the number of short β-particles emitted at wide angles from the main track is greater than the number of long-ranged β-particles emitted at small inclinations. The name collisional β-radiation fits the phenomenon better than δ-radiation. A method of evaluating the Avogadro number suggests itself from the results. R. A. MORTON.

Determination of the absorption coefficient of the very penetrating radiation. W. KOLHÖRSTER (Z. Physik, 1926, **36**, 147—149).—The

author compares his own results for the absorption coefficient of the highly-penetrating radiation in air and in water with those of Millikan and Missowsky and Tuwim. The mean value of the absorption coefficient of the radiation in water is calculated to be $2{\cdot}2\times10^{-3}$ per cm., corresponding with a wave-length of 2X. (2×10^{-11} cm.) and a potential of 6×10^{-6} volts. E. B. LUDLAM.

Potassium and the heat of the earth. A. HOLMES and R. W. LAWSON (Nature, 1926, **117**, 620—621).—The average velocity of the β-rays emitted by potassium is computed to be 0·85 *c*, in agreement with Hahn's value, 0·90 *c*; the velocity of β-rays from rubidium is taken as 0·60 *c*, the corresponding kinetic energies being $7{\cdot}30\times10^{-7}$ and $2{\cdot}04\times10^{-7}$ erg, respectively. Corrected values for the half-periods are 15×10^{11} and 10^{11} years, respectively. Rubidium is negligible geologically, but the heat generated by potassium in cal. per g. of average rock per year is $3{\cdot}22\times10^{-6}$, corresponding values for uranium and thorium being $4{\cdot}74\times10^{-6}$ and $3{\cdot}45\times10^{-6}$, respectively. The value $22{\cdot}5\times10^{6}$ years emerges for the time required for the accumulation of 270 cal./c.c. of basaltic material. A. A. ELDRIDGE.

Balance in radiophysiological equilibria shifted by *l*-adrenaline towards the α-side and by *d*-adrenaline towards the β-side. H. ZWAARDEMAKER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 93—94).—Potassium, which has a β-ray activity, is the origin of the microradioactivity of animal tissues necessary for certain functions, but it may be replaced by other radioactive elements in radio-equivalent quantities. The α- and β-activities of these, however, are antagonistic in a biological system, and a radiophysiological equilibrium may thus be established equivalent to the complete absence of radioactive elements if both types are present. This equilibrium may be disturbed by modifying the sensitivity of the organ to one or other of the two radiations. Thus natural *l*-adrenaline sensitises to the α-radiation, equilibrium again being restored by the addition of an excess of a β-ray compound. Experiments have been made with synthetic *d*-adrenaline, and this has been found to increase sensitivity towards β-radiations so that the addition of an α-ray element is necessary to restore equilibrium. This appears to be the first instance of a qualitative difference in the behaviour of *d*- and *l*-adrenaline. M. S. BURR.

Transmutation of elements. A. SMITS (Nature, 1926, **117**, 620).—There is no spectroscopic evidence of the formation of hydrogen or helium even when a quartz lead lamp is run at 60 amp., although the lamp shows different properties in burning and sparking. A. A. ELDRIDGE.

Mathematical-statistical investigation of the sub-electron. II. H. DAECKE (Z. Physik, 1926, **36**, 143—146; cf. A., 1925, ii, 258, 349).—The experimental values for the unit charge, $4{\cdot}77\times10^{-10}$ e.s.u., vary among themselves by as much as 10%. Five sets of observations were analysed by means of the correlation coefficient. There is apparently some dependence of the value on the radius of the charged particle. E. B. LUDLAM.

Spinning electrons and the structure of spectra. J. C. SLATER (Nature, 1926, **117**, 587).—A conception of electronic structure based on the idea of light quanta appears capable of giving a consistent explanation of the energy of the electron (cf. Goudsmit and Uhlenbeck, Naturwiss., 1925, Nov. 20). It is suggested that the electron's field itself is virtual, and that its energy consists of a quantum, which is permanently attached to it, revolving about it. Consistency with the radiation theory is attained by determining the path of the electronic quantum in the same way as the path of a quantum in a radiation field. A. A. ELDRIDGE.

Spinning electrons. A. S. EDDINGTON (Nature, 1926, **117**, 652).—Since the idea of a spinning electron does not involve any transport of mass or energy with speed faster than that of light, it is not invalidated by the relativity theory. The spinning electron represents a state of the world—distribution of charge-and-current vector—which, whilst differing from that of an electron at rest, is equally static and unchanging. It has already been suggested that the electron contains a space-like, instead of a time-like, charge-and-current vector, J^{μ}. A. A. ELDRIDGE.

[**Spinning electrons.**] O. W. RICHARDSON (Nature, 1926, **117**, 652).—A consideration of Kronig's objections (this vol., 448) to the view that the electrons in the atom possess an inherent magnetic moment. It is suggested that the electron loses its angular momentum in the process of nucleus formation, either by transferring it to the nucleus as a whole, or by radiating it away. The magnitude of the mechanical gyromagnetic anomaly requires the existence of a quantised spin of the nucleus. Further, the statement as to the foundation of the Bohr magneton resting on the orbital motions of electrons which can be treated solely as point charges moving with velocities small compared with that of light is too narrow. A. A. ELDRIDGE.

[**Spinning electrons.**] A. F. LINDEMANN (Nature, 1926, **117**, 652—653).—The idea that protons and electrons are rotating at speeds given by the usual quantum condition has been employed, but not developed, in attempting to explain the stability of nuclei with their excess positive charge. The necessary assumptions cannot, however, be based on any exact calculation without making hypotheses about the internal forces. A. A. ELDRIDGE.

[**Spinning electrons.**] J. FRENKEL (Nature, 1926, **117**, 653—654).—The application of the spinning quantised electron to the problem of the multiplet structure of spectral lines and that of the anomalous Zeeman effect (Uhlenbeck and Goudsmit, this vol., 215) involves a paradox, a solution of which is given, fuller publication being promised elsewhere. A. A. ELDRIDGE.

Thermodynamics and statistics of quantum processes (intensity of spectral lines). W. HEITLER (Z. Physik, 1926, **36**, 101—119).—Radiation

is treated as a chemical substance and the law of mass action is applied. An expression is obtained for the thermodynamic probability of a radiation process and applied to the calculation of the intensity of spectral lines in two series of the alkalis, with satisfactory agreement with experimental data. The summation rule for multiplets can also be deduced.

E. B. LUDLAM.

Half-integral vibrational quantum numbers in the magnesium hydride bands. W. W. WATSON (Nature, 1926, **117**, 692—693).—It is shown that the vibrational quantum numbers in the magnesium hydride band system must be given half-integral values. A. A. ELDRIDGE.

Hydrogen spectrum from the point of view of the new quantum mechanics. W. PAULI, jun. (Z. Physik, 1926, **36**, 336—363).—Mathematical. The new quantum mechanics of matrices originated by Heisenberg leads to the correct results for the terms of the Balmer series and avoids the difficulties encountered by the Bohr treatment in dealing with the effect of crossed electric and magnetic fields on the electron orbits. E. B. LUDLAM.

Quantisation of the perfect monatomic gas. E. FERMI (Atti R. Accad. Lincei, 1926, [vi], **3**, 145—149).—To effect the quantisation of the molecules of a perfect gas, these must be in such conditions that Sommerfeld's law is applicable to their motion. In addition, it appears necessary, for the calculation of systems containing elements indistinguishable among themselves, to assume some complement to Sommerfeld's law. Consideration of other similar systems leads the author to assume that in the perfect gas there can be at most a molecule the movement of which is characterised by certain quantum numbers. This assumption leads to an acceptable theory of the quantisation of the perfect gas, and in particular furnishes a reason for the diminution of the specific heat at low temperatures and gives the exact value for the entropy constant of the perfect gas. T. H. POPE.

Energy gradations in the ideal model of a monatomic gas. E. SCHRÖDINGER (Sitzungsber. Preuss. Akad. Wiss., 1926, 23—36; cf. A., 1925, ii, 951).—Theoretical. By means of the following hypothesis, quantum conditions for the gas as a whole instead of merely for its constituent molecules can be deduced. Since, according to Planck's fundamental assumption (A., 1925, ii, 495), $N!$ states of the gas coincide, the distance between the permissible energy gradations must be constant, and, measured in phase volumes, be equal to $N!\,h^{3N}$, and the lowest stage is assumed to be zero. The magnitude of the molecules and forces between them are not taken into account.

R. CUTHILL.

Change of mass in the two-body problem. G. VON GLEICH (Z. Physik, 1926, **36**, 150—160).—Mathematical. The usual formula for change of mass is not rigorously correct, but only an approximation; it is not the same for a gravitational as for an electric field. It also needs modification to represent correctly the fine structure of spectral lines.

E. B. LUDLAM.

Test of the correspondence principle based on the prediction of the absolute intensities of spectral lines. R. C. TOLMAN and R. M. BADGER (Physical Rev., 1926, [ii], **27**, 383—396).—A fuller account of work already published (see this vol., 451).

Relation between atomic volume and atomic number. C. DEL FRESNO (Z. anorg. Chem., 1926, **152**, 25—34).—With increasing atomic number, the number of principal quantum groups in the atom of an element increases, and a corresponding increase in atomic volume may be expected. The force binding the electrons also increases with increasing atomic number, and this should tend to decrease the atomic volume; thus for elements with equal numbers of principal quantum groups (elements in the same period), the atomic volume should diminish as the atomic number increases. It is deduced that the difference in atomic volume between successive members of a group of the periodic classification will be greater for higher than for lower periods when the difference in atomic number remains constant; when the difference in atomic number changes, the difference in atomic volume will change in the contrary direction. This is found to hold for all 17 groups of Paneth's periodic table (Z. angew. Chem., 1923, **36**, 407), with the exception of the alkaline-earth and nitrogen groups, in which barium and nitrogen have irregular values. Thus in the group lithium, sodium, potassium, rubidium, and cæsium, the differences of atomic number are 8, 8, 18, and 18, and the differences of atomic volume are 11·1, $<22{\cdot}4$, $>10{\cdot}9$, $<14{\cdot}2$, in accordance with the rule. Considering only elements in the principal groups, those in the third group have the lowest atomic volumes in each period.

A. GEAKE.

Periodic system and the alkyl compounds of the elements. A. VON GROSSE (Z. anorg. Chem., 1926, **152**, 133—148).—Collation of published data on the physical properties of the alkyl compounds of the elements shows that well-marked periodic changes take place in passing through the groups of the periodic system. Thus the equivalent volumes of the corresponding compounds fall to minima at group IV, then rise again to group VII; in every group, the equivalent volume increases with the atomic weight and, in aliphatic compounds, with the number of carbon atoms in the organic radical. The b. p. and, as far as data have been published, the m. p. of the compounds rise in each group with an increase in the atomic weight; in the first and second periods, the b. p. falls with an increase in the atomic number, whereas in the other periods it falls from groups I to IV, then rises again to group VII. Comparison of the chemical properties and stability of the alkyl compounds of the elements shows that only those elements the valency electrons of which are confined to one quantum orbit form typical alkyl compounds. This is the case with all elements except those anomalous on Bohr's view. Typical alkyl compounds should therefore be prepared containing the alkaline-earth elements, gold, gallium, indium, and thallium. A. R. POWELL.

Spectroscopy of the extreme ultra-violet. T. LYMAN (J. Franklin Inst., 1926, **201**, 553—562).—A review of recent work.

Ascription of band spectra to chemical substances based on experiments with flames. R. EISENSCHITZ and A. REIS (Z. Physik, 1926, **36**, 414—425).—Experiments were carried out with flames maintained at an approximate temperature by varying the amount of diluting gas, and the flames were separated into their two distinct cones by means of a glass cylinder; excess of oxygen or of a reducing gas could be employed. The flame spectrum of copper consists of two spectra superposed, one due to the oxide, which is strongest in the green region, but contains feeble bands in the red and violet; this is the one which gives the usual colour to the flame containing copper. It is a common error to ascribe the green flame to copper halide; the halogen is only effective in bringing more copper into the flame. Copper chloride, undecomposed in presence of excess of chlorine, appears violet. In a reducing flame, *e.g.*, hydrogen or carbon monoxide from a coal fire, the "metal" spectrum is obtained, consisting of sharp, well-separated bands in the blue and violet. The moment of inertia of the radiator is small and may possibly be due to copper hydride. The red and green bands of calcium are due to an emitter which does not contain oxygen; the iron bands are produced by an oxide. At 1800°, the vapours of calcium oxide and copper oxide are partly dissociated, the oxygen pressure being between 10^{-4} and 10^{-1} atm.

E. B. LUDLAM.

Absorption of light by tungsten and molybdenum atoms in the primary and metastable states. H. B. DORGELO (Z. Physik, 1926, **36**, 467—471).—The absorption tube was an argon discharge tube with tungsten or molybdenum cathode which was vaporised by bombardment with ions. The absorption was photographed by means of a spectrograph and Lummer-Gehrcke plate. Molybdenum showed absorption by the metastable quintuplet S and D terms and tungsten by lines corresponding with combinations of the quintuplet D terms with the septulet S term. E. B. LUDLAM.

Moment of inertia of carbon monoxide. C. SCHAEFER and B. PHILIPPS (Z. Physik, 1926, **36**, 399).—The separation between the single bands of the absorption spectrum at 2·35 μ was found to be 30·55 $\mu\mu$, giving a value of $14{\cdot}8\times10^{-40}$ gm. cm.^{2} for the moment of inertia, verifying the result $14{\cdot}6\times10^{-40}$ obtained by Burmeister from the band at 4·6 μ.

E. B. LUDLAM.

Absorption of ultra-violet rays by aldehydes. S. A. SCHOU (Compt. rend., 1926, **182**, 965—967).—The absorption spectra of formaldehyde, acetaldehyde, propaldehyde, and chloral in aqueous solutions, and of the first three in hexane solutions have been studied. Absorption is strongest in hexane solutions, owing to the production of hydrates in water, the amounts formed, as estimated from the difference in absorption, being 26% and 50% for acetaldehyde and propaldehyde, respectively. These aldehydes show an absorption band at 2800 Å., but extreme ultra-violet absorption is in all cases very feeble if the materials are highly purified. From this absorption, the amount of enolic form in a fresh, neutral aqueous solution is estimated at less than 1/15,000, but is greatly increased by the presence of a trace of alkali.

J. GRANT.

Absorption of light by simple carboxylic acids in the ultra-violet. H. LEY and H. HÜNECKE (Ber., 1926, **59**, [*B*], 510—524).—In connexion with earlier experiments on the optical behaviour of amino-acids (A., 1924, i, 1341), the relationships of the absorption curves of simple carboxylic acids, their esters, and salts have been examined, together with the effect of physical conditions (nature of solvent, temperature, etc.) on the absorption. With methyl acetate, absorption is least in water and greatest in hexane, whereas alcohol occupies an intermediate position. With ethyl acetate, similar observations are recorded, whilst with ethyl mono-, di-, and tri-chloroacetate the influence of solvent becomes progressively less marked. Ethyl glycollate is most transparent in water, least in alcohol, so that the optical effect of the solvent is strikingly influenced by the constitution of the ester. The cause of the action of the solvent is probably the formation of solvates by the union of water, alcohol, etc. which possess strong residual affinities with the strongly unsaturated carbonyl groups. In hexane, which is practically saturated, the ester exists in almost the same manner as in the vaporous state. When solvents are arranged according to their influence on the absorption of acids (acetic, chloro-, and trichloroacetic, and glycollic) the sequence is not the same as that observed with the esters. Direct comparison of the results is rendered difficult, since, in consequence of presence or absence of association, the carboxylic acids are not present in the different media in a comparable state. Further, solvate formation is probably not an identical process with acids and their esters, since with the former the hydroxyl group is involved, whereas this is not true to the same extent with the alkoxyl group. The absorption of simple carboxylic acids is displaced towards the region of shorter wave-length by salt formation with strong bases; between aqueous and alcoholic solution, the difference is slight in the sense that the aqueous solution is less absorbent.

The optical observations do not give any indication of the existence in solution of an equilibrium between two undissociated forms of the carboxylic acids. Whereas in many cases the absorption curves with increasing transparency fall in the sequence ester, acid, salt, indicating thus an equilibrium between true acid (with absorption of a salt) and pseudo-acid (with ester-like absorption), this sequence is not observed with the methyl and ethyl trichloroacetates, whilst the curves for methyl acetate and acetic acid in aqueous solution intersect. Whilst it is quite possible that neutralisation of a carboxylic acid is accompanied by deep-seated change in the molecule, the observed effect of salt formation on the spectrum is of the same order as that produced by a change of medium.

With methyl phenylacetate a broad band is

observed in alcoholic solution which is also present in aqueous solution, but becomes resolved into narrow bands in hexane. Comparison of the effect of the solvent on the spectra of methyl acetate and methyl phenylacetate leads to the resolution of the spectrum of the latter into two components, one of which is attributable to the PhC: group, the other to the carbonyl group. With phenylacetic acid and its salts, the two regions of absorption are still apparent, and these are influenced in quite dissimilar manners by change of solvent. H. WREN.

Absorption spectra of various derivatives of salicylic acid. J. E. PURVIS (J.C.S., 1926, 775—778).—In a continuation of previous work (this vol., 108) the absorption spectra of lithium, calcium, zinc, copper, and uranyl salicylates, lithium *o*-acetoxybenzoate, 3-nitrosalicylic, 3 : 5-dinitrosalicylic, 5-sulphosalicylic, 5-aminosulphosalicylic, and 5-nitrosulphosalicylic acids, sodium 3-nitro-5-aminosalicylate, hexamethylenetetramine salicylate, and hexamethylenetetramine have been examined. Consideration of the results obtained with salicylic acid and its various coloured and colourless salts leads to the conclusion that the specific absorption depends on the nature of the acidic and basic radicals, changes in the nature of one or the other producing alterations in the position and the intensity of the bands characteristic of each. The author has already shown (A., 1924, ii, 6) that the absorption bands of didymium in the visible region undergo changes in intensity with changes in the nature of the associated negative radical. Introduction of a nitro-group into the nucleus intensifies and shifts the less refrangible band of the acid, but lessens that of the more refrangible band. These results are not unlike those observed (A., 1915, ii, 607) with some nitro-compounds of benzoic and cinnamic acids. Replacement of the hydrogen atom of the hydroxyl group in lithium salicylate produces a change similar to that in salicylic and *o*-acetoxybenzoic acids and in the corresponding salts of theobromine etc. J. S. CARTER.

Relative positions of the absorption bands of a pigment dissolved in various colourless solvents. A. SZILÁRD (Biochem. Z., 1926, **170**, 185—200).—The pigment chosen for this work was the dimethyl ester of hæmatoporphyrin. The rule of Kundt was generally confirmed, that with increasing molecular refractive power of the solvent the adsorption bands of the pigment are displaced towards the red end of the spectrum. In the series of normal alcohols, this displacement was greater for the bands of longer than for those of shorter wave-length. The same obtained in less degree for the homologous series of ethyl esters of the fatty acids. In the case of a normal alcohol and an ethyl ester of the same number of carbon atoms (having similar molecular refractive power), the bands at the red end were displaced in an opposite sense to those at the violet end of the spectrum. The same differences were found in a series of isomeric alcohols. The extent of the differences between the positions of the bands in the case of a pair of isomeric alcohols or ethers depended on the extent of the structural differences between the isomerides. Substances of the same molecular refractive power which are not isomeric may show wide differences in the positions of the absorption bands. The rule of Kundt is less marked in the benzene series than in that of the normal alcohols. R. K. CANNAN.

Absorption spectra of condensed nuclear hydrocarbons. N. S. CAPPER and J. K. MARSH (J.C.S., 1926, 724—730; cf. A., 1925, ii, 470, 625).—Complete elimination of anthracene from phenanthrene and fluorene is possible only by light treatment, with consequent formation of dianthracene. The two substances were purified by refluxing concentrated xylene solutions by the heat from a silica mercury vapour lamp, the sparingly soluble dianthracene being readily separated. Repeated light treatments and separations are necessary. The pure substances are not fluorescent and give absorption curves which differ from those of previously examined impure specimens. The absorption spectra of anthracene, 9-phenylanthracene, 1 : 2-benzanthracene, chrysogen, octahydroanthracene, and bisdiphenylene-ethylene have also been examined. The chief feature of the spectra of simple polynuclear hydrocarbons is a series of rather narrow bands between 3000 and 4000, which show a constant frequency difference of about 140 waves/mm. This frequency is the same as that of the most prominent band in the infra-red spectrum of most hydrocarbons. There is some doubt as to whether this common frequency difference is due to CH: or C:C, and it is suggested that it is a frequency to which both can resonate. Fluorene gives a spectrum similar to that of *o*-xylene or other simple substituted benzene derivative. Bisdiphenylene-ethylene shows only a broad band in the blue region, an undeveloped one at about 3600 and another at about 4100. The spectrum of stilbene consists of a single broad band at about 3300; in phenanthrene, the double linking becomes aromatic and six narrow bands occupy the same region. The effect of an ethenoid linking is thus to cause a fusion of the bands characteristic of benzene nuclei. The hydrocarbon believed by Homer and Purvis (J.C.S., 1910, **97**, 1155) to be 1 : 2 : 7 : 8-dibenzanthracene, has an absorption curve very similar to those of stilbene and bisdiphenylene-ethylene, and it is hence considered unlikely that the substance in question has the structure assigned to it by these authors. J. S. CARTER.

Extinction of the resonance fluorescence of sodium vapour. R. MANNKOPFF (Z. Physik, 1926, **36**, 315—324).—The reduction in the intensity of the secondary radiation excited by fluorescent radiation produced in sodium vapour was measured by comparison with the exciting light which had been reduced in intensity by means of two Nicol prisms. The effect of the presence of a mixture of neon and helium, of nitrogen, and of hydrogen was determined and the number of effective collisions calculated. The value for the radius of the excited sodium atom was found to be 1·7 times that calculated by Thomas (A., 1924, ii, 433) for the radius of the orbit of the electron. E. B. LUDLAM.

Prolonged fluorescence of solid and dissolved uranium salts. F. PERRIN (Compt. rend., 1926, **182**, 929—931).—When uranyl salts are crystallised in violet light, they exhibit a green luminosity of sufficient persistence to be observed in a phosphoroscope, but the same phenomenon cannot be detected thus in solutions of these salts. Hitherto, this has been regarded as due to the direct action of the solid state on the nature and persistence of the luminescence, and as a brief phosphorescence in the case of solids and a fluorescence in solution. It is now argued that fluorescence and phosphorescence should not be distinguished by the greater or lesser persistence of emission, but by the action of change of temperature and of infra-red radiation, and that the luminosity of uranyl salts should be regarded as a true fluorescence.

Of solutions of uranyl salts, that of the sulphate in water containing an excess of sulphuric acid shows the greatest fluorescence. The fluorescence of the sulphate is considerably greater when dissolved in pure sulphuric acid, being only one fourth or one fifth that of the solid salt. The average life of the luminosity is about 5×10^{-4} sec. The luminosity is regarded as a "prolonged fluorescence" analogous to the brief fluorescence of dyes such as fluorescein, of which the persistence of luminosity is of a much smaller magnitude. Fluorescence of the uranyl salts is considerably reduced by the addition of various substances such as halide salts, organic acids, etc. Mere traces of hydrochloric acid or of alcohol greatly diminish the fluorescence of the sulphate when dissolved in sulphuric acid. C. J. STILL.

Yield of energy in fluorescence radiation from fluorescein solution by excitation contrary to Stokes' law. S. VALENTINER and M. RÖSSIGER (Z. Physik, 1926, **36**, 81—91).—The band exciting the fluorescence overlaps the band so produced, and if fluorescein is illuminated by light in this overlapping region, some fluorescent radiation is produced which is of shorter wave-length than the exciting light, contrary to Stokes' law. The relation between the energy of monochromatic incident light in this region to that of the fluorescent light has been investigated, and the yield is found to diminish as the wave-length of the exciting light increases. The violation of Stokes' law is explained as due to absorption of successive quanta, and the reduced yield with increasing wave-length is explained on the supposition that a smaller proportion of the quanta absorbed is effective in producing fluorescence.

E. B. LUDLAM.

Coloured derivatives of tetraphenylmethane. VIII. Relation of fluorescence and of solution-colour of the aminocarbazones in different colourless solvents to other optical properties of the latter. F. KEHRMANN, H. GOLDSTEIN, and F. BRUNNER (Helv. Chim. Acta, 1926, **9**, 222—226; cf. A., 1904, ii, 528, 797; 1917, i, 591).—Spectroscopic examination of solutions of 7-amino-5 : 5-diphenyl-3-carbazone and of 7 : 9(or 1 : 9)-diamino-5 : 5-diphenyl-3-carbazone (A., 1925, i, 430) in benzene, chloroform, carbon disulphide, ether, acetone, pyridine, methyl alcohol, and ethyl alcohol shows a progressive displacement of the head of the main absorption band from the blue to the red end of the spectrum. Displacement towards the red follows, in general, decreasing molecular refractivity of the solvent. The molecular dispersion value shows no general relation to the displacement. Solvents with a high dielectric constant shift the band towards the red; a low dielectric constant is associated with displacement towards the blue. The general character of the absorption bands is unaltered. The displacement is more marked in the case of the monoaminocarbazone. M. CLARK.

Chemiluminescence. H. KAUTSKY (Trans. Faraday Soc., 1926, **21**, 591—594, and Z. physikal. Chem., 1926, **120**, 230—233).—See A., 1925, ii, 1026.

Phosphorescent sulphides of zinc. A. A. GUNTZ (Ann. Chim., 1926, [x], **5**, 157—198; cf. Tomaschek, A., 1921, ii, 588).—The phosphorescence of zinc sulphide when pure has been shown to be slight and is enhanced by the addition of minute traces of copper or of manganese. The effect of other metals is due to the copper they contain as impurity, the presence of 10^{-5} part of copper being sufficient to give a brilliant phosphorescence. Zinc blende has a more intense and yellow fluorescence, but less phosphorescence than wurtzite. Salts of the alkali and alkaline-earth metals also exert a stimulating effect, but differ from metals in that excess of the salt does not inhibit the phosphorescence. A pressure of 6000 kg./cm.^{2} destroys the phosphorescence, which is recovered on heating to a temperature sufficiently high to allow of the formation of the necessary crystal network. The addition of cadmium sulphide dilutes the zinc sulphide and changes the colour of the phosphorescence towards the red, whilst the addition of zinc oxide changes it towards the violet region of the spectrum. The following mixture, finally heated at 1080° for half an hour to form wurtzite, gives good results: 7×10^{-5} part of copper, $2—3\times10^{-2}$ part of sodium chloride, sodium sulphate, and barium chloride to 1 part of zinc sulphide.

F. G. SOPER.

Refractivity, ionisation potentials, and absorption spectra. R. A. MORTON and R. W. RIDING (Phil. Mag., 1926, [vii], **1**, 726—731).—A discussion of the physical significance of the frequency term ν_0 in the dispersion formula of Sellmeier, and of the attempts of Herzfeld and Wolf (A., 1925, ii, 182) and of Davis (*ibid.*, 933) to express the dispersion by a formula involving two or more frequency terms. It is concluded that no satisfactory two-term formula can be obtained until the existing data for absorption spectra are extended further into the vacuum region. It is suggested that the formula proposed by Baly and Morton (A., 1924, ii, 714) employing the frequency of an accurately measured absorption band in the near ultra-violet and leading to a frequency in the extreme ultra-violet which is closer to the value calculated from the ionisation potential than that obtained from the Sellmeier formula, reproduces the known data most accurately. A. E. MITCHELL.

Variation of the dielectric constant of liquid and solid hydrogen with temperature. W. WERNER and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 34—43).—By a modification of Wolfke and Onnes' method (A., 1925, ii, 630) determinations of the dielectric constant of liquid and solid hydrogen have been made. At b. p. 20·36° Abs., $\varepsilon=1{\cdot}2311$, with a probable error of about 0·02%. This is larger than the values obtained by other investigators, but is in agreement with the value calculated from optical data. Near the m. p., $\varepsilon=1{\cdot}2553$, and its variation with temperature is approximately linear. The dielectric constant of solid hydrogen near the m. p. is 1·206—1·209 and decreases with temperature. M. S. BURR.

Changes in volume in the formation of inorganic compounds. E. MOLES (Anal. Fis. Quím., 1925, **23**, 524—539).—Chlorides may be divided into three classes, according as the molecular volume is (i) less than, (ii) greater than, or (iii) equal to the sum of the atomic volumes of the constituent atoms. In the first group, which corresponds with elements occupying positions in the periodic table one or two places after the inert gases, the heat of formation per atom of chlorine is greater than 50 cal. In the second group, corresponding with elements occupying positions in the periodic table from one to five places before the inert gases, the heat of formation per atom of chloride is less than 50 cal. In the first and second groups, the contraction or dilatation increases with the atomic weight. Similar regularities are observable in the permanganates. In the cobaltammines, ammonia, water, and chlorine obey the additive law, and the same is true of the carbonyl group in the metallic carbonyls. G. W. ROBINSON.

Volume contraction in the formation of aliphatic compounds at the absolute zero. W. HERZ (Z. anorg. Chem., 1926, **152**, 99—100).—The molecular volume of aliphatic compounds at the absolute zero, calculated from their densities (A., 1919, ii, 391; this vol., 117), is always less than the sum of the atomic volumes of the constituent atoms calculated from carbon 5·31 (Z. anorg. Chem., 1918, **104**, 134), oxygen 10·20, and hydrogen 9·60 (A., 1919, ii, 220). For a number of aliphatic hydrocarbons, alcohols, acids, and esters, the contraction, expressed as a percentage of the molecular volume, tends to constancy, varying from 52·5% to 81·8%. A. GEAKE.

Scattering of light in gaseous and liquid chlorine. W. H. MARTIN and A. F. W. COLE (Trans. Amer. Electrochem. Soc., 1926, **49**, 349—354).—The ratio of the intensity of the light scattered by gaseous chlorine at 20·5° and 140 cm. to the intensity of the light scattered by ether vapour at 25° and 36·6 cm. is found to be 0·99, in good agreement with the value calculated by means of the Rayleigh formula. For the two liquids at 20° and under their own vapour pressures, the value is 1·77, whereas Einstein's formula requires 1·13. The depolarisation factor, *i.e.*, the ratio of the intensity of the weak image to that of the strong image when the light scattered at right angles to the direction of the exciting beam is observed through a double-image polarising prism, is 0·041 for liquid chlorine and 0·24 for gaseous chlorine. R. CUTHILL.

Depolarisation of diffused light by organic substances. J. CABANNES and J. GRANIER (Compt. rend., 1926, **182**, 885—888).—The factor of depolarisation of scattered light, ρ, was determined with an accuracy of 5% for a series of organic substances in both the liquid and gaseous states (cf. A., 1925, ii, 1030). The light was previously filtered through quinine. The depolarisation limit, ρ_0 (cf. *ibid.*), varies only very slightly on passing from gaseous methane to hexane, the mean value 0·016 being found. Ganesan found 0·030 for the series pentane to octane (*ibid.*, 643), but the previous value, confirmed for hexane, is considered to hold up to octane. The value 0·042 was obtained for benzene. The values of ρ_0 increase when the filter is not used, because of the fluorescence excited by radiations of wavelengths of 3600—4000 Å. In the case of *cyclo*pentene and thiophen, ρ could be determined only for red light. S. K. TWEEDY.

Rotatory power and p_H values of molybdomalic acid complexes. Physico-chemical applications of polarimetry. E. DARMOIS (Bull. Soc. chim., 1926, [iv], **39**, 621—643).—The neutralisation of dimolybdomalic acid by organic and inorganic bases is investigated by the methods previously described (cf. Honnelaitre, A., 1925, i, 509). Neutralisation proceeds exactly as with sodium hydroxide. The crystalline lithium ($n=12$), ammonium ($n=5$), potassium ($n=5$), barium ($n=12$), calcium ($n=18$), methylamine, diethylamine, aniline ($n=1$), and *p*-toluidine *salts* were isolated (n is the number of molecules of water of crystallisation determined by cryoscopy in sodium sulphate decahydrate; cf. A., 1923, ii, 831); the copper and nickel *salts* were not obtained crystalline. The rotatory power of these salts in solution varies with concentration, slowly at high, and rapidly at low, concentrations; the molecular rotation is approximately the same for all salts at corresponding concentrations, especially when the latter are high, in conformation with Oudemans' law. This is due to the presence of the common ion $(4MoO_3,2C_4H_4O_5)''''$. The same holds for the rotatory dispersions. A partial hydrolysis of the complex occurs, which explains these results. The action of acids, salts, and esters on solutions of the salts of maximum stability (determined by p_H measurements) was investigated. The action of acids varies according to their tendency of forming complexes with molybdic acid. By means of rotatory dispersion measurements, the relative strengths of acids which do not form such complexes may be determined approximately. The results obtained may be explained by the reactions: $[4MoO_3,2C_4H_4O_5]Am_4+4HX \rightleftharpoons 4AmX+[4MoO_3,2C_4H_4O_5]H_4 \rightleftharpoons 3MoO_3+MoO_3,2C_4H_6O_5$. The method is applied to the determination of sulphuric acid in vinegar.
S. K. TWEEDY.

Rotatory dispersion of camphor. L. LONGCHAMBON (Compt. rend., 1926, **182**, 769—771).—A criticism of the work of Lucas (this vol., 337), chiefly on the grounds of misuse of Lowry and Cutter's

formula for the rotatory power of camphor dissolved in acetone (A., 1925, ii, 356). R. CUTHILL.

Anomalous dispersion and absorption of electric waves. S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 47—53).—The dielectric constants and absorptions for electromagnetic waves of 6·1 metres are recorded for some aliphatic alcohols and for acetone over the temperature range 60° to −90°. Whereas acetone behaves normally, the alcohols show anomalous absorption of the waves accompanied by anomalous dispersion of the electromagnetic oscillations. This is attributed to the presence of the hydroxyl group. S. K. TWEEDY.

Relation between the closing of electronic groups in the atom and the chemical valency. H. G. GRIMM and A. SOMMERFELD (Z. Physik, 1926, **36**, 36—59).—The Stoner–Main Smith classification of subgroups in the atom is known (Sommerfeld, Physikal. Z., 1925, **26**, 70) to be supported by the optical as well as the *X*-ray spectra; further evidence of this is adduced; for the designation of the terms the system of Russell and Saunders is preferred. The closing (completion) of a sub-group is shown by the third quantum number j being zero for the fundamental term. The spectra of nickel and platinum differ remarkably from that of palladium, indicating a less stable arrangement in the two former. Hence in the atomic core of Ag^+ the 18-group must be more stable ($j=0$) than in Ni^+ and Au^+; this conclusion is supported by the spectra (which with copper and gold, but not silver, show many unclassified lines) and also by the higher valencies of the two former.

The relative stability and completeness of the Stoner sub-groups, and the number of electrons they contain, are:

$$\underset{2}{n_{11}} : \underbrace{n_{21}, n_{22}}_{6} : \underbrace{n_{32}, n_{33}}_{10}$$

the relative stability depending mainly, as it does in the Bohr system, on the second quantum number, but the number of electrons being 2, 6, 10, instead of 6, 6, 6. The 8-shell (n_{11}, n_{21}, n_{22}) has the greatest stability; the 2-shell (n_{11}) is very stable in helium, and considerably stable in the heavier elements; the 4-shell (n_{11}, n_{21}) has a stability of a different kind, leading to the formation of non-polar compounds. These conclusions are supported by chemical as well as spectral evidence.

The physical meaning of valency is clear in the simple ions; in the non-polar compounds, and especially in the oxides in which the highest valency is shown, it may be taken to mean the number of the outer electrons of an atom engaged in attaching the other atoms. A table shows that the valencies of the typical and the B elements are as a rule either those of the periodic group, or two (rarely four) less. This is particularly marked in group IV and in the three elements following mercury. This indicates the completeness of a helium shell of 2 electrons, especially when next to an 18-shell.

The stability of a 4-shell ($2\times n_{11}+2\times n_{21}$), although not indicated by isolated atoms, is proved by examining the crystal structures of compounds of the type AB, where A and B have 8 valency electrons between them. Their lattices are of two types: (*a*) ionic, close-packed (NaCl and CsCl type with 6 or 8 atoms surrounding one), (*b*) non-polar, with 4 atoms round one (diamond and wurtzite lattices). In the 4th group, carbon, silicon, germanium, tin (lead doubtful) are all (*b*), whilst the elements of the A sub-group (titanium, zirconium, cerium, hafnium, thorium), none of which has this 4-shell, are all, like many other metals, close-packed. The same holds for their compounds: CSi occurs as diamond and wurtzite lattice, whilst TiC and ZrC are of the NaCl type. Of compounds of 3rd and 5th group elements, AlN and AlSb are (*b*), whilst ScN is (*a*); of those of the 2nd and 6th groups, BeO, ZnO, ZnS, ZnSe, CdS, and HgS are (*b*), and CdO and the oxides and sulphides of magnesium, calcium, strontium, and barium are (*a*); of those of the 1st and 7th groups, all the alkali halides and all the silver halides except the iodide are (*a*), but AgI, CuCl, CuBr, and CuI are of the diamond type. It may be assumed that each "tetrahedrally bound" atom (*i.e.* in the diamond and wurtzite lattices) is related not only to its 4 neighbouring atoms, but also to 8 electrons. Thus in BeO the oxygen must lend electrons to the beryllium, although definite charges cannot be assigned as in $Be^{--}O^{++}$, until it is known how long each electron remains in each atom. Ott and others have shown that the intensities of the *X*-ray reflexions are compatible with this, and definitely against such a formula as $Be^{++}O^{--}$. The change from the ionic to the non-polar lattice accords with the view of Fajans and Joos (Z. Physik, 1923, **23**, 1; A., 1923, ii, 750; Z. Krist., 1925, **61**, 18) that such change is due to a deformation of the electronic orbits of the anion by the cation, which is greater the larger the charge, the smaller the cation, and the larger the anion. Hence the tendency to ionisation falls as the centre of the periodic table is approached; it is greater when the cation belongs to an A subgroup; and in any one group it increases as the atomic number of the cation rises (MgO and AgCl are ionic, not BeO or CuCl), and as that of the anion falls (all the silver halides are ionic except the iodide).

The disappearance of this tetrahedral lattice with its "giant" molecules as soon as the average number of valency electrons exceeds 4 (as in N_2, O_2, F_2, C_2N_2, NO) is due to the appearance in these compounds of the n_{22} orbits. The energy of transformation of the ionised into the non-polar form can be calculated on Born's principles, making a probable assumption as to the lattice energy of the solid.

Thus $Cl^+Cl^-=Cl\text{–}Cl+ca.$ 100 Cal.
$I^+Cl^-=I\text{–}Cl+30$ Cal.

A similar cyclic process is developed to determine whether the tetrahedral structure is more stable than the polar; but the data for its application are lacking.

N. V. SIDGWICK.

Valency theory. H. BURGARTH (Z. Elektrochem., 1926, **32**, 157—162).—An attempt is made to account for the valencies of the first two groups of eight elements of the periodic classification by assuming that each atom has eight non-electrical valencies, four of which are of *A* type and four of *B* type, such that *A*- and *B*-valencies are oppositely directed and

may neutralise each other. When less than eight electrons are present in the outer atomic shell, the normal valency shown by the non-ionised atom is due to free, or unneutralised *A*-valencies. Further, when an atom gains or loses electrons, the valency is then partly of "ionogen" type and partly of free *A* type. Thus, for lithium and sodium, one *B*-valency is assumed to be bound to the outer shell of the neutral atoms; this leaves three *B*-valencies and four *A*-valencies free in each case, *i.e.*, one free *A*-valency after neutralisation. Similarly, beryllium, boron, and carbon have two, three, and four free *A*-valencies in excess. For nitrogen and phosphorus, one *A*-valency is bound as well as four *B*-valencies, so that here three free *A*-valencies are left over, whilst oxygen and fluorine have, respectively, two and one free *A*-valencies. The free *A*-valencies thus agree with the normal valency series.

When sodium becomes an ion by the loss of an electron, it loses a free *A*-valency, but gains a positive ionogen valency, so that its valency number is not changed in the process; magnesium, aluminium, and carbon behave similarly by the loss of one or more electrons. The theory is developed and applied to other elements. The results are set out in the form of a table, which shows the leading valencies exhibited by the elements, as well as of the corresponding ions formed by loss or gain of electrons.

The theory is also applied to the structural formulæ of benzene, of compounds of bivalent carbon, and of the acids and oxy-acids of chlorine, sulphur, and phosphorus, and to other cases. C. H. D. CLARK.

Constitution of nickel carbonyl and the nature of secondary valency. A. A. BLANCHARD and W. L. GILLILAND (J. Amer. Chem. Soc., 1926, **48**, 872—882).—Certain non-metals, and probably non-metals in general, react with nickel carbonyl as though they combine with the nickel alone, the carbonyl groups escaping as carbon monoxide. Thus bromine and nickel carbonyl react in the gaseous state, or in solution, rapidly and quantitatively, thus: $Ni(CO)_4+Br_2=NiBr_2+4CO$. With sulphur, the main reaction is $2Ni(CO)_4+3S=Ni_2S_3+8CO$, and proceeds very slowly (cf. Dewar and Jones, J.C.S., 1904, **85**, 203). The oxidation product formed when nickel carbonyl or its solutions are kept in air consists of a basic carbonate together with small amounts of formate (cf. Thorne, A., 1924, ii, 766). The carbonate, however, is apparently derived from the carbon dioxide in the air, since in the presence of oxygen and water only, nickel oxide and carbon monoxide alone are formed, exactly analogous to the above cases. A small quantity of the carbon monoxide reacts with the water to form formic acid. Either constituent of nickel carbonyl can react alone with substances, leaving the other constituent uncombined (cf. this vol., 603) so that only secondary valency is exerted.

A structure for the extremely volatile carbonyls is proposed, based on the Lewis–Langmuir theory, in which the metal atom is sheathed with eighteen electrons, the eight lateral pairs of which are shared with the carbonyl groups. The octets of the latter are completed, when necessary, by their corners swinging together to share a pair of electrons. The formation of nickel carbonyl is due to the rearrangement of electrons into layers which give greater stability; the layers involved in primary valency usually become octets, and those involved in secondary valency are often larger than octets. This distinction is not sufficiently universal, however, to serve as a means of classification. S. K. TWEEDY.

Electron affinity of the halogens. E. B. LUDLAM (Trans. Faraday Soc., 1926, **21**, 610—611, and Z. physikal. Chem., 1926, **120**, 256—260).—See A., 1925, ii, 1018.

Distribution of size of particles in disperse systems. A. GYEMANT (Z. Physik, 1926, **36**, 457—466).—A formula is obtained for the size of particles based on the assumptions that stable systems result from the aggregation of smaller particles. This aggregation is the result of collisions and reaches a limit which is determined by the boundary potential, the electric charge, and the degree of hydration. E. B. LUDLAM.

Eka-cæsium and a suggestion about radiation and the elements. F. H. LORING (Nature, 1926, **117**, 448—449).—Re-measurement of the *X*-ray line previously given as $1\cdot032\pm0\cdot005$ yields the value 1·029 Å.; since films tend to shrink on development, it is believed that this is the $L\alpha_1$ line of eka-cæsium (87), and not the $L\beta_1$ mercury line, 1·0458 Å. Elements of low atomic number may be regarded as having absorbed corpuscular radiation; possibly even there may be an intermediate state in which some elements spontaneously absorb "radiation" and emit it radioactively. Such considerations may account for the radioactivity of potassium and rubidium, since there is no evidence that these elements are contaminated with elements 85 and 87, or that the latter are radioactive. Examination of manganese phosphate yielded copper lines and two faint lines 1·433 and 1·233 Å., presumably the $L\alpha_1$ and $L\beta_1$ lines of element 75. Whether or not these lines are the combined $K\alpha_1$ and $K\alpha_2$ lines of zinc and the $L\alpha_1$ line of mercury, the method may be applied to detect traces of element 87 in potassium and rubidium. A. A. ELDRIDGE.

Forces of chemical affinity. Crystal structure in the light of the new atomic models. A. C. CREHORE (Phil. Mag., 1926, [vii], **1**, 786—827).—The atomic models suggested by the author (A., 1922, ii, 438) and the expressions obtained for the electrostatic force acting on a first electron due to a second in any position (Phil. Mag., 1925, [vi], **49**, 839) have been employed in an examination of the grouping of atoms in a space lattice. It is shown that solid hydrogen cannot form either a simple cubic or a face-centred cubic lattice, and it is suggested that no element in the crystalline state can form a simple cubic lattice. It is shown also that carbon cannot crystallise in any lattice which has a centre of symmetry. It is concluded also that hydrogen cannot form a similar lattice to diamond. The author's models give a very close approximation to the diamond lattice for carbon. It is suggested that crystalline hydrogen may be a cubic lattice of about $4\cdot36\times10^{-8}$ cm. on an edge, at

the corners of which are groups of four hydrogen atoms in the form of a regular tetrahedron of about $0{\cdot}58\times10^{-8}$ cm. on an edge. A. E. MITCHELL.

Chemical effects with crystals. VIII. Etching and solution phenomena with borax. F. RINNE and R. GRÄFE (Ber. Sächs. Ges. Wiss. Math. Phys. Kl., 1925, **76**, 275—293; from Chem. Zentr., 1925, II, 2124; cf. A., 1924, ii, 257, 265).—Etching studies with crystals of borax in water at 17—18° demonstrated their monoclinic holohedral symmetry. The same result was obtained in growth and solution experiments using spheres and cubes. G. W. ROBINSON.

Rubidium (cæsium)-silver-gold halides. J. VOGEL (Monatsh., 1926, **46**, 265—271).—The results of Wells (A., 1923, ii, 32) are confirmed. Rubidium and cæsium show no tendency to replace one another in these triple halides. On account of the great difference in solubility and crystal form of the rubidium and cæsium triple chlorides, a method is given for the separation of these elements which is spectroscopically complete. W. THOMAS.

Isomorphous relationship of cuprous and silver halides. E. REICHEL (Monatsh., 1926, **46**, 355—382).—Cuprous and silver chloride and bromide do not possess the same crystal structure. The miscibility of the chlorides even at higher temperatures is limited. Silver halide recrystallised from a solution containing cuprous halide shows no traces of cuprous salts; cuprous salts, on the other hand, contain traces of silver salts. The iodides are largely, if not totally, miscible. This seems to be due to their identical lattice structure. Two types of mixed crystals are obtained from a hydriodic acid solution: the γ-mixed crystals, which consist of a mixture of α-silver iodide and γ-cuprous iodide, and also the β-mixed crystals, which apparently consist of an isomorphous mixture of β-silver iodide and β-cuprous iodide. Mixed crystals rich in cuprous iodide show a marked photo-luminescence in ultra-violet light. W. THOMAS.

Rubidium (cæsium)-silver-gold halides. F. EMICH (Monatsh., 1926, **46**, 261—263).—A summary (cf. preceding abstracts). W. THOMAS.

Crystal lattice pores. J. KOENIGSBERGER (Physikal. Z., 1926, **27**, 215—217).—Consideration of the physical properties of a number of crystalline substances leads to the view that these are not entirely homogeneous. It is probable that "pores" or cavities and sub-microscopic particles of solid impurity are arranged in an orderly manner in the space lattice. J. S. CARTER.

***X*-Ray diagrams of mixed crystals.** G. FRIEDEL (Compt. rend., 1926, **182**, 741—744).—Theoretical. It is shown that the direction of the diffraction maxima in the above can be accounted for without assuming that the lattice of a mixed crystal has a constant parameter equal to the mean of those of the constituent crystals; indeed, such an assumption is theoretically unsound. Similar considerations apply to twin-crystals such as quartz. R. CUTHILL.

Crystalline and amorphous states in the alkali metals. C. C. BIDWELL (Physical Rev., 1926, [ii], **27**, 381—382).—Fading of the *X*-ray diffraction patterns indicates that when lithium is heated from 20° to 110°, incomplete disintegration of the crystal lattice takes place. A. A. ELDRIDGE.

Crystal structure of carborundum. I. Modification II. II. Modification I. III. Modification III. H. OTT (Z. Krist., 1925, **61**, 515—531; **62**, 201—217; **63**, 1—18).—I. The polymorph known as II is the commonly occurring and most stable form of carborundum. Its symmetry is hexagonal. Rotation *X*-ray photographs show the axes to be $a=3{\cdot}09$, $c=15{\cdot}17$ Å.; 6 molecules to the cell. Discussion of the halvings on these photographs leads to the conclusion that all the carbon atoms and all the silicon atoms, respectively, lie on similar lattices of the diamond type, one of which is so displaced against the other along the hexad screw-axis that each carbon atom is tetrahedrally surrounded by 4 silicon atoms and *vice versa*. The minimum interatomic distance is 1·90 Å.

II. The polymorph known as I is shown to be of trigonal symmetry, and its cell, unlike that of II, is rhombohedral. Stated, however, in hexagonal terms, the cell has $a=3{\cdot}09$, $c=37{\cdot}9$ Å.; 15 molecules to the cell. The arrangement of the atoms is again tetrahedral, minimum distance 1·90 Å., and differs from that of II only in that some of the tetrahedral groups are screwed about the *c*-axis, whence the long *c*-spacing. Most of the specimens of I appear, from the *X*-ray results, to contain inclusions of II, which points to partial conversion of the former into the latter.

III. The rare modification known as III has dihexagonal symmetry; $a=3{\cdot}09$, $c=10{\cdot}09$ Å.; 4 molecules to the cell. The atoms are arranged like those of I and II, except that whereas the structure of I may be compared to a twinning of two diamond lattices, that of III resembles a twinning of two wurtzite lattices. Although carborundum, unlike diamond, shows residual rays and is a conductor of electricity, considerations of intensity in the photographs of all three modifications make it probable that the lattice is built up, not of ions, but of neutral atoms. W. A. CASPARI.

Crystal structure of duralumin. R. J. ANDERSON (J. Franklin Inst., 1926, **201**, 465—483).—The face-centred cube lattice of duralumin containing 4% of copper shows $d_{100}=4{\cdot}046$ Å., which is identical with that of aluminium itself. With 6% of copper, however, d_{100} sinks to 4·042 Å., and distortion of the lattice begins. From *X*-ray photographs, the growth of grains in duralumin on heat treatment and their fragmentation on tensile straining are demonstrated. W. A. CASPARI.

Crystal structures of beryllium oxide and beryllium sulphide. W. ZACHARIASEN (Z. physikal. Chem., 1926, **119**, 201—213).—The substances were examined in powder form by a photographic method. Beryllium oxide, whether prepared at 400° or 2000°, belongs to the hexagonal system, the unit cell containing 2 molecules and having the dimensions

a=2·694, c=4·392 Å. The space-group is C_{6v}^4 I, Be $(\frac{2}{3}, \frac{1}{3}, 0)$, $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$, O $(\frac{2}{3}, \frac{1}{3}, \frac{3}{8})$, $(\frac{1}{3}, \frac{2}{3}, \frac{7}{8})$. The results indicate that the lattice is atomic and not ionic.

Beryllium sulphide, d 2·36, crystallises regularly, having the zinc blende structure; a=4·85 Å.

L. F. GILBERT.

Variation of the angles of crystals during growth. E. S. HEDGES (J.C.S., 1926, 791—799; cf. Miers, A., 1904, ii, 114).—Experiments in which the variations of angle exhibited by the vicinal faces during crystallisation were investigated by immersing crystals of sodium potassium tartrate, magnesium sulphate, diammonium hydrogen phosphate, and sodium chlorate in their slightly supersaturated solutions, readings being taken with a special type of goniometer after various time intervals, show that during growth the number of such faces initially increases with time and then decreases, and that the positions of the faces undergo rapid variations, generally by replacement, but in certain cases by continuous progression. The vicinal faces of sodium chlorate are consistent with the symmetry of the crystal, and a method is devised to determine the true positions of the ideal cube faces even when they are absent. The slower the growth, the more closely does the crystal approximate to the ideal form, single perfect cube faces being developed on sodium chlorate by careful control of the rate of growth. These measurements lend additional support to the views of Miers (*loc. cit.*) on the cause of vicinal faces.

J S. CARTER.

Crystal structure of hafnium. W. NOETHLING and S. TOLKSDORF (Z. Krist., 1925, **62**, 255—259).—Hafnium is hexagonal close-packed, a=3·32, c=5·46 Å. Hull's results for the structure of zirconium are confirmed. CHEMICAL ABSTRACTS.

Single-crystal tungsten wire and the theory of recrystallisation. S. OHASHI (Nagaoka Anniversary Vol., 1925, 417—422; from Chem. Zentr., 1926, 1, 1701—1702).—To explain the mechanism of the separation of solid metal from a molten mass on cooling and the phenomena of recrystallisation, the author suggests that the arrangement of the atoms between the boundaries of two crystals determines the magnitude of the attraction between them so that the larger grains grow at the expense of the smaller and the average grain size increases with the time of crystallisation. Recrystallisation starting from one centre is interfered with by the growth of crystals from other nuclei, so that for the production of large single crystals this interference must be eliminated and growth confined solely to one neutral nucleus. By electrically heating tungsten wires which are maintained in slow motion between two clamps supplying the current, it is possible to convert the wires into single crystals or into a small number of large crystal grains. The relation between the temperature of recrystallisation, T, of tungsten and the time of heating, H, is given by the equation T=1250−250 log H. A. R. POWELL.

Structure of sperrylite. W. F. DE JONG (Physica, 1925, **5**, 292—301).—For platinum diarsenide, a_0=5·92 Å.; for d 10·602, the unit cube contains 4 platinum and 8 arsenic atoms. If it is assumed that the platinum, and also the arsenic, atoms are equivalent, there is dyakisdodecahedral symmetry (T_h^6), pyrite structure, with parameter u=0·38. Then the smallest distance between a platinum and an arsenic atom is 2·47, and between two arsenic atoms, 2·46 Å. CHEMICAL ABSTRACTS.

***X*-Ray goniometer. Crystal structure of glyoxaline compounds.** G. GREENWOOD (Min. Mag., 1926, **21**, 1—9).—By suitable modifications, the Bragg spectrometer can be adapted to function as a goniometer in which *X*-rays are the source of light and the ionisation chamber is the telescope. The apparatus lends itself to the examination of badly-crystallised specimens. Glyoxaline-4-sulphonic acid (tetragonal-scalenohedral) is found to have a=11·08, c=9·22 Å., d 1·838, 8 molecules per cell, and space-group D_{2d}^1. Glyoxaline (monoclinic) has a=7·67, b=5·44, c=5·12 Å., β=63° 11′, d 1·167, 2 molecules per cell. The space-group is probably C_{2h}^1, whence the molecule itself would appear to possess a plane of symmetry. W. A. CASPARI.

***X*-Ray examination of chitin.** H. W. GONELL (Z. physiol. Chem., 1926, **152**, 18—30).—Chitins from lobster, cuttle-fish, caterpillars, pupæ, mushrooms, and the marine worm *Aphrodite* give identical fibre-diagrams, yielding about 20 reflexions. The best photographs are obtained by loosening the chitin by means of glycerol and 25% hydrochloric acid and exposing through a single detached layer of chitin substance. The diagram from the marine worm *Eunice gigantea* stands apart and indicates a distinct kind of chitin. The cell-spacing along the fibre axis of the prevalent form of chitin is 10·4 Å.; the cell appears to be hexagonal, and on this assumption the a-spacing is 21·8 Å. Taking acetylglucosamine anhydride as the chitin molecule, and d 1·4, there are 18 molecules to the cell. W. A. CASPARI.

***X*-Ray comparison between lichenin and cellulose.** R. O. HERZOG (Z. physiol. Chem., 1926, **152**, 119—124).—The reflexions on the fibre-diagrams of lichenin and thrice-precipitated β-cellulose have been examined photometrically. The principal difference lies in the innermost reflexion; this is a double one, and the more intense component lies nearer the centre in the case of lichenin and farther from the centre in that of cellulose. Minor differences in spacing and intensity occur in other reflexions. It is inferred that the two substances, although similar, are not identical. W. A. CASPARI.

Crystalline character of cellulose acetate. E. OTT (Helv. Chim. Acta, 1926, **9**, 378—379).—The crystalline structure of cellulose triacetate is clearly indicated in the *X*-ray diagram, although the interference lines are of small intensity and are rather indistinct because of the smallness of the crystals (cf. Katz, Naturwiss., 1925, **4**, 164; A., 1925, i, 1245). Kahlbaum's commercial cellulose acetate gives a diagram similar to that obtained from specially purified material, but less distinct.

M. CLARK.

Dimorphism of furfuryl furoate. J. E. ZANETTI and P. F. KERR (J. Amer. Chem. Soc., 1926, **48**, 794—797).—Crystals of the β-form, m. p. 27·5°, stable at the ordinary temperature, are monoclinic-prismatic, d 1·395. Those of the unstable α-form are obtained with difficulty by cooling the fused substance; they are triclinic-pinacoidal, m. p. 19·5°, d^4 1·330, and on keeping gradually pass into pseudomorphs consisting of the β-form. W. A. CASPARI.

Electrical conductivity in single crystals and in crystal aggregates. A. SMEKAL (Z. Physik, 1926, **36**, 288—291).—It is maintained that the experimental results of Joffé and Zechnowitzer (this vol., 224) on strained crystals are all in agreement with the surface theory of electrolytic conduction in crystalline substances. E. B. LUDLAM.

Recrystallisation and recovery (improvement of the crystalline structure) of metals. G. MASING (Wiss. Veröff. Siemens-Konz., 1925, **4**, 230—243).—An analysis of the process of recrystallisation shows that formation of nuclei can be assumed to occur only to a limited extent. In normal (primary) recrystallisation, formation of nuclei has little effect on the structure except in making it less fibrous and is only an incidental phenomenon. In abnormal (secondary) recrystallisation, nucleus formation has a decisive influence, but the reason for the difference is unknown. In both cases, the formation of nuclei is a rare occurrence, and there is no reason to believe that it is more extensive in the secondary than in the primary recrystallisation. The molecular changes in the process of recovery of a metal are the same as in primary recrystallisation, as is shown by the fact that the former occurs at the temperature at which recrystallisation of the polycrystalline aggregates can be detected. The distinction between crystal recovery and the loosening of structure owing to changes in internal strain on heating is difficult, but it can be made by the means of Bauschinger effect and the temperature limit of this loosening of structure, since no such limit is observed with the internal strains. G. M. BENNETT.

Deformation lines in large and small crystals of ferrite. H. O'NEILL (J. Iron and Steel Inst., June, 1926, advance proof, 24 pp.; cf. B., 1924, 518).—Single crystals of α-iron containing 1·8% of silicon were deformed in compression and tension, the stress being applied along a quaternary axis. The surface and etch markings on a plane section were then examined, and, together with indentation tests and other work, lead to the following conclusions. A single crystal of α-iron may be cleaved parallel to cube faces, and there is also evidence of (112) cleavage. Under static deformation, it slips along one or more of the (112) planes. Movement along (112) planes results in little or no change in density, agreeing with the data for deformed single crystals, which in this respect differ from an aggregate of small crystals. If the layers of atoms move along the (112) planes for a distance of $0{\cdot}5a\sqrt{3}$, where a is the side of the cube, or a simple multiple of this, no change in orientation occurs, but if the movement takes place on successive planes for a distance $0{\cdot}577a$, the moved portion of the crystal is twinned with respect to the original, and Neumann lamellæ are formed. In an aggregate, the crystals slip along (112) and possibly also (001) planes. The nature of certain etch markings on deformed specimens is discussed in detail. W. HUME-ROTHERY.

Relation between lattice constant and density of iron–nickel alloys. A. ÔSAWA (J. Iron and Steel Inst., June, 1926, advance proof, 10 pp.).—The lattice constants, densities, and hardness of the complete series of iron–nickel alloys have been determined for annealed specimens and those dipped in liquid air. Annealed alloys containing less than 12% and more than 33% of nickel consist of single body-centred and face-centred cubic lattices, respectively, with simple substitution of iron and nickel atoms. Between these limits, the alloys are heterogeneous and both structures are shown; for specimens dipped in liquid air, the corresponding limits are 15% and 35% of nickel, respectively. The lattice constant of the body-centred α-iron is a=2·865 Å., and expands to 2·875 Å. in the alloy containing 32% of nickel, whilst the face-centred cubic lattice constant, which is a=3·538 Å. for pure nickel, expands to 3·600 Å. in the alloy containing 73% of iron. The addition of nickel to iron produces a marked increase in the hardness, which rises to a maximum at 21% and 27% of nickel in the annealed and severely cooled samples, respectively, showing the presence of martensite and austenite even in slowly cooled samples. W. HUME-ROTHERY.

Tensile strength of tungsten wires at high temperatures. R. TAJIME.—See B., 1926, 365.

Experiments with liquid helium. Properties of super-conducting metals in the form of thin films. G. J. SIZOO and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 971—976).—Films of tin, of thickness 0·3—0·5 μ, were prepared by cathode sputtering, and the change of electrical resistance with temperature was measured at temperatures down to that of liquid helium, in which region the resistance disappears at a rapid rate as the temperature falls. "Vanishing-point," or the temperature at which the resistance is half gone, is found to vary for different films, and also for the same film, due to agglomeration of the metal with time and consequent increase in resistance. In all cases, however, the vanishing point is 0·1—0·2° lower than that of ordinary tin wires, possibly due to differences in structure. The influence of current density has also been examined. A qualitative study of the disturbing effect of a magnetic field on the super-conductivity indicates that the threshold value of the field for these films cannot greatly differ from that of tin wires. In consideration of the view of Silsbee (J. Washington Acad. Sci., 1916, **6**, 597) that thin metallic films should have an abnormally high threshold value of the current, it is, however, improbable that the current is uniformly distributed through the film. Experiments with bismuth films did not indicate super-conductivity, even at temperatures as low as 1·24° Abs. M. S. BURR.

Theory of state of matter. IV. Molecular weight and critical data. F. SCHUSTER (Z. Elektrochem., 1926, **32**, 155—157; cf. A., 1925, ii, 951, 1142; this vol., 342).—The following relationship between the mol. wt., M, of a liquid at temperature $T°$ Abs. and its critical temperature T_c and critical pressure p_c is derived: $M=kdT_c/p_cA$, where d is the density of the liquid at $T°$ Abs., k is a constant, and A is $[1+(1-m)^{\frac{1}{3}}-\frac{1}{2}(1-m)]^3$, m being equal to T/T_c. In the expression of Berthelot, $k=11{\cdot}4$ and $A=2-m$. The author's expression is found to give approximately constant values of k for non-associating liquids, the average value being 22·5 at 0°. The values of the constant for twelve liquids are found to deviate from the mean value rather less than the corresponding Berthelot constants, and the value of the author's constant is approximately twice that of the Berthelot constant in the neighbourhood of the critical temperature. The equation is therefore applicable for reckoning the mol. wts. of non-associating liquids at temperatures as far as the critical temperature. The values of k are also evaluated by both methods for four common associating liquids.

C. H. D. CLARK.

Electric moment of carbon dioxide, ammonia, and sulphur dioxide. C. T. ZAHN (Physical Rev., 1926, [ii], **27**, 455—459).—Measurements with carbon dioxide, ammonia, and sulphur dioxide give the following values, respectively, for values of A and B in Debye's equation $(\epsilon-1)vT=AT+B$, where ϵ is the dielectric constant, T the absolute temperature, and v the specific volume: 0·000958, 0·003; 0·000768, 1·740; 0·001433, 2·167. Hence the corresponding values of the electric moment (in c.g.s., e.s.u. $\times 10^{18}$) are: 0·06, 1·44, and 1·611. It cannot, however, be stated definitely that carbon dioxide has an appreciable electric moment. A. A. ELDRIDGE.

Electrical resistance of sodium and potassium in the temperature region of liquid helium. H. R. WOLTJER and H. K. ONNES (Proc. Fourth Intern. Congress Refrigeration, 1924, **1**, 183—187*a*).—Sodium and potassium at 1·5° Abs. did not show super-conductivity as do mercury, lead, tin, indium, and thorium. CHEMICAL ABSTRACTS.

Specific electrical resistance of tungsten wires. J. TSUKAMOTO.—See B., 1926, 365.

Hall effect in evaporated films of iron, cobalt, nickel, palladium, and platinum. H. B. PEACOCK (Physical Rev., 1926, [ii], **27**, 474—483).—For films of iron (13—134 μμ), cobalt (11—166 μμ), and nickel (6—270 μμ) the Hall coefficients were, respectively, 1·4, 4·9, and 7·8 times the bulk values; for palladium (10—204 μμ) and platinum (6—36 μμ) the factors were 0·66 and 0·64. Iridium films have a positive Hall effect. The ratios of the specific resistances (film : bulk) were measured, as also were variations in the saturation of the Hall *E.M.F.* Films of the ferromagnetic metals, when heated, gave values approximating to those for the metals in bulk. The nature of the difference between evaporated films and bulk metal is considered. A. A. ELDRIDGE.

Physical properties of rubidium and cæsium and the resistance of potassium under pressure. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1925, **60**, 385—421).—See this vol., 232.

Effect of tension on the transverse and longitudinal resistance of metals. P. W. BRIDGMAN (Proc. Amer. Acad. Arts Sci., 1925, **60**, 423—449).—The change of resistance of nickel when the direction of the current is perpendicular to the stress is abnormal. Results are given for aluminium, gold, silver, copper, palladium, platinum, and iron, those for the first four being doubtful.

CHEMICAL ABSTRACTS.

Effects of torsion on the thermal and electrical conductivities of aluminium with special reference to single crystals. J. E. CALTHROP (Proc. Physical Soc., 1926, **38**, 207—213).—An attempt is made to measure changes produced by torsion in the conductivities of aluminium single crystals, and of annealed and hard-drawn wires. The hard wire gave a decrease in thermal conductivity of a few parts in 1000, but the single crystals showed less than 1 part in 1000 parts. Decreases in electrical conductivity were about the same for all specimens, and less than 1 part in 1000 parts. C. J. SMITHELLS.

Constitution of alloys of aluminium and magnesium from 32 to 48% magnesium. T. HALSTEAD and D. P. SMITH (Trans. Amer. Electrochem. Soc., 1926, **49**, 327—347).—Measurements of the resistance at 25° and 100° and of the thermo-*E.M.F.* of the above alloys show the existence of two regions of solid solution, viz., 36·8—38·8 and 39·4—43·0 atoms %, respectively, of magnesium, instead of the single β-field found by previous investigators (Hanson and Gayler, B., 1921, 13; Ohtani, *ibid.*, 1922, 377). The composition corresponding with the formula Al_5Mg_3 lies within the former field, but no simple stoicheiometric ratio falls within the latter field.

R. CUTHILL.

Thermoelectric element. O. HERMANN.—See B., 1926, 371.

Proof of a polarisation phenomenon on conduction of electricity through electrically double-refracting nitrobenzene. O. LOHAUS (Physikal. Z., 1926, **27**, 217—218).—Polarisation of nitrobenzene is held to be responsible for the discordant values of the Kerr constant reported by different observers. In consequence of polarisation, the field-strength in the immediate neighbourhood of the electrodes is much greater than in the interspace, and hence the double refraction is much more pronounced in the electrode zones than elsewhere. A small Kerr cell consisting of a drop of nitrobenzene in contact with two carbon plates 1 mm. apart was observed through a microscope fitted with two Nicol prisms. With an applied potential of 1000 volts and 300—400 magnification, the light intensity is observed to be greatest in the immediate vicinity of the cathode. The light intensity decreases very rapidly away from the cathode and at a distance 0·01 mm. is that of the remaining space between the electrodes.

J. S. CARTER.

Magnetic changes in iron and steel below 400°. W. H. DEARDEN and C. BENEDICKS (J. Iron and Steel Inst., June, 1926, advance proof, pp. 24).—The low temperature changes in iron and steel have been investigated by a magnetometric method in which small cylindrical specimens were heated while suspended at an angle of 45° to a magnetic field of 15 gauss, temperature–magnetisation curves being recorded photographically. Owing to the demagnetising effect of the induced poles, the absolute field within the specimen was only a small fraction of 1 gauss. Pure annealed electrolytic iron showed a sudden increase in magnetisation at about 250°, whilst the quenched material showed two similar changes at 225° and 345°, respectively. Carbon steels containing up to 1·25% of carbon and annealed at 910°, gave a very weak point at 130° corresponding with increased magnetisation, and a change at 210° in the direction of lower magnetisation, the latter change being due to cementite (Fe_3C). Steels quenched from 910° showed no signs of the cementite change at 210°, but gave weak changes at 120° and 260°, with a marked change at 330°, indicating loss of magnetisation. Quenched steels re-heated at 500° resembled annealed steels, whilst quenched specimens tempered at low temperatures (200—250°) still showed the 330° change together with other slight changes due to the austenite → martensite → troostite transformations, but although troostite contains cementite, the latter is too finely dispersed to give a magnetic effect, and the cementite change at 210° is shown only in quenched specimens tempered above 300°. All points were determined by heating curves, as cooling curves show marked hysteresis effects. W. HUME-ROTHERY.

Specific resistance and thermoelectric potential of steels differing only in carbon content. E. D. CAMPBELL and H. W. MOHR (J. Iron and Steel Inst., June, 1926, advance proof, 18 pp.).—Bars of standard steels were carburised and decarburised to give series of varying carbon content but fixed amounts of other elements. The specific resistance (ρ) was determined at 25°, and the thermoelectric potential against a bar of pure iron with hot and cold junctions at 25° and 0°, respectively. For the nearly pure iron–carbon steels made from "Armco iron," $\rho=10{\cdot}44+3{\cdot}7C$, where C is the percentage of carbon up to 1·1% and $\rho=14{\cdot}51+7{\cdot}8(C-1{\cdot}1)$ from 1·1% to 1·5% carbon. The thermoelectric potential increases uniformly up to 1·5% carbon at the rate of 2·3 microvolts for 1% of carbon. The corresponding equations for a perfectly pure iron–carbon series would be $\rho=10{\cdot}0+3{\cdot}7C$, and $\rho=14{\cdot}07+7{\cdot}8(C-1{\cdot}1)$. For a nickel steel (3·5% Ni, 0·63% Mn) ρ increases with rise of carbon content up to 0·92% carbon, at the rate of 5·7 micro-ohms for 1% carbon, compared with 3·7 for the pure iron–carbon series, indicating that the presence of nickel increases the solvent power of α-iron for carbides. The thermoelectric potential increases more slowly than in the pure iron–carbon series. In a chrome–nickel series (3·69% Ni, 1·5% Cr), ρ rises rapidly until the carbon concentration (miliatoms/c.c.) is equal to or slightly greater than that of the chromium, when the precipitation of double carbides causes a sudden drop in ρ, which falls to a minimum when the carbon concentration is twice that of the chromium. The thermoelectric potential increases three times as fast as in the iron–carbon series, until the carbon concentration is twice that of the chromium, after which the increase is less rapid. In the absence of nickel, a chrome–vanadium series (0·99% Cr, 0·2% V) shows a continuous fall in ρ down to a minimum when the carbon concentration is from 2·6 to 3·0 times that of the chromium and vanadium together. The thermoelectric potential at first increases more rapidly and later more slowly than in pure carbon steels. The above results referred to annealed steels; quenched specimens in general show higher values for both ρ and the thermoelectric potential, but the results are complex.
W. HUME-ROTHERY.

Thermomagnetic behaviour of ferrites. H. FORESTIER and G. CHAUDRON (Compt. rend., 1926, **182**, 777—779).—The ferrites of nickel, copper, lead, barium, calcium, cadmium, and zinc have been prepared by the method previously used for magnesium ferrite (A., 1925, ii, 1159). For the ferrites of nickel, copper, magnesium, barium, and lead, the magnetisation decreases with increasing temperature and disappears at the Curie point, and the heating and cooling curves coincide. Calcium and cadmium ferrites also give coincident curves, unless heated above the temperature of the Curie point, when this is found to be depressed on cooling, so that by keeping the substances for some time at the high temperature they are completely transformed into a paramagnetic form. Zinc ferrite gives a magnetisation–temperature curve with no discontinuity, and reversible throughout. The mean susceptibilities $\times10^3$ between 0 and 100 gauss for the different ferrites are: copper 102, ferrous 80, nickel 78, magnesium 54, calcium 42·5, barium 9·9, lead 1·2, and zinc 0·16. R. CUTHILL.

Measurement of the permeability and hysteresis of ferromagnetic substances for high frequencies and the fundamental equations for ferromagnetism. W. JAEGER and W. MEISSNER (Z. Physik, 1926, **36**, 161—168).—Theoretical discussion of the effect of rapidly alternating currents on iron. E. B. LUDLAM.

Magnetic properties of odd molecules. N. W. TAYLOR (J. Amer. Chem. Soc., 1926, **48**, 854—859).—Lewis' prediction that "odd" molecules are paramagnetic (cf. "Valence," 1923, p. 148) is confirmed experimentally for chlorine dioxide, thallium in mercury solution (in which it probably exists in the form of ions, Tl^+), diphenyl-α-naphthylmethyl, and sodium in liquid ammonia. S. K. TWEEDY.

Magnetic states of cobalt chloride. A. CHATILLON (Compt. rend., 1926, **182**, 765—767).—From susceptibility measurements with cobalt chloride in various states, the following figures for the number of magnetons and Curie points (Abs.), respectively, have been obtained: aqueous solution, 26, −12°; amyl alcohol solution, 23, 0°; ethyl alcohol solution, 23, 16°; solid crystallised from ethyl alcohol, 26, −16°; $CoCl_2,6H_2O$, from −80° to 50°,

25, −30°, and from 110° to 208·5°, 24, 14°; ignited solid, 25, 7°. R. CUTHILL.

Effect of complex ion formation on the magnetic susceptibility of paramagnetic salts in aqueous solution. S. S. SHAFFER and N. W. TAYLOR (J. Amer. Chem. Soc., 1926, **48**, 843—853).—The susceptibilities of nickelous chloride and bromide, copper nitrate and bromide solutions are lowered by the addition of substances which form stable complex ions with the metal ion. Nickelous chloride solution is rendered diamagnetic by potassium cyanide; with ammonia two molecular species of complex ions in equilibrium seem to be produced. The lowering of susceptibility by complex ion formation is roughly parallel to the firmness of the linkings between the metal atom and the atoms or groups in the co-ordinated position (cf. Pascal, A., 1913, ii, 544). These linkings are probably at least partly magnetic in character. S. K. TWEEDY.

Change in the magnetism of metallic hydroxides in contact with water. (MLLE.) S. VEIL (Ann. Chim., 1926, [x], **5**, 135—156).—The magnetic properties of the hydroxides of iron, chromium, copper, bi-, and ter-valent nickel change when the hydroxides are treated with water in sealed tubes at temperatures between 120° and 210°. With the exception of iron, the magnetic properties are then decreased. Further treatment beyond 12 hrs. has little effect, but when the hydroxide is redissolved in hydrochloric acid and reprecipitated, the modified magnetism persists, and a further change occurs on similar treatment with hot water. Successive treatments cause magnetic changes which tend towards a limit. If the modified ferric salt, before reprecipitation from hydrochloric acid solution as hydroxide, is recrystallised as a double salt with ammonium chloride, the cumulative effect of the treatment is destroyed. This observation is associated with the fact that crystalline, unlike amorphous, substances have constant magnetic properties. The ferric chloride solutions were examined ultramicroscopically, but all were optically void, and no difference in this respect could be observed between solutions resulting from successive treatments. The oxides derived from the hydroxides by calcination at low temperatures are generally less magnetic than the corresponding hydroxides. The effect of successive treatments is also evidenced in the oxides, the change in magnetic properties being in the same direction as those of the hydroxides. Nickel oxide, however, is much more magnetic when derived from the hydroxide treated with hot water than when obtained from the hydroxide precipitated in the cold. The significance of magnetic properties in relation to chemical composition is discussed. F. G. SOPER.

Magnetic properties of rare-earth oxides. E. H. WILLIAMS (Physical Rev., 1926, [ii], **27**, 484—486).—The magnetic susceptibility ($\times 10^6$) of pure cerium, holmium, and praseodymium oxides, respectively, is 0·14, 229, and 13·4 dyne cm. per g. (cf. *ibid.*, 1918, **12**, 158; 1919, **14**, 348). The values accord with Kunz's "resolution numbers."
A. A. ELDRIDGE.

Magnetic susceptibility of aqueous solutions of salts of the rare earths. H. DECKER (Ann. Physik, 1926, [iv], **79**, 324—360).—The magnetic properties of aqueous solutions of the rare earths have been studied by a differential method, and confirmation of earlier results has been obtained. The susceptibility in aqueous solutions is equal to that of the salts in the crystal state. Langevin's formula has been used to calculate the number of Weiss magnetons and of Bohr magnetons, but in neither case do the results yield whole numbers. Measurements with chromium, manganese, iron, cobalt, nickel, and cobalt have also been carried out. For the ferrous ion 25 Weiss magnetons were calculated and for the copper ion 10 magnetons. These figures confirm those of Weiss. For the other metals, the values lack quantitative significance owing to the difficulty of procuring preparations free from iron. The molecular susceptibilities of various anions have been evaluated. R. A. MORTON.

Refractive index of gases and vapours in a magnetic field. R. FRASER (Phil. Mag., 1926, [vii], **1**, 885—890).—Hydrogen, nitrogen, carbon dioxide, oxygen, and sodium vapour, at pressures so low that the period of the Larmor precession is at least of the same order as the mean time between collisions, show no change of refractive index when subjected to magnetic fields of 184 gauss. The experiments of Gerlach and Stern (Ann. Physik, 1924, [iv], **74**, 673; A., 1925, ii, 258) and of Glaser (A., 1925, ii, 642) indicate that gases and vapours are oriented in a magnetic field. The results indicate, therefore, that the atoms and molecules examined react to light in a manner independent of their orientation. A. E. MITCHELL.

Electro-optical investigation of sodium vapour. Corrections. H. KOPFERMANN and R. LADENBURG (Ann. Physik, 1926, [iv], **79**, 96).—Corrections to an earlier paper (cf. this vol., 216). J. S. CARTER.

Anomalous specific heats of vitreous substances. Boric anhydride and glycerol. M. SAMSOEN and P. MONDAIN-MONVAL (Compt. rend., 1926, **182**, 967—969).—A curve is shown relating the temperature to which a known weight of boric anhydride is heated, to the amount of heat yielded up by 1 g. during cooling to 15°. A marked break is shown at 218°, where the specific heat changes from 0·302 to 0·344. Another curve shows the relation between the heat absorbed by 1 g. of glycerol and the temperature to which it is previously cooled. A break occurs at −87°, where the specific heat changes from 0·107 to 0·535. In each case, the temperature of transformation differs from that obtained by dilatometric means by 25—27°. (Cf. A., 1925, ii, 1051.)
J. GRANT.

Present status of theory and experiment relating to specific heats and the chemical constant. F. I. G. RAWLINS (Proc. Physical Soc., 1926, **38**, 176—192).—The theoretical and experimental aspects of the specific heats of solids, liquids, and gases in the light of present knowledge are discussed. Possible lines of advance have been indicated for solids in view of the progress now being made in

X-ray crystallography, and the importance of further experimental work on compressibilities and elastic constants is suggested. Tentative views on the specific heat of liquids are given. In gases, the quantum theory of rotational heat is shown to fail to account satisfactorily for the behaviour of hydrogen at low temperatures. The chemical constant of monatomic and diatomic substances is discussed, both from a thermodynamical and from a statistical point of view. Current views on the nature of this constant are outlined. The theory of gaseous degeneracy and its bearing on specific heats and chemical constants is reviewed. C. J. SMITHELLS.

Law of heat of formation. H. COLLINS (Chem. News, 1926, **132**, 246—251, 262—266; cf. A., 1922, ii, 685).—The evidence on which the author bases his law of the heat of formation is summarised. Tabulated data are given for compounds of 43 elements showing a close agreement between the theoretical and observed values for the specific gravities and heats of formation of many compounds of these elements. A. R. POWELL.

Latent heat of vaporisation of liquid oxygen–nitrogen mixtures. L. I. DANA (Proc. Amer. Acad. Arts Sci., 1925, **60**, 241—267).—By means of the continuous flow method at constant pressure, and employing a special calorimeter of suitable construction, the latent heats of vaporisation at atmospheric pressure of liquid oxygen (50·01 cal.^{15}/g.), nitrogen (47·74 cal./g.), and their mixtures, have been determined. A latent heat is defined and measured which involves the change in heat content from the liquid state to the vapour state vertically above it on the vapour line in the temperature–composition diagram. CHEMICAL ABSTRACTS.

Heats of fusion of organic solvents of relatively low m. p. S. MITSUKURI (Bull. Chem. Soc. Japan, 1926, **1**, 30—34).—The following values of heats of fusion have been deduced from measurements of the f. p. of dilute solutions in certain organic solvents: chloroform, 2080 cal. (Beckmann and Faust, A., 1915, ii, 143, give 2100 cal.); acetone, 1300 cal.; methyl alcohol, 600 cal. (Maas and Waldbauer, A., 1925, ii, 492, give 1140 and 520 cal., respectively); carbon disulphide, 660 cal.; ethyl alcohol, 650 cal.; ethyl ether, 1400 cal. (whereas Beckmann and Waentig, A., 1910, ii, 581, give the value 2030 cal.). G. M. BENNETT.

Relation between composition and b. p. E. Q. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 870—872).—The b. p. at 760 mm., T_1° Abs., of most normal organic liquids and many inorganic non-electrolytes is given by $T_1=\sqrt{20{,}000m}$, where m is the sum of the number of atoms of each element multiplied by one less than the number of the row of the periodic table given by Hildebrand ("Solubility," 1924, p. 84) in which it occurs. The b. p. under a pressure of p atm., T_p, is given by $T_p=T_1/(1-0{\cdot}2\log p)$. Some classes of presumably normal liquids show small systematic deviations from these equations. S. K. TWEEDY.

Critical temperature of mercury. L. A. SAYCE and H. V. A. BRISCOE (J.C.S., 1926, 957—958).—The critical temperature of mercury calculated from the normal b. p. using the law of Guldberg and Guye (A., 1890, 1043) is 675°, and 1550° if calculated from surface tension data (Jouniaux, A., 1925, ii, 23). The data of Traube and Teichner (Ann. Physik, 1904, [iv], **13**, 620) indicate that this temperature is above 1000°. The present attempt to determine the critical temperature by heating mercury in a closed silica bomb has been unsuccessful, the bomb bursting at a temperature above 1000°. Immediately prior to bursting, the contrast between the opaque liquid and the transparent vapour was well defined. To overcome experimental difficulties, it is suggested that mercury might be enclosed in stout-walled silica vessels and heated to a higher temperature than the containing vessel by means of high-frequency eddy currents, the container being cooled below its softening point by conduction and radiation. J. S. CARTER.

Measurements of the surface tension of liquid helium. A. T. VAN URK, W. H. KEESOM, and H. K. ONNES (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 958—962).—The surface tension of liquid helium, in contact with its saturated vapour, has been measured by the method of capillary rise. The temperature was calculated from the vapour pressure (cf. Onnes and Weber, A., 1916, ii, 13). By plotting the molecular surface tension ψ_M against temperature, it has been shown that ψ_M increases linearly with decrease of temperature down to 2·4° Abs., below which it appears to approach a constant value in the neighbourhood of 1·5° Abs. The Eötvös constant for the straight portion of the curve is about 1, which is in accordance with the rule that the constant increases with the critical temperature, helium having the lowest constant and the lowest critical temperature. The deviation from a straight line probably indicates some peculiarity in the molecular attraction. M. S. BURR.

Drop-weight method for the determination of surface tension and the weight of the ideal drop. W. D. HARKINS (Nature, 1926, **117**, 690—691).—Polemical. The author insists that the weight of the ideal drop is given by $2\pi r\gamma$, where r is the radius of the tip and γ is the surface tension. Iredale (A., 1923, ii, 379) uses the formula $\pi r\gamma$, and also the incorrect relation $k^2=\gamma_1\rho_1/\gamma_2\rho_2$. A. A. ELDRIDGE.

Temperatures of equal surface tensions. W. HERZ (Z. anorg. Chem., 1926, **152**, 160—162).—The temperatures at which 46 organic liquids have surface tensions of 20 and 30 dynes per cm. have been obtained by interpolation and extrapolation from known data and the ratios of these temperatures to the critical temperature T_c of the liquid have been calculated. The ratio T_{20}/T_c varies from 0·59 to 0·69 in more than 40 cases and the ratio T_{30}/T_c from 0·46 to 0·58, the variation from the mean not exceeding 16% in the first case and 25% in the second. A. R. POWELL.

Crystallisation of glycerol. M. SAMSOEN (Compt. rend., 1926, **182**, 846—847; cf. this vol., 562).—Crystallisation nuclei do not appear in glycerol until the latter has undergone prolonged

cooling below −40°, the optimum temperature range being −50° to −55°. Traces of phosphorus pentoxide increase the number of nuclei, either by virtue of withdrawing water from the glycerol (the presence of less than 0·5% of water prevents the formation of nuclei) or by a specific action of its own. The rate of crystallisation of glycerol is zero below −25° and above +13°; it attains a maximum at −9°. The crushed crystals have m. p. 18·07°. S. K. TWEEDY.

Chemical constants of bromine. K. JELLINEK (Z. anorg. Chem., 1926, **152**, 16—24).—The determinations of Latimer and Hoenshel (this vol., 232) of the molecular heats of lead bromide and bromine at very low temperatures are utilised to calculate the chemical constant of diatomic bromine. The bromine pressure of lead bromide is calculated from the *E.M.F.* of an aqueous cell, from that of a cell containing the molten bromide, and from the reduction equilibrium. The values obtained for the chemical constant are 2·53 (18°), 2·34 (388—650°), and 2·71 (650°), respectively. From the molecular heat of bromine and its vapour pressure at the triple point, the calculated value is 2·75 (−4°). The mean value for diatomic bromine is 2·5±0·25, and for monatomic bromine, calculated from this and the dissociation equilibrium, 1·89±0·20. A. GEAKE.

Density and compressibility of acetylene. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 41—43).—The density of carefully purified acetylene was determined by Dumas' method at 0° and 25° for pressures, p, of 0·5—1·5 atm. The interpolated normal density for 1 atm. was 1·1747 at 0° and 1·0740 at 25°, the mean coefficient of expansion being 0·0037496. The values of pv at 0° are given by 1·0114−0·0114 p (cf. Howarth and Burt, A., 1925, ii, 818). By direct comparison of the behaviour of acetylene and hydrogen under pressure, the product pv was determined for the former up to a pressure of 12 atm. S. K. TWEEDY.

Density of boric oxide from a fractional crystallisation of boric acid. H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON (J.C.S., 1926, 954—955).—A previous paper (A., 1925, ii, 619) described a systematic fractionation of boric acid. Two end-fractions were converted into boric oxide glass and their densities compared by the flotation method (this vol., 219), the mean densities in the region 18—19° of the head and tail fractions being 1·79415 and 1·79445, respectively. The corresponding atomic weights of boron are 10·790 and 10·796. The beads of each sample showed variations in density amongst themselves, and little value is attached to the third decimal figure, the results merely indicating that fractional crystallisation of boric acid does not produce a change as great as 0·01 in the atomic weight of boron. J. S. CARTER.

Relations between temperatures, pressures, and densities of gases. S. F. PICKERING (U.S. Bur. Standards Circular No. 279, 1926, 1—85).—Calculations involving the relations between temperatures, pressures, volumes, and weights of gases are described. For use with high pressures, the simple gas equation may be corrected to the form $p_1v_1/F_1T_1 = p_2v_2/F_2T_2$, where p, v, and T have their usual significance, and F_1 and F_2 are correction factors depending on p_1 and T_1, and p_2 and T_2, respectively. Graphs are given showing the values for these correction factors for air, argon, helium, hydrogen, methane, neon, nitrogen, and oxygen, usually up to 200° and 200 atm. The different equations of state are reviewed. The equation of van der Waals is very inaccurate quantitatively except for neon. Dieterici's equation gives satisfactory agreement in the neighbourhood of the critical temperature, but for higher temperatures the equation of Berthelot is better. Various tables of correction factors, aqueous vapour pressures, critical constants, etc. are given, with an extensive bibliography. Graphs showing the volumes of gases delivered from cylinders at different pressures are included. W. HUME-ROTHERY.

Vapour pressure of ozone at very low temperatures. A. L. SPANGENBERG (Z. physikal. Chem., 1926, **119**, 419—438).—The vapour pressure has been measured between −193° and −183°, both statically and by the transport method. The results are representable by Nernst's formula, $\log p = -\lambda_0/4{\cdot}571\ T + 1{\cdot}75 \log T - \varepsilon T/4{\cdot}571 + C$, where p is the vapour pressure in mm., T the temperature Abs., and λ_0, the heat of vaporisation per g.-mol. at 0° Abs., =3700 cal.; ε, a constant, =0·05099; and C, the chemical constant, =5·850. If p is in atm., C=2·97. This formula gives b. p. −112·3°/760 mm. The values of the molecular heat of vaporisation in cal., λ, calculated from the vapour pressures, give by extrapolation the above value for λ_0, and can be represented by the formula $\lambda = \lambda_0 + 3{\cdot}5090\ T - 0{\cdot}051166\ T^2$. R. CUTHILL.

Vapour pressures of chlorine dioxide. F. E. KING and J. R. PARTINGTON (J.C.S., 1926, 925—929).—The vapour pressures of pure chlorine dioxide, obtained by heating silver chlorate in a current of chlorine at 85—95°, have been determined from the f. p., −59°, to the b. p., +11°, the vapour pressure at the f. p. being 10 mm. A fair approach to a straight line is obtained on plotting values of log p against $1/T$ Abs. The value of the latent heat of evaporation of liquid chlorine dioxide, calculated from data in the region of the b. p., is 6520 cal. per mol. The Trouton constant is 23, the values calculated from the two formulæ of Nernst and from that of Wartenberg being 20·85, 21·3, and 20·2, respectively. The ratio of the absolute temperatures corresponding with vapour pressures of 760 mm. and 200 mm. is 1·114, the value shown by Ramsay and Young to correspond with normal liquids. There is thus very little, if any, association in the liquid state, the formula in both the liquid and gaseous states being ClO_2. J. S. CARTER.

Study of sodium and potassium salts. L. HACKSPILL and R. GRANDADAM (Ann. Chim., 1926, [x], **5**, 218—250).—The vapour pressures of the chlorides of sodium and potassium have been determined over the temperature range 800—1100°. The vapour-pressure curve of mixtures of these salts has also been constructed, and its form indicates that the sodium salt can be separated from the potassium salt

by fractional distillation. Iron interacts with salts and hydroxides of sodium and of potassium at 1000° to form the alkali metal. The cyanides reduce metallic oxides to the metal at temperatures varying between 560° and 750° with simultaneous formation of the alkali metal. The m. p. of potassium cyanide, purified by recrystallisation from liquid ammonia, is 634·5°± 0·3° and that of sodium cyanide 563·75°±1°.

F. G. Soper.

Evacuation of carbon dioxide and water. N. R. Campbell (Phil. Mag., 1926, [vii], **1**, 762—768).—When a cooled trap is used for removing mercury vapour during an evacuation, other substances may condense in the trap and establish in the system a vapour pressure large enough to be appreciable but so small as to retard the rate of evacuation. With a trap cooled in liquid oxygen boiling at atmospheric pressure, carbon dioxide is condensed, whilst if solid carbon dioxide is used, water is condensed. By maintaining the trap at 78° Abs. by boiling the oxygen under reduced pressure, or between 108° and 150° Abs. by means of solid mercury cooled by liquid oxygen, pressures less than 10^{-7} mm. can be attained rapidly even in the presence of carbon dioxide and water vapour. The utilisation of the vapour pressure of carbon dioxide at 90·2° Abs. as a convenient standard for calibrating ionisation gauges is suggested.

A. E. Mitchell.

Equation of state of solid substances (metals) in connexion with their compressibility and with the pressure and temperature coefficient of this quantity. J. J. van Laar (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 95—112).—Van der Waals' equation of state may be applied to solids by introducing a term λ, referring to the "static" virial of repulsion, necessitated by the fact that, in a solid, the molecules are bound to definite positions of equilibrium. The equation for solids thus becomes $p+a/v^2=(\lambda+RT)/(v-b)$. If b be regarded as a function of v, it is found that the pressure and temperature coefficients of the compressibility coefficient of copper can be calculated with considerable accuracy.

M. S. Burr.

Change in the coefficient of dilatation of substances in the amorphous state. M. Samsoen (Compt. rend., 1926, **182**, 517—519; cf. A., 1925, ii, 1051).—The coefficients of cubic dilatation of a large variety of amorphous organic substances, carried out, using mercury as the dilatometric liquid, agreed with those resulting from Chévenard's method. This latter was used in the case of "orca," whilst for glycerol, displacements were read directly in a calibrated semi-capillary tube. In all cases, a change in the coefficient of dilatation was noted at the temperature at which the viscosity was about 10^{14} c.g.s.u., the new value never being less than twice the old. It is supposed that this is produced by the elimination (by means of the effect of Newtonian attraction on the molecules at a particular viscosity) of the factor which goes to make up the dilatation coefficient of a liquid as distinct from that of a solid; *i.e.*, the value is greatest for the liquid state. This anomaly is too general to be associated with allotropic change alone, but must be a general property of amorphous substances.

J. Grant.

Behaviour of nitrogen according to the law of corresponding states. A. T. van Urk (Proc. Fourth Intern. Congress Refrigeration, 1924, **1**, 79—80A; Leiden Comm., No. 169C; cf. following abstract).—The curves show a bend in the neighbourhood of the critical temperature and density. As the bend of the deviation curve displaces itself towards greater values of log λv with increasing temperature, it is probable that the same bend exists also at higher temperatures, if measured at greater densities. The deviation curve of the points measured by Bridgman (Proc. Amer. Acad. Arts Sci., 1924, **59**, 173) cuts the zero axis with a positive slope, whilst the author's curves show that the slope at smaller densities is negative.

Chemical Abstracts.

Behaviour of oxygen according to the law of corresponding states. H. A. Kuypers (Proc. Fourth Intern. Congress Refrigeration, 1924, **1**, 69—71A; Leiden Comm., No. 169B).—By means of the equation of state in which the normal volume has been taken as a unit of volume, the pv_A values of all isotherms have been calculated for the densities of all isotherm points measured. The differences of the measured and calculated pv_A, expressed in percentages of the latter, are represented graphically.

Chemical Abstracts.

Rotation entropy of di- and poly-atomic gases. K. Szél (Z. Physik, 1926, **36**, 292—299).—A formula based on Planck's investigation of the physical structure of the phase-space leads to results which for high temperatures agree with those obtained by other workers by quite different methods.

E. B. Ludlam.

Experimental test of the degradation of monatomic gases. W. Meissner (Z. Physik, 1926, **36**, 325—335).—When compressed helium at 15° Abs. was allowed to expand, the proportion liquefied was found to be 0·19 of the whole. This is much more than is to be expected from the calculation based on the theory of corresponding states. The theories of Nernst, Einstein, and Planck are discussed. It is not possible to say whether the divergence between the experimental result and the theory of corresponding states is due to degradation of the gas.

E. B. Ludlam.

Binary liquid mixtures. G. Weissenberger, F. Schuster, and O. Zack (Z. angew. Chem., 1926, **39**, 270—271).—The partial vapour pressures at 20° of the more volatile constituents of mixtures of phenol with trichloroethylene, *s*-dichloroethylene, chloroethylene, and ethylidene chloride are greater than those calculated according to Raoult and van 't Hoff. Thus molecular compounds are not formed. None of these chlorinated hydrocarbons contains the trichloromethyl group, which has a specific relation to aromatic hydrocarbons. The ethyl and, especially, the methyl esters of acetic acid have less than the calculated vapour pressures when mixed with phenol. Molecular compounds are formed, the active atoms being the hydroxyl hydrogen of the phenol and the carbonyl oxygen of the esters. Tetrahydronaphthalene does not form compounds either with these esters or with trichloroethylene, ethylidene chloride, or carbon tetrachloride.

A. Geake.

Viscosity and turbulence. C. CAMICHEL, L. ESCANDE, and M. RICAUD (Compt. rend., 1926, **182**, 881—883).—The viscosity coefficients for petrol, water, and sucrose solutions were determined in the turbulent condition of flow by the Poiseuille method. The similar behaviour of viscous fluids in the turbulent region is confirmed. The curves connecting the pressure difference with the mean rate of flow approach each other on passing from the turbulent to the non-turbulent condition. The observations are extended to gyratory turbulence in fluids. S. K. TWEEDY.

Coefficients of viscosity of certain pairs of isofluid liquids. V. A. UNKOVSKAJA and E. D. VOLOVA (J. Russ. Phys. Chem. Soc., 1925, **57**, 107—123).—Measurements of the viscosity at 20°, 40°, and 60° of various binary mixtures are recorded. For the system chlorobenzene–bromobenzene the simple mixture rule values of the fluidity are distinctly greater than those observed, the divergence attaining a maximum value for mixtures which contain rather more than 50 mol. % of the bromo-compound; the divergence increases with rise of temperature to 1·6% at 60°. Similar relations are shown by *iso*butyl acetate–ethyl *iso*valerate; the maximum deviation corresponds with 50 mol. % and reaches 0·5% at 20°. Ethyl propionate and *iso*butyl formate and ethyl butyrate and ethyl *iso*butyrate behave similarly. Mixtures of propyl acetate and ethyl propionate give a rectilinear fluidity isotherm at 40°, but at 20° the mixture containing about 25 mol. % of the former component exhibits a fluidity 0·2% greater than the calculated value (cf. Biron and Morguleva, A., 1914, ii, 174; Biron, Nitikin, and Jakobson, *ibid.*, 175). T. H. POPE.

Mutual solubility of liquids. III. Mutual solubility of phenol and water. IV. Mutual solubility of *n*-butyl alcohol and water. A. E. HILL and W. M. MALISOFF (J. Amer. Chem. Soc., 1926, **48**, 918—927).—Agreement is expressed with Kablukov and Malischeva's criticism (A., 1925, ii, 768) of Hill's method of determining mutual solubility by the indirect volumetric method.

The mutual solubility of phenol and water was determined between 20° and the critical solution temperature, which was found to be 65·85°, corresponding with 34% of phenol.

The mutual solubility curve for *n*-butyl alcohol and water, which was determined from the quadruple point, −2·95°, falls between the curves for *iso*- and *sec.*-butyl alcohols. The critical solution temperature is 125·15°, corresponding with a concentration of 32·5% of *n*-butyl alcohol. S. K. TWEEDY.

Absorption of hydrogen chloride and sulphur dioxide in sulphuric acid and acetic acid. V. ČUPR (Pub. Fac. Sci. Univ. Masaryk, 1926, No. 68, 1—17; cf. A., 1925, ii, 655).—The absorption of hydrogen chloride in aqueous solutions of 0—100% acetic acid at 0° and 25°, in 62% and 98% sulphuric acid at 40° and 68°, and in 96% sulphuric acid at various temperatures, has been determined. The absorption of sulphur dioxide has been determined in aqueous solutions of 0—100% acetic acid at 27°, and in 0—97% sulphuric acid at 41° and 62°. The absorption isotherms for sulphur dioxide and hydrogen chloride in the sulphuric acid solutions show minima at concentrations corresponding with the hydrate H_2SO_4,H_2O. The minima flatten with increasing temperature and vanish at about 60—65°. It is suggested that the changes in absorption are connected with the formation of the hydrate, which dissociates at higher temperatures, since no minima occur in the corresponding isotherms for acetic acid, which forms no hydrate in aqueous solutions. C. J. SMITHELLS.

Solubility measurements on ampholytes. H. VON EULER and K. RUDBERG (Arkiv Kemi, Min., Geol., 1926, **9**, No. 18, 1—6).—See A., 1925, ii, 853.

Fat solvents. C. E. BILLS (J. Biol. Chem., 1926, **67**, 279—285).—The miscibility and colour reactions of five different fats with a large number of organic substances have been studied and the results tabulated. C. R. HARINGTON.

Osmotic pressure of solutions. V, VI, and VII. M. LEVALT-EZERSKI (J. Russ. Phys. Chem. Soc., 1925, **57**, 151—160; cf. this vol., 120).—The f.-p. depression for any solution is given by $\Delta t = a(p-p')/p'$, where $a=EN$, and the osmotic pressure by $P=b(p-p')/p'$, where $b=1240$ if P is expressed in atmospheres. This equation is in complete agreement with the results of Berkeley and Hartley's measurements of the osmotic pressures of potassium ferrocyanide (cf. A., 1916, ii, 518; 1919, ii, 271). T. H. POPE.

Expression for the reaction of aqueous solutions. I. M. KOLTHOFF (Biochem. Z., 1926, **169**, 490—493).—A criticism of Giribaldo (this vol., 125). E. C. SMITH.

Spectrography of potassium trihalides. P. JOB (Compt. rend., 1926, **182**, 632—634).—The existence in aqueous solution of the ions I_3', Br_3', $ClBr_2'$, BrI_2', and ClI_2' is demonstrated by a spectrographic method (cf. A., 1925, ii, 389, 471, 887). Approximate equilibrium constants are given. S. K. TWEEDY.

Chemical sorption. I. S. LIEPATOV (Z. anorg. Chem., 1926, **152**, 73—90; cf. A., 1925, ii, 385, 957, 1059).—Hydrated manganese dioxide, starch, and nitroalizarin are acidic and do not adsorb acids. Hydrated manganese dioxide is the most acid of the three and adsorbs bases and the basic constituents of salts containing either organic or inorganic anions. Nitroalizarin adsorbs the basic constituent from salts containing organic anions, but not from those containing inorganic anions, and starch adsorbs only free bases. For the adsorption isotherm, the equation $dc_2/dc_0=k_1(m-c_2)+k_2c_2$ is recommended, where c_0 is the initial concentration of solute, c_2 the amount adsorbed, and m the amount required to saturate the adsorbing material. If $k_1-k_2=wk$, this becomes $wk=1/c_0 \log_e m/(m-wc_2)$. For the adsorption by starch of potassium hydroxide from solutions in 80% alcohol, the rate of adsorption is highly dependent on the concentration. For a given time, the value of wk is independent of the concentration. After 15 min., w is greater than 1 and k_2 has therefore a negative

signification, but after a longer time w becomes less than 1, corresponding with purely physical processes assuming an important rôle. The rate of adsorption depends on the difference in concentration of solute between the outer and inner surfaces of the adsorbent, *i.e.*, it is a diffusion velocity. Specimens of nitroalizarin prepared by two different methods adsorbed copper acetate to different extents, and from the measurements it is concluded that they differ physically but not chemically. Increasing temperature greatly accelerates adsorption. For the adsorption of sodium hydroxide by hydrated manganese dioxide, which has been shown to be a chemical process (cf. Pavlov, A., 1925, ii, 507), the temperature coefficient is very small owing to the absence of diffusion processes. Nitroalizarin adsorbs only the basic constituents of salts, the whole of the acid constituent remaining in the solution. The colour of the nitroalizarin is changed by adsorption and varies continuously with the initial concentration of the solute. The adsorption by hydrated manganese dioxide of the basic constituents of potassium and barium chlorides shows no tendency to reach a maximum with increasing initial concentration. The adsorption of salts which are hydrolysed by water tends towards a maximum, and is diminished by the addition of acid. The reversibility or otherwise of adsorption depends on the nature of the products formed in the process.

A. GEAKE.

Chemical nature of adsorption. K. C. SEN (Biochem. Z., 1926, **169**, 192—199).—Adsorption of salts or ions from solution is influenced by the nature of the adsorbent, and negative ions may be taken up rapidly by negatively charged surfaces. The presence of a readily adsorbed anion favours the adsorption of a cation. Adsorption of a negative ion stabilises a negatively charged sol, and in accordance with the above increases the total salt adsorption. Anions are differently adsorbed from solutions containing different cations, which is contrary to what would be expected on the basis of Freundlich's theory.

C. RIMINGTON.

Adsorption of carbon dioxide by activated coconut charcoal. H. ROWE (Phil. Mag., 1926, [vii], **1**, 659—670; cf. this vol., 345).—The rate of adsorption of carbon dioxide by activated coconut charcoal at 20° for low initial pressures (2×10^{-2} to $1{\cdot}5\times10^{-1}$ mm.) has been determined, using the apparatus previously described. The charcoal was completely freed from gases at 450°; after cooling, a known volume of carbon dioxide was admitted and the pressure measured at intervals up to 24 hrs. The time required to attain equilibrium increased with the initial pressure. The pressure–time curves consist of two parts, the initial rapid fall of pressure being due principally to adsorption, the later slow fall to absorption. The latter portion of the curve is exponential, showing that the absorption follows the diffusion law. The rate of adsorption has been determined also for samples of charcoal containing initially some adsorbed gas. In general, adsorption and absorption processes are both indicated, but below a definite equilibrium pressure, and definite concentration of the gas in the charcoal, adsorption alone is operative. Absorption begins only when the concentration of the gas in the charcoal has reached this limiting value.

A. B. MANNING.

Physical properties of active charcoals, and the heat effect of wetting active charcoals with liquids. H. HERBST (Kolloid-Z., 1926, **38**, 314—321).—The various factors affecting the adsorptive power of active charcoals are discussed. Other things being equal, the adsorptive power naturally depends on the percentage of free carbon in the charcoal, of which the specific gravity is a measure. A good capillary structure is not the sole criterion of adsorptive power; it must go hand in hand with the presence of unsaturated carbon molecules. Charcoals with low porosity, such as coconut and walnut charcoals or those prepared at too high a temperature (above 1100°) and thus "graphitised," show the phenomenon of "ultraporosity," *i.e.*, only the smallest molecules are adsorbed, since larger ones cannot enter the capillaries. In order, therefore, to obtain a measure of the true activity in such cases, hydrogen must be used. The adsorption of substances from solution is influenced by the nature of the solvent. A charcoal which shows activity towards a gas may show none towards a solution, because the solvent may have a low wetting power. Conductivity measurements afford a satisfactory means of detecting the transition from the α to the β ("graphitised") charcoal. *X*-Ray investigations in this connexion are liable to ambiguity in interpretation. A search for another transition at higher temperatures would be of interest. The determination of porosity by comparison of the true and apparent specific gravities, and the heat of wetting of a charcoal with liquids are discussed.

N. H. HARTSHORNE.

Wetting adsorption. Adsorption of deformable substances. O. BARTSCH (Kolloid-Z., 1926, **38**, 321—328).—A stalagmometric method for determining the adsorption of oleic acid is described. From the results of measurements with a variety of adsorbents, it is shown that the wettability of the adsorbents by water and by oleic acid is of great influence on the process. The thickness of the layer of adsorbed oleic acid can amount to many thousand molecules. Having special regard to the deformability of the adsorbed liquid particles under the influence of the phase boundary forces, an explanation is given of the formation of powerfully adsorbed layers, without invoking the assistance of molecular attraction, and without conflicting with Langmuir's theory of a unimolecular layer.

N. H. HARTSHORNE.

Experimental verification of Gibbs' adsorption equation by observing the adsorption by mercury of its own ions from solution, and its bearing on Nernst's theory of electrode potential. R. K. SCHOFIELD (Phil. Mag., 1926, [vii], **1**, 641—658).—The changes in concentration of mercurous ions in a solution of mercurous sulphate, produced by a stream of drops of mercury falling through it, have been determined, using a modification of Patrick's constant-flow adsorption tube (A., 1914, ii, 249). The quantity of mercurous ions adsorbed per unit area of mercury is identified with the number of ions which on the Nernst theory of electrode potential

are deposited on the mercury surface, and impart to it their charge. The variation of surface tension with applied potential of a mercury surface in contact with the same solution has also been determined in a capillary electrometer similar to that used by Smith (A., 1900, ii, 330), and Gibbs' equation has been used to calculate the ionic adsorption from the slope of the electro-capillary curve. The satisfactory agreement between the two sets of values for the ionic adsorption constitutes a quantitative verification of Gibbs' adsorption equation. The relation between different views of the mechanism of the electrode potential is briefly discussed. The surface charge may be regarded as set up by a flux of electricity across the surface, producing, in accordance with Faraday's laws, the same quantity of mercurous sulphate as would be adsorbed from solution had no electric flux taken place. A. B. MANNING.

Electric adsorption. S. MOKRUSCHIN and O. ESSIN (Kolloid-Z., 1926, **38**, 307—310).—In reference to Mukherjee's conception of the nature of electric adsorption (Trans. Faraday Soc., 1921, **48**, 108), the authors discuss the probability of a molecule or ion presenting a favourable pole or charge to the adsorbing surface when colliding with it. The equation $m=S(1-1/2^n)$ is deduced, where m is the number of molecules adsorbed by an "elementary surface," n the number of molecules colliding with that surface, and S the number of "elementary surfaces." The equation, with certain developments, is applied to the experimental results of Ghosh and Dhar (A., 1924, ii, 733) for the adsorption by freshly-precipitated barium sulphate of chloride, dichromate, oxalate, arsenite, bromate, thiosulphate, nitrite, ferricyanide, and iodate ions, and is found to be in excellent agreement with them. N. H. HARTSHORNE.

Adsorption of electrolytes by cotton yarn. Theory of mercerisation. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 31—47).—The behaviour of cotton towards electrolytes is analogous to that of starch. Acids are very slightly adsorbed, this action being most marked for medium concentrations of the acids. Alkalis, on the other hand, are readily adsorbed, and when the solutions are dilute, the adsorption follows the ordinary formula. On account of the swelling of the yarn, adsorption of alkali from concentrated solution follows a more complex course, the curve showing an abrupt change in direction, due, not to chemical action, but to change in structure of the yarn caused by the swelling. The presence of electrolytes either diminishes or affects but little the adsorption of alkali by cellulose, any diminution of the adsorption being closely related to the decreased swelling of the cellulose. The results indicate that adsorption of alkali by cellulose must be regarded as a chemical adsorption. T. H. POPE.

Adsorption of alkali by cellulose. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 48—54; cf. preceding abstract).—Sodium and potassium hydroxides are absorbed by cellulose in very nearly the same proportions, but barium hydroxide is adsorbed in much larger quantities. The adsorption of alkalis by cellulose is expressed by the ordinary adsorption equation, but is said to involve a chemical reaction of hydrolytic nature. T. H. POPE.

Influence of adsorbents on surface tension. L. JENDRASSIK (Biochem. Z., 1926, **169**, 178—185).—The surface tension of crystalloid and colloid solutions, measured by a static method, is decreased by wiping the surface with filter-paper. Disturbance of the surface by allowing the solutions to flow from a pipette restores the figure to its normal value. The phenomenon appears to be due to an alteration of the physical equilibrium of the solution such as a concentration of the surface layer. Talc lowers the surface tension of some solutions and raises that of others. C. RIMINGTON.

Hyperbola method for the measurement of surface tensions. A. FERGUSON and I. VOGEL (Proc. Physical Soc., 1926, **38**, 193—203).—When a liquid lies between two plates inclined to one another at a small angle, its surface has a hyperbolic section, from the measurement of which its surface tension can be calculated. The method has long been known, but has recently been improved by Grünmach (Physikal. Z., 1910, **11**, 980). Errors arise, however, from the difficulty of determining the horizontal and vertical axes of co-ordinates, and according to the present paper this difficulty is met by plotting two linearly related functions of the observations, the surface tension being deduced from the co-ordinates of the resulting mean straight line and the angle between the plates. The latter may be measured either directly or by calibration with a liquid of known surface tension. C. J. SMITHELLS.

Electrical phenomena at interfaces. K. C. SEN (Z. anorg. Chem., 1926, **152**, 221—224; cf. this vol., 122).—Examples are quoted from the work of Powis (A., 1915, ii, 137) and of Mukherjee (A., 1925, ii, 1149) in support of the author's view of the behaviour of antagonistic ions in the coagulation of colloids and the inversion of emulsions. In many cases, the antagonistic effect of the ions may be masked by the electrical conditions at the interface. A. R. POWELL.

Spectrometrical measurement of the increase of thickness of surface films [on metals]. G. TAMMANN and G. SIEBEL (Z. anorg. Chem., 1926, **152**, 149—159).—When polished nickel surfaces are heated in a stream of air at constant temperature, the oxide film increases in thickness according to the equation $t=ae^{by}-a$, where y is the thickness of the film in time t, a is a constant independent of the temperature, and b is the decrease in oxygen concentration in the successive oxide layers. The rate of thickening of the film varies with the temperature according to the equation $b_T=2{\cdot}64e^{-0{\cdot}00626(T-(273+45))}$. These facts indicate that the oxide film adsorbs a thin gas layer, the oxygen content of which is maintained constant by continual replenishment from the air, but the rate of diffusion of oxygen through this film does not follow the ordinary diffusion law. The thickening of the oxide film on copper in air follows the same law as that of nickel only after the film has reached a thickness equivalent to an air

layer 400 μμ thick (cf. Tammann and Köster, A., 1922, ii, 831). A. R. POWELL.

Electrical properties and permeability for ions of membranes. VIII. Permeability of dried collodion membranes for non-electrolytes. A. FUJITA (Biochem. Z., 1926, **170**, 18—29).—As was found in the case of univalent cations (A., 1925, ii, 131), the rates of diffusion of a number of non-electrolytes through dried collodion membranes follow the same series as that obtained with moist membranes, but the differences between individual rates are much magnified. A substance which diffuses through moist membranes at less than half the rate for potassium chloride is unable to diffuse through the dried membrane. Ammonia, in contrast to the ammonium ion, exhibits an exceptionally large rate of diffusion. The permeability for water is shown to be of the same order as that for other easily permeable substances. R. K. CANNAN.

Cryoscopy in sodium sulphate [deca]hydrate. E. PIERRET (Bull. Soc. chim., 1926, [iv], **39**, 590—602; cf. Darmois and Périn, A., 1923, ii, 831).—The technique of Lowenherz's cryoscopic method in sodium sulphate decahydrate is improved (cf. A., 1896, ii, 149). Sodium salts and non-electrolytes behave normally. The method is applicable to salts which react chemically with the solvent, provided small depressions are used and the decomposition products are known. Complete double decomposition appears to occur in such cases, but with sulphates double compounds are formed. *E.M.F.* measurements confirmed the complete double decomposition in the case of cupric chloride. The constant for the solvent, determined with carbamide is 33·7. The experimental results for some metallic salts are recorded; mol. wts. less than 200 may be determined to 0·5% by the method. S. K. TWEEDY.

General colloid chemistry. XIX. Constitution of silicic acid sols. II. W. PAULI and VALKÓ (Kolloid-Z., 1926, **38**, 289—300; cf. A., 1925, ii, 521).—Silicic acid sols as prepared by Grimaux (Compt. rend., 1884, **98**, 105) by the saponification of tetramethyl orthosilicate are not completely free from electrolytes, but the latter may be removed by electrodialysing the sol for a few hours. The products have a hydrogen-ion concentration of 1·3 to $3·4\times10^{-5}N$ and a specific conductivity of 4·6 to $13·6\times10^{-6}$ mho. The composition of the colloid particles may be represented by the formula $[x(SiO_2+nH_2O),ySiO_3H']+yH^{\cdot}$, already advanced for the Graham sol in the previous communication. The number of molecules associated with one charge (x/y in the formula) varies between 6000 and 15,000 for the Grimaux sols, *i.e.*, about ten times the values found for the Graham sols. This difference is attributed to the fact that the latter sol is prepared in a solution having a high hydrogen-ion concentration, whilst in the former case the solution is practically neutral. Grimaux sols with 1—2% SiO_2 are stable for some weeks. Jellies form gradually, but they may be redispersed merely by shaking; the conductivity, however, remains unchanged. In migration velocity determinations by the direct macroscopic method, the velocity of the sol-electrolyte boundary is influenced greatly by the nature of the electrolyte. The migration velocity of the particles in the Graham sol is estimated to be 20×10^{-5}, and in the Grimaux sol 10×10^{-5} cm./sec. All the particles carry charges. The addition of potassium chloride or barium chloride diminishes the velocity, whilst sodium hydrogen carbonate increases it. In the latter case, a considerable increase in the charge number of the particles takes place. The decrease of conductivity brought about by the addition of hydrochloric acid to silicic acid sols is due to a decrease in the hydrogen-ion concentration consequent on the formation of positively charged particles according to the scheme $[x(SiO_2+nH_2O),ySiO_2H^{\cdot}]+yCl'$. N. H. HARTSHORNE.

Selenium and tellurium dispersoid solutions with varying particle size. R. AUERBACH (Kolloid-Z., 1926, **38**, 343—347).—From cryoscopic measurements, it is found that metalloid selenium dissolves in pyrosulphuric acid as diatomic molecules. Metalloid selenium of any degree of dispersion changes at 130° into a metallic modification. In a molecularly dispersed solution, this change is due to a breaking down of Se_2 molecules into single atoms. It is accompanied by a colour change from green to yellow. By the addition of water to solutions of Se_2 in pyrosulphuric acid, with consequent increase in the particle size, at 20° the colour changes from green through yellow and red to violet, and the metalloid is then precipitated, whilst above 130° the colour change is from yellow, through red, to blue and the metallic form is deposited. In both cases, the colour change is in accordance with Ostwald's colour-dispersity rule. If, however, the yellow metallic solution is coagulated at the ordinary temperature, the first result is the re-formation of the Se_2 molecules accompanied by the change from yellow to green, *i.e.*, in opposition to the colour-dispersity rule. After this, the colour changes proceed in the normal manner and finally the metalloid is precipitated.

Tellurium, in accordance with its metallic character, dissolves in pyrosulphuric acid only as single atoms. On coagulation the colour changes from red, through violet, to blue, in accordance with Ostwald's rule. Spectrophotograms of selenium (in both forms) and of tellurium solutions are shown and their relation to the cryoscopic results is indicated.

N. H. HARTSHORNE.

Thermal synthesis of colloids. I. Colloidal sulphur. A. GUTBIER (Z. anorg. Chem., 1926, **152**, 163—179).—When superheated sulphur vapour free from air is passed into air-free water, a white sulphur sol is formed containing up to 0·082% S. The sol has an acid reaction due to the presence of traces of polythionic acids and hydrogen sulphide; it exhibits the Tyndall phenomenon and Brownian movement and appears to be of a polydisperse nature. The sols are stable for 2—6 weeks, according to the degree of dispersion; no sulphur can be extracted from them by organic solvents, but the sulphur that slowly precipitates on keeping readily dissolves in carbon disulphide and appears to be the S_λ form. A sol containing 0·022% S had d_4^{20} 1·003, σ^{20} 1·012, η^{25} 1·02, and under the influence of a current at 110—220 volts the particles of sulphur migrated

towards the anode. Sols with a higher sulphur content (up to 0·85%) were obtained by condensing sulphur vapour in dilute solutions of organic protective colloids, *e.g.*, a 0·5% solution of saponin or a 1·0% solution of starch. A. R. POWELL.

Preparation of a pure gold sol. W. M. BENDIEN (Chem. Weekblad, 1925, **23**, 168).—Sols suitable for examining the effects of electrolytes can be obtained without dialysis by employing Bredig's dispersion method in a solution of 0·0001*N*-hydrochloric acid, diluting with five times the volume of conductivity water, and neutralising with the exact equivalent of potassium hydroxide. S. I. LEVY.

Colloid chemistry of clay and kaolin. K. NISHIKAWA (Kolloid-Z., 1926, **38**, 328—333).—The reason for the necessity of the moistening and air-drying stages in the making of coherent articles from clay is thought to lie in gel formation, which causes the particles to become mechanically linked to one another, possibly by sharing water of hydration. To throw light on this point, measurements of the viscosity of various German and Japanese clay and kaolin suspensions under different pressures have been made. At high pressures, *i.e.*, with small times of flow, the Hagen–Poiseuille law was found to hold, but with low pressures the viscosity was relatively very much greater, the effect being more marked the more concentrated the suspension. This behaviour is the same as that observed in the gelatinisation of gelatin, agar, and other strongly hydrated solutions, and indicates the influence of "structure viscosity." A graphical method for indicating the extent to which a clay suspension exhibits structure viscosity is described. It is found that the clay showing the greatest structure viscosity also shows the least diminution in volume on drying. Ostwald's equation for solutions showing structure viscosity, viz., $p_K{}^n \times t_K = K$, where p_K is the pressure, n a constant greater than 1, t_K the time of flow, and K a constant, is found to hold for lower values of t_K.
N. H. HARTSHORNE.

Polychromism of sulphur. WO. OSTWALD and R. AUERBACH (Kolloid-Z., 1926, **38**, 336—342).—Cryoscopic measurements with the clear blue solutions of sulphur in pyrosulphuric acid show the molecules to be diatomic. It is to be assumed that blue solutions in other solvents (*e.g.*, hot glycerol) also contain the sulphur in this form, which is thus much more highly dispersed than in most organic solvents in which the molecules are octatomic. There are two series of sulphur solutions of varying degrees of dispersity and varying colour. One is obtained, *e.g.*, by the progressive dilution of pyrosulphuric acid–sulphur solutions with water, and the second, *e.g.*, by the decomposition of thiosulphates with acid. The first series begins with the highly-dispersed S_2 molecules and passes through the colloid range to coarse dispersions. The second begins at the smallest colloid particles and finishes also at coarse suspensions. The colours of the first series start at pure ultramarine blue and pass to green, then to opalescent yellow, red, violet, then to a very turbid and impure blue and green, and finally to yellow, macroscopic sulphur. In the second series the latter colours are more readily reproducible. They commence with the opalescent yellow and thereafter follow the same order. Sulphur solutions with sufficiently wide variations of dispersity thus pass through the visible spectrum twice, and so furnish an inorganic and purely dispersoid–chemical analogue to the colours observed by Piccard with organic salts. The colour changes are produced by the movement of three absorption bands, two of which were previously postulated by Ostwald. In molecularly dispersed (S_2) solutions, all these bands are in the region of photographic spectroscopy, two in the ultra-violet, and one in the visible part. With decreasing dispersity, the bands shift towards the longer wave-lengths, in accordance with Ostwald's colour-dispersity rule. The analogy between the sulphur solutions and ultramarine sols is emphasised and discussed. In many respects, the investigations confirm the conclusions of von Weimarn.
N. H. HARTSHORNE.

Method of determining the particle size of colloidal solutions. A. SOÓS (Kolloid-Z., 1926, **38**, 300—306).—A colloidal solution may be considered to consist of a number of equal layers, in each of which the projection of the particles is just sufficient to cover the plane of the layer. Generally, a given thickness of solution does not contain a whole number of these "complete" layers, so that if light rays are passed through the solution, the emerging light is made up of two components, for in passing through the "incomplete" layer a portion of the light beam encounters the particles and suffers change (a reduction in amplitude) and the remainder passes through unhindered. The intensity of the emergent light is not therefore directly proportional to the thickness, but is an isoperiodic function of it, producing a wave-like curve in which the wave-lengths are equal to the depth of a "complete" layer. This depth (h) can be shown to be connected with the radius of a particle (r) by the equation $r=3ch/4s$ (assuming that the particles are spherical), in which c is the concentration of the solution and s the specific gravity of the particles. The method thus developed theoretically has been tested with gold and silver hydrosols, using the yellow rays from a mercury-vapour lamp, and measuring the intensity of the emerging radiation by means of a polarisation spectrophotometer. The wave-like form of the curves obtained by plotting thickness of solution against the angular reading of the analyser is clearly marked. The values of the particle size thus obtained are about one hundredth of those given by the Zsigmondy ultramicroscopic method. This discrepancy is thought to be due to the fact that in the latter and other ultramicroscopic methods, only the large particles are counted, and distribution of the total quantity of substance amongst these leads to results which are far too high. This source of error has previously been recognised, but not its magnitude. It is pointed out that the above equation is not strictly true, since the projections of the particles can cover one another before they cover the whole field, but it is anticipated that the correction so involved would not be large. N. H. HARTSHORNE.

Influence of non-electrolytes on the precipitation of colloids by electrolytes and on the adsorption of ions. K. C. SEN (Kolloid-Z., 1926, 38, 310—314).—The coagulation of manganese dioxide sol by copper sulphate and by silver nitrate in the presence of ethyl alcohol and of sucrose has been studied. Sucrose and ethyl alcohol stabilise the sol against copper sulphate, the former to a high, and the latter to a low degree. With silver nitrate, sucrose exerts no appreciable effect, whilst ethyl alcohol sensitises the sol. The adsorption of copper sulphate and silver nitrate by air-dried hydrated manganese dioxide is increased considerably by the addition of the above non-electrolytes. The conclusion of Weiser (A., 1925, ii, 108), that adsorption of a non-electrolyte lowers the adsorption of an electrolyte, is not therefore generally valid. The effect of non-electrolytes on colloids is discussed, and it is shown that the above cases are anomalous and not susceptible to any simple explanation. The nature of the non-electrolyte is evidently of some significance.

N. H. HARTSHORNE.

Influence of some stable colloids on the flocculation of colloidal suspensions. A. BOUTARIC and (MLLE.) G. PERREAU (Rev. gén. Colloid., 1926, 4, 33—39, 75—78).—A more detailed account of work already published (A., 1925, ii, 1155).

Anomalous flocculation of clay. A. F. JOSEPH and H. B. OAKLEY (Nature, 1926, 117, 624).—Highly purified clay suspensions show no anomalous behaviour in flocculation by calcium and sodium hydroxides, but the necessary concentrations differ. Calcium compounds are much more powerful flocculants than those of sodium. If gradually increasing quantities of mixtures of chloride and hydroxide are added to a dilute clay suspension, the flocculating effect at first increases very rapidly with the concentration, then rapidly decreases, and then permanently increases. A. A. ELDRIDGE.

Dispersoidological investigations. VI. Cellulose dispergation in concentrated aqueous solutions of strontium thiocyanate, bromide, and chloride. P. P. VON WEIMARN and K. AOKI (Rep. Imp. Ind. Res. Inst., Osaka, 1925, 6, No. 10, 11—33).—Normal dispergation curves, the velocity of dispergation increasing with rising temperature, were obtained in experiments at 130—160° or 170—180° with 1 g. of cellulose in 100 c.c. of aqueous solutions of strontium thiocyanate saturated at 25°, 50°, or 75°. At constant temperature the velocity increases with increasing concentration of salt. Increase in the amount of cellulose added prolongs the time required for complete dispergation. Similar results were obtained for strontium bromide and chloride, but the rate of dispergation was much smaller.

CHEMICAL ABSTRACTS.

Dispersoidological investigations. VII. Cellulose dispergation in concentrated aqueous solutions of barium thiocyanate and bromide. P. P. VON WEIMARN and S. KATAOKA (Rep. Imp. Ind. Res. Inst., Osaka, 1925, 6, No. 10, 37—44).—The rate of dispergation of cellulose in barium thiocyanate solution is increased by rise of temperature, but reduced by exclusion of air and avoidance of stirring. Barium bromide does not effect the complete dispergation of cellulose. CHEMICAL ABSTRACTS.

Dispersoidological investigations. VIII. Cellulose dispergation in concentrated aqueous solutions of calcium bromide and chloride. P. P. VON WEIMARN and S. OTSUKA (Rep. Imp. Ind. Res. Inst., Osaka, 1925, 6, No. 10, 47—60; cf. preceding abstracts).—Cellulose is readily dispergated by saturated solutions of calcium bromide, less readily by those of the chloride. CHEMICAL ABSTRACTS.

Dispersoidological investigations. IX. Ability of thiocyanates and halides of alkaline-earth metals to produce dispergation of cellulose. P. P. VON WEIMARN (Rep. Imp. Ind. Res. Inst., Osaka, 1925, 6, No. 10, 63—67; cf. preceding abstracts).—The activity decreases in the order: salts of calcium, strontium, barium; thiocyanates, iodides, bromides, chlorides.

CHEMICAL ABSTRACTS.

Dispersoidological investigations. X. Cellulose dispergation in aqueous sodium citrate and calcium chloride solutions of extremely low concentrations. P. P. VON WEIMARN and H. HORI (Rep. Imp. Ind. Res. Inst., Osaka, 1925, 6, No. 10, 71—79).—A study of "dispersoidal solutions of the second kind," dilute solutions of cellulose in cold salt solutions, incapable of gelatinising on cooling. With sodium citrate, maximum dispergation is observed in 0·025—0·05 millimolar solutions; with calcium chloride, in 0·025 millimolar solutions.

CHEMICAL ABSTRACTS.

Colloid-chemical experiments on cholesterol. R. STERN (Klin. Woch., 1925, 4, 1650—1651; from Chem. Zentr., 1926, I, 324).—The precipitation of cholesterol from aqueous dispersions by dilute solutions of proteins does not involve any electrical effect, but is due to the dehydration of the particles of the decidedly hydrophobic cholesterol sols. J. S. CARTER.

Colloidal particles in alternating fields of various frequencies. O. BLÜH (Ann. Physik, 1926, [iv], 79, 143—144).—An earlier investigation (this vol., 23) on the dependence of the mobility of colloidal particles on the frequency resulted in a discrepancy between experiment and theory which is now accounted for mathematically. R. A. MORTON.

Swelling of caoutchouc and the constitution of the solvent. J. SALKIND (Ber., 1926, 59, [B], 525—528).—The maximum weight of liquid absorbed per unit weight of raw caoutchouc is independent of the chemical constitution of the isomeric esters, ethyl formate, and methyl acetate, but varies greatly with the structure of the three esters, $C_4H_8O_2$ (propyl formate, ethyl acetate, and methyl propionate), and the four esters, $C_5H_{10}O_2$ (*iso*butyl formate, propyl acetate, ethyl propionate, and methyl butyrate). With vulcanised rubber, the swelling is less pronounced but otherwise similar. The maximum increases with increasing mol. wt. of ester, and with isomeric esters the highest maxima are observed in the presence of a long, straight carbon chain. The radical of the acid appears to exert a greater influence than that of the alcohol. There does not appear to

be even an approximate parallelism between swelling and dielectric constant, surface tension, or density of the ester, so that in these cases Ostwald's expression $\sqrt[n]{QD}$=const. (in which Q, D, and n are the swelling pressure, dielectric constant, and a constant depending on the medium) does not appear to hold (cf. A., 1921, i, 733). The rates of swelling, calculated from the formula $K=1/t \cdot \log a/(a-x)$, diminish fairly regularly with the time and are approximately the same for isomeric esters. H. WREN.

Kinetics of the swelling and de-swelling of gels. S. LIEPATOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 55—64).—Measurements of the rate of absorption of water by glue and by gum tragacanth show that, when the swelling of a gel is not complicated by any secondary change, its velocity is given by the equation $K=1/t \cdot \log_e m/(m-Q)$, where m is the weight of the dry gel and Q the quantity of water absorbed by the gel in time t. Similar measurements of the absorption in presence of dilute solutions of potassium hydroxide, hydrochloric acid, or potassium dichromate or ferricyanide show that, when the swelling is accompanied by a secondary process, its velocity is more suitably expressed by $K=1/t \cdot \log_e m/(m-\gamma Q)$, where γ is the velocity constant of the secondary process. The latter equation embraces all known cases of the swelling of gels.

The velocity of de-swelling of a swollen gel in a medium such as alcohol depends on the rate of diffusion of water (1) from the inner to the outer layers of the gel and (2) into the surrounding liquid. This process is continuous, and its velocity is given by $K=1/(a-E)t \cdot \log_e (a-z)E/(E-z)a$, or, in some instances, more accurately by $\gamma K=1/(a-E)t \cdot \log_e (a-\gamma z)E/(E-\gamma z)a$, where a indicates the original amount of water in the gel, and E and z indicate the amounts of water which the gel gives up in infinite time and time t, respectively. These equations are in good agreement with the results obtained when glue is immersed in 40% formaldehyde solution or in methyl or ethyl alcohol, and with all other known cases of the dehydration of gels. T. H. POPE.

Method for rapid determination of cataphoresis. R. H. HUMPHRY (Kolloid-Z., 1926, **38**, 306—307).—An apparatus for rapidly ascertaining the charge on colloidal particles in non-aqueous sols consists of two aluminium plate electrodes immersed in a transparent vessel containing a non-conducting liquid which in some cases is the dispersion medium of the sol to be examined. The sol is allowed to flow in a fine stream from a capillary, either downwards or upwards, according to its density, in the space between the electrodes. On switching on the current, having conveniently a potential drop of 400 volt/cm., deviation of the stream towards one electrode or the other is observed. If, as in nickel–toluene or –paraffin sols, particles of both signs are present, the stream develops a fan-shaped form. N. H. HARTSHORNE.

Alcoholysis of salts of weak acids and weak bases in ethyl and methyl alcohol, and dissociation constants of basic ions. H. GOLDSCHMIDT and E. MATHIESEN (Z. physikal. Chem., 1926, **119**, 439—473; cf. A., 1922, ii, 135; 1924, ii, 825).—For all the bases examined, the value of the ratio, [base][acid]/[cation of base], is greater in ethyl alcohol and in water than in methyl alcohol, and in some cases greater in ethyl alcohol than in water and in others less. Addition of water to the alcoholic solutions represses the alcoholysis, but the effect is not adequately explained by the theory previously proposed (A., 1922, ii, 135), and appears to depend on a change in the dissociation both of the acid and of the basic ion. The former change is nearly the same for all the acids, but the latter varies for different bases, apparently being to some extent determined by the ratio of the dissociation constants of the basic ion in water and in the particular alcohol concerned.

R. CUTHILL.

Distribution equilibrium, degree of dissociation, and electromotive force. E. SIEGLER (Ann. sci. Univ. Jassy, 1926, **13**, 360—390).—From direct determinations of λ/λ_∞, and from the constancy of the ratio of the specific conductivities, the degree of dissociation in two mixed liquids is found to be the same when the electrolyte is in distribution equilibrium in the two solvents. The Krüger–Walden formula is applicable only to strong, but not to weak electrolytes. Between the two phases in distribution equilibrium the *E.M.F.* is zero. The connexion between dielectric constant of a liquid and the potential of a metal immersed in it exists also for mixed liquids.

E. B. LUDLAM.

Apparent dissociation constants of creatine and creatinine. G. S. EADIE and A. HUNTER (J. Biol. Chem., 1926, **67**, 237—244).—The apparent basic dissociation constant of creatine, as determined by electrometric titration with hydrochloric acid at 20°, is $9{\cdot}6\times10^{-12}$; that of creatinine, similarly determined, is $6{\cdot}3\times10^{-10}$. C. R. HARINGTON.

Ionisation constant of creatinine. C. P. MCNALLY (J. Amer. Chem. Soc., 1926, **48**, 1003—1009; cf. A., 1921, i, 515).—The ionisation constant of creatinine has been calculated (*a*) from measurements of the hydrogen-ion concentration in creatinine hydrochloride solutions, (*b*) from the hydrolysis of creatinine hydrochloride in aqueous solution, as measured by the conductivity of aqueous solutions of creatine hydrochloride, alone and in presence of an equivalent of creatinine, and (*c*) from measurements of the distribution of creatinine between aqueous acetic acid and ether. The values obtained are $7{\cdot}0\times10^{-10}$ at 25°, and $10{\cdot}1\times10^{-10}$ at 40°.

F. G. WILLSON.

Equilibrium between cupric ion, cuprous ion, and metallic copper. (MISS) F. FENWICK (J. Amer. Chem. Soc., 1926, **48**, 860—870).—The concentrations of cupric and cuprous ion in equilibrium with metallic copper at 25° were determined in perchlorate and sulphate solutions, the concentration range being 0·18—0·82*M* in the first case and 0·22—0·67*M* in the second (cf. Luther, A., 1901, ii, 301). Measurements of the *E.M.F.* of the cells: $Cu|Cu^+$ in equilibrium solution $|Hg_2^{++}$ in equilibrium solution $|Hg$ and $Hg|Hg_2(ClO_4)_2+HClO_4|HClO_4+AgClO_4|Ag$, together with certain simplifying assumptions, gave 1×10^6 for the equilibrium constant $[Cu^{++}]/[Cu^+]^2$. Variable values were obtained for this constant when

the cuprous ion was assumed bivalent. The following standard molal electrode potentials at 25° were calculated: $Cu|Cu^+$, −0·522 volt, and $Cu|Cu^{++}$, −0·167 volt. The cell $H_2|HClO_4|HClO_4+Hg_2(ClO_4)_2|Hg$ was also investigated. S. K. TWEEDY.

Dissociation of antimony pentachloride. H. BRAUNE and W. TIEDJE (Z. anorg. Chem., 1926, **152**, 39—51).—The dissociation of antimony pentachloride was determined by measuring the pressure at constant volume in a quartz bulb, heated in an electric furnace. The antimony pentachloride was previously purified by distillation at a pressure of 10 mm. Between 120° and 260°, the results are expressed by the equation $\log K_p=-3570/T+9740$, from which the heat of the gaseous reaction $SbCl_3+Cl_2=SbCl_5$ is calculated to be 16,320 cal. for a mean temperature of 200°. At the lower temperatures, equilibrium is attained very slowly, and above 300° dissociation was complete. The vapour pressure of antimony trichloride was determined from 104° to 155°, and of the pentachloride from 52° to 84°, and straight-line relationships were obtained between $\log p$ and $1/T$. The calculated heats of evaporation are 11,550 cal. for a mean temperature of 120° and 11,050 cal. for a mean temperature of 70°, respectively. With the aid of these values, the heat of the gaseous reaction is calculated from Thomsen's determination of the heat of formation of the liquid pentachloride from the solid trichloride at 20° to be 17,000 cal. A. GEAKE.

Influence of pressure on equilibrium in binary systems. III. *m*-Chloronitrobenzene, *m*-bromonitrobenzene, and their mixtures at high pressures. N. A. PUSHIN (Z. physikal. Chem., 1926, **119**, 400—404; cf. A., 1925, ii, 277).—The influence of pressures up to 2500 kg./cm.^{2} on the m. p. of the above compounds and of mixtures of the two containing, respectively, 30 and 50 g.-mol. % of *m*-bromonitrobenzene has been studied by the pyrometric method previously described (*ibid.*, 38). Over the whole range of pressures the compounds form a continuous series of solid solutions, for which the solidus and liquidus curves lie very close together. R. CUTHILL.

Distillation of heterogeneous ternary mixtures. I. System water–benzene–toluene. J. BARBAUDY (J. Chim. Phys., 1926, **23**, [iv], 289—320).—The saturated solution of benzene in water contains 0·504, 0·295, and 0·247 parts of benzene per 100 of solution at 107·4±1°, 74·3±0·05°, and 57·0±0·1°, respectively. At 69·25°, the numbers for the aqueous and benzene layers are 0·281 and 99·721, respectively. The saturated vapour curves of binary and ternary mixtures of water, benzene, and toluene have been determined by the partial condensation at fixed temperatures of previously superheated vapours. For the binary systems, the results agree with the theoretical equation $m_A=100\pi_A/P=f(t)$, where m_A is the molecular percentage of the constituent *A*, *P* the total pressure of the mixed vapour, and π_A the vapour pressure of the pure constituent *A* at the particular temperature *t*. For ternary mixtures, a corresponding equation $m_{Aq}/\pi_{Aq}=m_c/\pi_c=100/P$ can be used, where the molecular percentages refer to water and to the total hydrocarbons, respectively. The distillation and condensation of various mixtures are discussed with reference to triangular diagrams and space models. The triangular diagram is divided into two fields by a line which separates mixtures which on distillation leave a residue of water, from those which leave a residue of toluene. W. HUME-ROTHERY.

Equilibrium in the capillary layer. J. D. VAN DER WAALS, jun. (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 868—870).—Theoretical. A modification of van der Waals' calculation of the free energy of a substance in the transition layer separating the liquid from the vapour phase. M. S. BURR.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XII. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1925, **28**, 858—867; cf. A., 1925, ii, 1063).—A further consideration of osmotic equilibria in ternary systems separated by a semi-permeable membrane. Systems are discussed in which a component other than water diffuses through the membrane. M. S. BURR.

Equilibria in systems in which phases are separated by a semi-permeable membrane. XIII. Isotonic curves in ternary systems in which separation into two or three liquids is obtained. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 84—92).—Theoretical. A continuation of previous work on equilibria. M. S. BURR.

Thermodynamics of surface actions. II. Variation of surface tension with pressure. L. GAY (J. Chim. Phys., 1926, **23**, [iv], 321—352; cf. A., 1925, ii, 539).—Theoretical. Equilibrium between phases in mutual contact is discussed on the assumption that the pressure on each phase depends on the surfaces of contact. Equations are given connecting surface tension and pressure with the absorption ratio, which is defined as the total excess or defect of a constituent (per unit surface area) in the whole thickness of a surface layer, divided by the total quantity which would be present if the phases were of constant composition up to their geometrical interfaces. The validity of the equations with varying degrees of absorption is discussed. W. HUME-ROTHERY.

Vapour pressure and heat of dilution of aqueous solutions [of carbamide]. E. P. PERMAN and T. LOVETT (Trans. Faraday Soc., 1926, **22**, 1—19).—See this vol., 127.

Free energy of hydrogen fluoride. R. A. MORGEN and J. H. HILDEBRAND (J. Amer. Chem. Soc., 1926, **48**, 911—918).—From the hydrogen fluoride vapour pressures over fused potassium hydrogen fluoride, which are given between 226° and 348° by the equation $\log p(\text{mm.})=-2150/T+5·94$, and the *E.M.F.* between 223° and 272° of polarised electrodes in the same electrolyte, at which the reaction taking place is $H_2(1\text{ atm.})+F_2(1\text{ atm.})=2HF(p\text{ atm.})$, the free energy of hydrogen fluoride, ΔF, is calculated. By graphical extrapolation, $\Delta F_{298}=-32,500$ cal. for $p=1$ atm.; extrapolation with the aid of Latimer's equation for the entropy of diatomic gases (A., 1921,

ii, 380) gives the more probable value −31,800 cal. The figure obtained from the entropy and heat of reaction is −33,600 cal. Assuming ΔF_{298} is −31,800 cal., ΔF_{298} for $\frac{1}{6}(HF)_6$ is calculated to be −35,000 cal. (cf. Simons and Hildebrand, A., 1924, ii, 848). The escape of hydrogen fluoride from fused potassium hydrogen fluoride causes the formation of a more or less immiscible, viscous phase of dipotassium hydrogen fluoride, $(KF)_2,HF$. S. K. TWEEDY.

Heat of dilution of salts at very low concentrations. W. NERNST and W. ORTHMANN (Sitzungsber. Preuss. Akad. Wiss., 1926, 51—56).—The demands of the theories of Debye and Hückel (A., 1923, ii, 459) and of Ghosh (A., 1922, ii, 125) require that, at very low concentrations, the heats of dilution of salts of the same type should be the same. The present measurements show that whilst the heats of dilution of lithium chloride, calcium chloride, zinc sulphate, and calcium dithionate are positive, those of potassium chloride, potassium nitrate, and calcium nitrate are negative. There is no numerical agreement between the observed values and those calculated from the Debye–Hückel equation even after correction has been made for the electrostriction of the solution. J. S. CARTER.

Relation of Arrhenius between osmotic pressure and latent heat of evaporation. K. SCHREBER (Z. Elektrochem., 1926, **32**, 149—150).—Arrhenius, in deducing the relation between osmotic pressure and latent heat of evaporation, made a false assumption, viz., that in the vapour space the temperature is uniform. The temperature of the vapour arising from the surface of a solution, T_s, is not the same as that from the pure solvent, T. It is deduced that the osmotic pressure $\pi=rs(T_s-T)/AT$, where r and A are derived from the Clausius–Clapeyron equation, written in the form $V\times dp=r\times dt/AT$, and s is the density of the vapour. C. H. D. CLARK.

Equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion. H. R. RAIKES, A. F. YORKE, and F. K. EWART (J.C.S., 1926, 630—637).—The equivalent conductivity was measured at 18° and 10°, and the values for infinite dilution were found to be 217·0 and 180·2, respectively. Using Washburn's value for the mobility of the sodium ion, the calculated mobility of the hydroxyl ion is 173·8 and 144·3 at the two temperatures. Special care was taken to prevent ingress of carbon dioxide, and the water used had a conductivity of approximately 0·085 gemmho.

Electrical conductivity of iodo-bromine solutions of potassium iodide. V. A. PLOTNIKOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 135—142).—The solubility of potassium iodide in bromine is increased considerably by addition of iodine, and when 40% of the latter element is present, exceeds 6·5%. In spite of the low dielectric constant of the solvent, the solutions exhibit marked electrical conductivity (cf. Plotnikov and Rokotjan, A., 1913, ii, 378); for a 5% solution of the iodide in a solvent containing 36·9% of iodine, the specific conductance is 0·028, the value for a corresponding aqueous solution being 0·034. For medium concentrations the specific conductance of these solutions is greatly increased by the addition of iodine and potassium iodide. Thus, for solutions containing iodine and potassium iodide in quantities corresponding with the formula KI_{11}, increase in the concentration from 18% to 38% causes the specific conductance to increase 250-fold. When, however, the solution approaches saturation, further addition of iodine and the iodide produces little change in the conductivity. When the mixed solutes agree with the formula KI_9, the molecular conductivity diminishes on dilution of the solution.

The electrical conductivity of solutions of potassium iodide in mixtures of iodine and bromine may be explained by the formation of ionised complex polyiodides. T. H. POPE.

Electromotive behaviour of cupric oxide. R. E. W. MADDISON (Trans. Faraday Soc., 1926, **22**, 27—33).—See this vol., 130.

Effect of the electrode material on oxidation potentials. J. A. V. BUTLER, W. E. HUGH, and D. H. HEY (Trans. Faraday Soc., 1926, **22**, 24—26).—See this vol., 129.

Photovoltaic cells with unalterable electrodes. S. SCHLIVITCH (Compt. rend., 1926, **182**, 891—893).—The *P.D.* between illuminated and non-illuminated platinum wires immersed in the same salt solution has been measured. The light source was a quartz mercury-vapour lamp, the infra-red radiation being filtered out. Potassium and ammonium dichromate and sodium nitrate solutions were used. The illuminated electrode is always negative with respect to the other. The *P.D.* increases on prolonged illumination and falls when the illumination ceases. With concentrated solutions of the two last-named salts, the *P.D.* changes sign after cessation of the illumination (cf. Rule, this vol., 361). S. K. TWEEDY.

Kinetic activation as a factor in gas reactions. W. TAYLOR (Trans. Faraday Soc., 1926, **22**, 20—23).—See this vol., 124.

Interaction of nitric oxide and hydrogen and the molecular statistics of termolecular gaseous reactions. C. N. HINSHELWOOD and T. E. GREEN (J.C.S., 1926, 730—739).—A homogeneous change between nitric oxide and hydrogen in the region of 1100° Abs. has been measured, and is shown to be termolecular. It is supposed that the reaction takes place in two stages: (*a*) $2NO+H_2=N_2+H_2O_2$, (*b*) $H_2O_2+H_2=2H_2O$; or (*a*) $2NO+H_2=N_2O+H_2O$, (*b*) $H_2+N_2O=N_2+H_2O$. The velocity coefficient of the homogeneous reaction at 826° is within 10% of $1·0\times10^{-7}$, and the heat of activation is 44,000 cal. At pressures below 300 mm. of each of the gases, there is a small amount of surface reaction, which becomes relatively more important at still lower pressures. Molecular statistics of termolecular gaseous reactions are discussed at length, from the point of view of the theory of activation. H. BURTON.

Velocity-temperature coefficient in liquid media. H. ESSEX and O. GELORMINI (J. Amer. Chem. Soc., 1926, **48**, 882—894).—The velocity coefficients for the following reactions in organic solvents were determined between 10° and 60°:

(*a*) $NPhMe_2+MeI=NPhMe_3I$; (*b*) $C_5H_5N+MeI=C_5H_5NMeI$; and (*c*) $Et_3SBr=Et_2S+EtBr$ (cf. von Halban, A., 1909, ii, 722). The critical increment E ($=RT^2\times d\log_e k/dT$) shows a maximum for reactions (*a*) and (*c*) in nitrobenzene at 35°; it is practically independent of temperature for reaction (*a*) in benzyl alcohol, and, over the range 25—45°, for all three reactions in *s*-tetrachloroethane. At 55°, E is abnormally high for reaction (*c*) in the latter solvent. The values of E run parallel with those of E' calculated from the equation $d\log_e(k/\sqrt{T})/dT=E'/RT^2$, which is derived from the expression of Trautz for the velocity coefficient of a bimolecular gas reaction (cf. A., 1918, ii, 151). The results indicate in general that the energy of activation of isolated reactions in solution is independent of T, observed deviations being attributed to abnormalities in the solvent.

S. K. Tweedy.

Reaction between hydroxylamine and ferric chloride. A. D. Mitchell (J.C.S., 1926, 336—350).—The velocity of the interaction of hydroxylamine and ferric chloride in acid solution has been investigated and the influence of the products of change on the velocity determined; the course of the reaction was followed by determination of the ferric salts present by the method of Hahn and Windisch (A., 1923, ii, 262), and it can be represented approximately by the differential equation $dx/dt=k(a-x)^2(b-x)/(h+3x/2)^2(f+x)$, where a, b, h, and f represent the initial molar concentrations of ferric ions, hydroxylamine, hydrogen ions, and ferrous ions, respectively. In the absence of acid and ferrous ions, the initial velocity is very high, but this is rapidly reduced by the accumulation of hydrogen and ferrous ions, which exercise a retarding influence. Neutral salts slightly depress the velocity coefficient. An equilibrium as an intermediate stage is postulated to explain the decelerating influence of hydrogen and ferrous ions, which is probably of the type $2Fe^{\cdots}+NH_3OH^{\cdot}\rightleftharpoons Fe^{\cdot\cdot}+2H^{\cdot}+(Fe, H, NOH)^{\cdots}$, the complex then breaking down slowly, forming nitrous oxide. Rise of temperature is supposed to shift the equilibrium in a sense favourable to the reaction, thus accounting for the abnormally high temperature coefficient, which is 6·5 for 10°.

E. E. Walker.

Termolecular reactions. Reduction of silver acetate by sodium formate. A. Coutie (J.C.S., 1926, 887—893).—Noyes and Cottle's work (A., 1899, ii, 205) on the reduction of silver acetate by sodium formate affords no proof that the reaction is of the third order. Reinvestigation of the experimental conditions and the use of a slightly modified velocity equation have proved the reaction to be essentially termolecular.

H. Burton.

Variation of the hydrolysis constant of sucrose with the concentration. H. Colin and (Mlle.) A. Chaudun (Compt. rend., 1926, **182**, 775—776; cf. A., 1925, i, 233).—The initial rate of hydrolysis of sucrose by acids is raised or lowered by the addition of glycerol according as the acid is strong or weak, respectively. It is suggested that the reaction occurs by formation of a complex of sugar, water, and hydrogen ions, which then breaks up at a rate proportional to its own concentration and that of the anion of the acid.

R. Cuthill.

Theory of catalysis. II. Kinetics of mutarotation. II. H. von Euler and A. Ölander (Z. anorg. Chem., 1926, **152**, 113—132; cf. A., 1925, ii, 876).—In continuation of earlier work, the velocity of mutarotation of α-glucose has been determined at 20° in solutions of different p_H value between p_H 0·52 and p_H 9·19. The region of maximum stability of dextrose at 20° is p_H 4·83 and at 5° p_H 5·19, and the corresponding values of the specific reactivity of the dextrose anion are 66 and 7·1. Using the same nomenclature as in the previous paper, the values at 20° of the coefficients A and B are $4\cdot15\times10^{-11}$ and $18\cdot6\times10^{-2}$, respectively, $k_0=0\cdot00620$ and $K_b=2\cdot4\times10^{-17}$. The temperature coefficients of r_{q_1}, r_{q_2}, and r_{q_3} are 24,000, 18,300, and 5000 cal., respectively, and of K_a and K_w 12,400 and 14,400, respectively. On the assumption that the reaction velocity k_0 is controlled by the amphoteric ions, it is shown that $h_0=h_i\sqrt{r_{q_1}/r_{q_3}}$, where h_0 is the p_H at maximum stability and h_i that at the isoelectric point (cf. Kuhn, A., 1925, ii, 49). The symmetrical nature of the curves (mutarotation–p_H) shows that dextrose functions as a very weak acid and also as a very weak base.

A. R. Powell.

Hydrolysis in the systems TiR_4–H_2O. I. A. Athanasiu (Bul. Chim., Soc. Româna Stiinte, 1924, **27**, 81—144).—The systems titanium tetrachloride–water and titanium tetrabromide–water show continuous progressive hydrolysis, the hydrolyse being complete at maximum temperatures and dilutions. Solutions were prepared either by allowing the halides to fall drop by drop into water mechanically agitated and cooled in freezing mixtures, or by emulsifying the halides first with highly-purified paraffin and extracting the emulsions with ice water, the second method giving more consistent results; the degree of hydrolysis was determined by conductivity measurements. The rate of hydrolysis increases with temperature and dilution, and platinum exercises a catalytic effect; the rates of hydrolysis determined were for the chloride $K_v=0\cdot34\times10^{-4}$ and $1\cdot79\times10^{-4}$ for dilutions 10 and 20, respectively, at 25°, and for the bromide $K_{10}=0\cdot15\times10^{-3}$; the reaction is bimolecular, indicating a series of "consecutive" reactions between the colloidal and aqueous phases. The presence of alcohol diminishes the degree of hydrolysis and retards the rate. The results are plotted cubically, with the three rectangular axes expressing, respectively, concentration, temperature, and degree of hydrolysis.

S. I. Levy.

Determination of the rate of hydrolysis of sparingly soluble esters. R. C. Smith and H. A. Paterson (J.C.S., 1926, 940—941).—The rate of hydrolysis of propyl acetate, ethyl propionate, propyl butyrate, benzyl acetate, benzyl propionate, and phenyl acetate has been determined by a simple modification of the usual method. The results for the first three show fairly good agreement with those obtained by the ordinary method. The solubilities of the last three have been determined.

H. Burton.

Velocity of decomposition of solids. II. Rate of dissociation of cadmium carbonate. M. CENTNERSZWER and B. BRUŽS (Z. physikal. Chem., 1926, **119**, 405—418; cf. A., 1925, ii, 685).—At a given temperature, the rate of this reaction first increases for a time which is the shorter the higher the temperature, then passes through a maximum, and finally decreases in accordance with the simple unimolecular law. If, however, the products of dissociation are allowed to recombine, on heating again the period of induction is absent. It is suggested in explanation that the induction period is due to a polymorphic change of cadmium carbonate near its dissociation temperature, occurring according to the simple exponential law, and with a calculated temperature coefficient of 3·06 for 10°. For the second stage of the process, the temperature coefficient of the velocity constant is 2·02 for 10°, from which it is concluded that the decomposition of solids is a purely chemical process, not a process of diffusion. Previous compression of the carbonate does not affect the rate of its decomposition. R. CUTHILL.

Sorption kinetics. J. K. SYRKIN and L. I. BERNSTEIN (Z. anorg. Chem., 1926, **152**, 105—112).—The amount of iodine adsorbed by 1 g. of carbon from 20 c.c. of solutions of iodine in methyl alcohol, ethyl acetate, and benzene was determined after 5, 15, 30 min., and 24 hrs. at 22·5°. The actual weight of iodine adsorbed in a given time increases with increasing initial concentration, but the percentage amount diminishes. The adsorption was greatest from methyl alcohol and least from benzene, and the dielectric constants of the three solvents are in the same order. A. GEAKE.

Liquid-line corrosion. E. S. HEDGES (J.C.S., 1926, 831—833).—Evidence is brought forward to show that the enhanced corrosion occurring at the liquid line when strips of metals are immersed in liquids having either a chemical action or a solvent effect on them, is due to a film of liquid at the junction of the metal and liquid. Similar results were obtained either in the presence of oxygen at the surface or in an atmosphere of hydrogen. Excessive corrosion occurs also with marble in dilute acids, even when the evolution of gas is sufficient to cause an upward streaming of the soluble product. The hypothesis of Spring (A., 1890, ii, 328) is supported by these results. H. BURTON.

New type of gaseous catalysis. S. C. LIND and D. C. BARDWELL (Science, 1925, **62**, 593—594).—Helium, neon, and argon have, equally with nitrogen, the power of causing the polymerisation of acetylene in the presence of radon, introduced as an ionising source. Nitrogen and argon also catalyse the synthesis of water. Argon, but not carbon dioxide, catalyses the oxidation of carbon monoxide. Compton supposes that when the inert gas has a higher ionisation potential than the reacting gas, the reaction, *e.g.*, $Ne^+ + C_2H_2 = Ne + C_2H_2^+$ takes place, the acetylene then behaving as if it had been originally formed by an α-particle collision. A. A. ELDRIDGE.

Catalysis of the reaction between arsenious acid and permanganic acid and its analytical application. R. LANG (Z. anorg. Chem., 1926, **152**, 197—206).—Very small quantities of potassium iodide, potassium iodate, or silver chloride accelerate the reaction between arsenious acid and permanganate, so that it takes place practically instantaneously on mixing the two solutions. For the titration of arsenious acid with permanganate the solution should be either 0·5—2*N*-hydrochloric acid or at least 0·5*N*-sulphuric acid, and should contain about 1 g. of sodium chloride per 100 c.c.; 1 drop of a 0·0025*N*-solution of potassium iodide or iodate is added, and the liquid titrated directly with permanganate to a pale pink colour, or the end-point may be obtained potentiometrically. The converse method for determining permanganate gives accurate results only when the end-point is determined potentiometrically; the arsenious acid is added to the sulphuric acid solution of permanganate until the latter becomes green; 1 g. of sodium chloride is added, followed by 1 drop of the catalyst, and the titration is finished as usual. For the determination of chromic acid, an excess of arsenious acid is added, followed after 1 min. by the catalyst, and the excess is then titrated with permanganate. Vanadyl salts in hydrochloric acid are determined by adding manganese sulphate and an excess of permanganate and titrating potentiometrically with arsenious acid, using 1 drop of 0·0025*M*-potassium iodide solution as catalyst. A. R. POWELL.

Mechanism of the oxidation of manganese [in a manganous salt] to permanganic acid by the Proctor–Smith reaction. A. TRAVERS (Compt. rend., 1926, **182**, 972—973).—The reaction $7AgNO_3 + 3(NH_4)_2S_2O_8 + 6H_2O \rightleftharpoons 3Ag_2O_2,AgNO_3 + 3(NH_4)_2SO_4 + 3H_2SO_4 + 6HNO_3$, is used to illustrate the instantaneous oxidation in the cold to permanganic acid which takes place when a manganous salt is added to the reagents producing the above reaction. Thus if 10% of acid is previously added to the silver nitrate, the silver compound is produced in a black, colloidal form; the manganous salt upsets the equilibrium, which is restored gradually, the liquid appearing wine-red in colour owing to the superposition of the violet of the permanganic acid on the black silver compound. A further addition of manganous salt again reverses the reaction, and the true violet of the permanganic acid is seen, followed by the above changes. The silver peroxide–nitrate plays the part of a catalyst. J. GRANT.

Autoxidation and anti-oxygenic action. Catalytic action of nitrogen compounds. C. MOUREU and C. DUFRAISSE (Compt. rend., 1926, **182**, 949—951).—The authors develop their theory (cf. A., 1925, ii, 561) of the relation between the oxidisability of an element and the catalytic properties it confers on the molecule. Comparison is drawn between the affinities for oxygen of nitrogen and phosphorus, in this respect the two extreme elements of the nitrogen group. It is concluded that the catalytic properties of oxygen are shown most markedly when it is combined in a molecule. J. GRANT.

Production of hydrogen chloride from chlorine and steam in the presence of carbon. B. NEUMANN and R. DOMKE.—See B., 1926, 358.

Production of hydrogen bromide from bromine and water vapour in the presence of carbon. B. NEUMANN, W. STEUER, and R. DOMKE.—See B., 1926, 358.

Autoxidisable system as an example of catalysis by heavy metals. E. WERTHEIMER (Fermentforsch., 1926, **8**, 497—517).—The oxidation of α-naphthol and *p*-phenylenediamine to indophenol-blue is taken as an example of catalysis by heavy metals and also as a model of cell respiration. Substances which form complex salts with or precipitate the heavy metals—such as hydrogen cyanide or sulphide—inhibit the oxidation. Among other substances, amino-acids also inhibit the oxidation, and the inhibition caused by the various amino-acids runs parallel to their respective ease of complex salt formation. The addition of a heavy metal removes the inhibition, and the quantitative relation is stoicheiometric. The oxidation system has an optimum between p_H 8 and 9. At about this reaction the anions inhibit the oxidation in the following order $CNS > I > Cl > PO_4 > NO_3 > CH_3{\cdot}CO_2 > SO_4$, and the cations in the order $Na > NH_4 > Cs > K > Mg > Ca$. At p_H 4, however, anions and cations accelerate oxidation, the acceleration of the anions being in the order $I > CNS > Cl > PO_4 > SO_4$. The activity of the ions in the Hofmeister series depends on the influence of these on the dispersion condition of the heavy metal.

H. I. COOMBS.

Comparison of the catalytic oxidation of hydrocyanic acid and ammonia. L. ANDRUSSOV (Ber., 1926, **59**, [*B*], 458—461).—A parallelism exists between the combustion of ammonia and hydrocyanic acid, since, in accordance with the schemes $NH_3+O_2=NH_3O_2=HNO+H_2O$ and $HCN+O_2=HCNO_2=HNO+CO$, nitroxyl is formed in each case and subsequently becomes decomposed in accordance with the equation $2HNO \rightleftharpoons H_2+2NO$; all these reactions are reversible. Nitroxyl can also react with ammonia or hydrocyanic acid, yielding either water or carbon monoxide and di-imide, which immediately decomposes into nitrogen and hydrogen. This reaction explains the formation of large quantities of nitrogen at a platinum contact at temperatures below 600°, whereas at higher temperatures the reactions leading to the production of nitric oxide are predominant. The period of contact with the catalyst necessary for the accomplishment of these reactions is very short (about 10^{-4} sec.). At temperatures above 550° with prolonged time of contact production of nitrogen is also due to thermal decomposition of ammonia, nitric oxide, nitroxyl, or hydrocyanic acid. The influence of this type of change can be almost nullified by suitably increasing the velocity of the gas current.

H. WREN.

Catalytic oxidation of ammonia. L. ANDRUSSOV.—See B., 1926, 318.

Preparation of the catalyst for Heslinga's determination of the elements. J. C. M. SAUERBIER (Chem. Weekblad, 1926, **23**, 168—169).—The catalyst prepared in the ordinary way contains manganese sulphate and carbonate; the latter make the results for carbon dioxide too high, especially if the material analysed contains much hydrogen. A satisfactory catalyst is obtained by addition of potassium permanganate to the equivalent quantity of manganous sulphate in nitric acid solution; the precipitate is washed, dried, and heated at 300°. It is advantageous to use a mixture of air and oxygen instead of air alone.

S. I. LEVY.

Behaviour of centres of activity of saturated surfaces during the initial stages of unimolecular reactions. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1926, **23**, 172—182; cf. A., 1925, ii, 804, 983; this vol., 250).—Decrease in pressure of the reactant has little effect on the velocity of unimolecular reactions on saturated catalysing surfaces, whilst inert diluents cause a marked decrease. This may be explained on the basis of Langmuir and Frenkel's theories of adsorption taken in conjunction with the modern theory of centres of activity on the catalysing surface, since the molecules of inert gas will be adsorbed by the active centres to an extent depending on their relative concentration and other factors, and will thus retard the adsorption of the reacting molecules. This explanation is confirmed qualitatively by experimental evidence, and the quantitative relations have now been worked out theoretically, independently of the mechanism of chemical change. If p be the fractional pressure of the reactant in the mixture, and v the fractional reaction velocity, then $1/v=(1-\lambda)+\lambda/p$; $\lambda=(\tau_0''e^{\mu_0''/RT}/\tau_0'e^{\mu_0'/RT})(M_1/M_2)^{\frac{1}{2}}$, where M_1 and M_2 are the mol. wts., τ_0' and τ_0'' the vibration frequencies perpendicular to the catalysing surface, and μ_0' and μ_0'' the heat of desorption per g.-mol. of reactant and diluent, respectively. Thus, although λ is independent of the pressure for homogeneous centres, it is independent of the temperature only if the heats of desorption of the two molecules are equal. If λ be very large, then v becomes small and the diluent acts as a catalytic poison. In general, when the diluent is a strong poison, its heat of desorption is much greater than that of the reactant, so that, with increase of temperature, the poisoning effect is reduced. This has often been observed experimentally. When λ is small, very little reduction occurs in the reaction velocity, and if $\lambda=1$, the two types of molecules behave similarly, except that one can react and the other cannot, and $v=p$, *i.e.*, the reaction velocity is proportional to the partial pressure of the reactants. The expression may be extended to multimolecular reactions and the composition of the adsorbed film in contact with a given gaseous atmosphere may be calculated. Experimental evidence confirms the expressions deduced.

M. S. BURR.

Oxidations on charcoal. W. M. WRIGHT (Proc. Camb. Phil. Soc., 1926, **23**, 187—190).—The rate of autoxidation of activated sugar charcoal is independent of the pressure of oxygen. It thus appears to take place on very active parts of the charcoal surface which are always saturated with oxygen, the rate of reaction being equal to the rate of evaporation of carbon dioxide from these. Attempts made to

measure the area of the autoxidisable surface by fractional poisoning with potassium cyanide or amyl alcohol indicate that not more than 0·38% of the surface is autoxidisable. The oxidation of oxalic acid on the surface of sugar charcoal is not coupled with autoxidation of charcoal, since this can be inhibited by poisoning without affecting the rate of the first reaction. It is due, however, to a larger, less active surface. These two surfaces are also found, but relatively more active, on blood charcoal. The small, highly active surface probably contains iron, and is preferentially poisoned by potassium cyanide. The temperature coefficients of each of the active surfaces have been determined, and hence the heats of activation. The activity of nitrogen-free charcoals is increased by the introduction of small quantities of iron, contrary to the statement of Warburg (A., 1924, ii, 466). The introduction of nitrogen has been shown to increase the specific surface of the charcoal, so that nitrogenous charcoals are, in general, more efficient catalysts than pure sugar charcoals. The iron–carbon–nitrogen complex also appears to be more active catalytically than the iron–carbon union. M. S. Burr.

Formation of hydrogen peroxide from electrolytic gas by optically-excited mercury atoms. K. F. Bonhoeffer and S. Loeb (Z. physikal. Chem., 1926, **119**, 474—476; cf. Taylor and Marshall, A., 1925, ii, 1078).—Hydrogen peroxide has been detected as an intermediate product in the reaction between hydrogen and oxygen induced by optically-activated mercury atoms. R. Cuthill.

Influence of an illuminated mercury surface on the Franck–Cario reactions. H. S. Hirst (Proc. Camb. Phil. Soc., 1926, **23**, 162—171).—When hydrogen, enclosed in silica tubes over mercury, unites with such gases as oxygen, ethylene, and carbon monoxide, under the influence of ultra-violet light, the velocity of reaction is greatly increased by illuminating the mercury surface with light strong in the line λ=2536·7 Å., and is approximately proportional to the area of surface illuminated. No such effect is observed with mercury vapour alone. The formation of a film of mercuric oxide or other reaction product on the surface of the mercury reduces its catalytic efficiency. The black oxide film is obtained only when hydrogen is present with oxygen. In the case of nitrogen–hydrogen mixtures, hydrazine and ammonia have been detected in the reaction products, and in hydrogen–oxygen mixtures hydrogen peroxide and water, probably indicating that these reactions proceed in steps. No definite conclusions can be reached as to the mechanism of the phenomena observed. It is probably related, however, to the observations of Franck and Cario (A., 1922, ii, 809) on the production of an activated hydrogen by collisions of the second kind with mercury atoms primarily activated close to the metal surface by absorption of resonance radiation of wave-length 2536·7 Å. M. S. Burr.

Direct oxidation of manganous ion to permanganate. A. N. Campbell (Trans. Faraday Soc., 1926, **22**, 46—51).—See this vol., 366.

Electrolytic deposition of antimony from acid and alkaline solutions. J. Lukas and A. Jílek (Chem. Listy, 1926, **20**, 63—67, 130—132, 170—173).—To obtain bright, firmly-adherent deposits of antimony from acid solutions, the substance, containing less than 0·3 g. of antimony, is dissolved in 3 c.c. of concentrated sulphuric acid; water is added and the solution treated with 12·5 g. of ammonium citrate, 2 g. of disodium hydrogen phosphate, and 2 c.c. of hydrazine hydrate, and electrolysed for 2 hrs. at 70—90°, using a current of 1 amp. at 1·6—2·1 volts and a rotating anode. If a stationary anode is employed, the electrolysis should be conducted with 0·5 amp. for 3 hrs. The citrate may be replaced by 11 g. of sodium potassium tartrate, but the deposits then obtained are not quite so brilliant. Good deposits are produced also by using ammonium instead of sodium phosphate and neutralising the solution (to methyl-orange) with ammonia before adding the hydrazine hydrate. A. R. Powell.

Electrolytic water. [Anodic oxidation of chromic oxide.] R. Saxon (Chem. News, 1926, **132**, 310).—Traces of chromic acid are formed by the anodic oxidation of chromic oxide in pure water; addition of manganese dioxide to the chromic oxide increases slightly the yield of chromic acid. Much more rapid oxidation ensues in the presence of calcium or potassium hydroxide or both. In solutions of alkali chlorides containing a little chrome alum, chromic oxide is rapidly oxidised at the anode to chromic acid. A. R. Powell.

Present position in photochemistry. E. K. Rideal (Trans. Faraday Soc., 1926, **21**, 652—656, and Z. physikal. Chem., 1926, **120**, 313—319).—A summary of the discussion before the Faraday Society, October, 1925.

Conclusions from recent work on photochemistry. D. L. Chapman (Trans. Faraday Soc., 1926, **21**, 547—553, and Z. physikal. Chem., 1926, **120**, 163—173).—See A., 1925, ii, 1078.

Elementary processes of photochemical reactions. J. Franck (Trans. Faraday Soc., 1926, **21**, 536—542, and Z. physikal. Chem., 1926, **120**, 144—156).—See A., 1925, ii, 1077.

Formation of polar compounds by photochemical reactions. W. A. Noyes, jun. (Trans. Faraday Soc., 1926, **21**, 569—572, and Z. physikal. Chem., 1926, **120**, 196—201).—See A., 1925, ii, 1081.

Photosensitisation and mechanism of chemical reactions. H. S. Taylor (Trans. Faraday Soc., 1926, **21**, 560—568, and Z. physikal. Chem., 1926, **120**, 183—195).—See A., 1925, ii, 1078.

Photochemical sensitisation. A. Berthoud (Trans. Faraday Soc., 1926, **21**, 554—559, and Z. physikal. Chem., 1926, **120**, 174—182).—See A., 1925, ii, 1083.

Fundamental laws of photochemistry. I. Plotnikov (Trans. Faraday Soc., 1926, **21**, 484—488, and Z. physikal. Chem., 1926, **120**, 69—74).—A review of the subject in which the Wittner–Nernst–Wegscheider theory of the effect of the intensity of the light and Einstein's photochemical

equivalent theory are condemned, in favour of the quantum theory with the Grotthus–van 't Hoff law of chemical absorption as a fundamental basis. J. GRANT.

Einstein's law of photochemical equivalence. N. R. DHAR and B. K. MUKERJI (Trans. Faraday Soc., 1926, **21**, 489—493, and Z. physikal. Chem., 1926, **120**, 75—82).—See A., 1925, ii, 1075.

Confirmation of the Einstein law of photochemical equivalence in a very simple photochemical reaction. F. WEIGERT and L. BRODMANN (Trans. Faraday Soc., 1926, **21**, 453—458, and Z. physikal. Chem., 1926, **120**, 24—31).—See A., 1925, ii, 1075.

Einstein's law of photochemical equivalence. A. J. ALLMAND (Trans. Faraday Soc., 1926, **21**, 438—452, and Z. physikal. Chem., 1926, **120**, 1—23).—See A., 1925, ii, 1074.

Law of photochemical equivalence and place of the quantum theory in relation to the atomic theory and energetics. D. BERTHELOT (Trans. Faraday Soc., 1926, **21**, 463—474, and Z. physikal. Chem., 1926, **120**, 38—57).—See A., 1925, ii, 1022.

Function of radiation in unimolecular reactions. H. S. HIRST and E. K. RIDEAL (Trans. Faraday Soc., 1926, **21**, 508—511, and Z. physikal. Chem., 1926, **120**, 103—108).—Theories of the function of radiation in unimolecular reactions are discussed. It is suggested that the energy of activation of the molecules is present in a system as the internal molecular energy contributing to the internal molecular heat content. The problem is therefore the explanation of the mechanism by which energy is transferred between molecules in accordance with Maxwell's distribution law. If the explanation is in the emission and absorption of radiation of frequencies making up the various possible quantum states of the internal specific heat, as well as in the slow method of collision, it is necessary ultimately to accept quanta travelling solely along the Poynting vector connecting the molecules (cf. Sir J. J. Thomson's theory of light). The alternative explanation favoured is a theory of fluctuations analogous to those of energy and density observed in colloid particles under Brownian movement. This arises from the formation of active molecules in a time corresponding with the vibration period of the oscillator, and manifested by the sudden disappearance and appearance of the same amount of energy in different parts of the vessel. J. GRANT.

Relations between the velocity of photochemical reactions and wave-length. P. LASAREV (Trans. Faraday Soc., 1926, **21**, 475—476, and Z. physikal. Chem., 1926, **120**, 58—59).—Further data are given in support of the author's earlier conclusion that the velocity of photochemical reactions is proportional to the absorbed energy and independent of the wave-length of the activating light. J. GRANT.

Photochemical reactions and methods of measuring them. I. PLOTNIKOV (Trans. Faraday Soc., 1926, **21**, 637—643, and Z. physikal. Chem., 1926, **120**, 291—301).—The limitations of the Grotthus–van 't Hoff photochemical absorption law, and of Beer's law on which it depends, are discussed. The former may not be applied without objection except in the rare cases of substances having one narrow spectral line claimed wholly by photochemical absorption. In its simplest form it obtains solely within the line of "pure photochemical absorption," where the temperature coefficient and reaction velocity constant are independent of the wave-length. In the case of the distribution between two or more components of the light absorbed, the total absorbed light may be divided in the ratio of the partial absorption to the sum of both absorptions. Complications are introduced also by the absorption of chemically active light by photochemically non-active components, and by the presence of several photoactive components. Pure light reactions obeying photochemical laws, and unaccompanied by dark reactions obeying mass action laws, are rare. Consequently all factors which determine or disturb the course of reaction must be taken into account beforehand. J. GRANT.

Yield of photochemical reactions with complex light in comparison with that obtained with the component lights. M. PADOA (Trans. Faraday Soc., 1926, **21**, 573—574, and Z. physikal. Chem., 1926, **120**, 202—204; cf. A., 1924, ii, 322).—In the formation of hydrogen chloride from its elements the photochemical activity of white light is greater than that of the spectrum and of the component monochromatic lights in the ratios 1·56 : 1 and 1·62 : 1, respectively. The yield is independent of the extent of the zone illuminated with white light, but diminishes as the spectrum is widened. In the bromination of cinnamic acid, the total effect of exposure of different portions of the liquid to the separate component rays is 172% and 189% of that of white light in chloroform and carbon tetrachloride solutions, respectively. On exposure of the same portion of the liquid to all the rays, the corresponding values are 284% and 366% if the rays of smallest wave-length are used first, and 233% for both solvents for the reverse order. If the effect of the induction period is eliminated by allowing the rays to act always on fresh solutions and with equal photochemical intensities, the corresponding values are 320% and 169%. The use of a light filter passing only 45% of the luminous energy produces, in chloroform solution, an action equal to that of white light. J. GRANT.

Relation between velocity of photochemical reactions and dielectric constant. C. WINTHER (Trans. Faraday Soc., 1926, **21**, 595—596, and Z. physikal. Chem., 1926, **120**, 234—235).—See A., 1925, ii, 1082.

Photo-activity of chlorine. W. TAYLOR (Trans. Faraday Soc., 1926, **21**, 614—619, and Z. physikal. Chem., 1926, **120**, 261—267).—See A., 1925, ii, 1079.

Rôle of water in the photosynthesis of hydrogen chloride. R. G. W. NORRISH (Trans. Faraday Soc., 1926, **21**, 575—580, and Z. physikal. Chem., 1926, **120**, 205—213).—See A., 1925, ii, 1080.

Rôle of water vapour in the photosynthesis of hydrogen chloride. J. CATHALA (Bull. Soc. chim., 1926, [iv], **39**, 612—620).—The curve proposed by Coehn and Jung to represent their results on the catalytic influence of water vapour on the synthesis of hydrogen chloride is shown to be meaningless, and consequently Norrish's theory of this catalysis is erroneous. Apart from this, the theory is contrary to experience. It requires, moreover, that the induction period produced by traces of ammonia should be proportional to the total volume of gas and inversely proportional to the illuminated surface. The former, however, does not follow exclusively from this theory, and the experiment cited by Norrish in support of the second statement is interpreted as indicating the period to be independent of the illuminated surface. The objections raised by Norrish to the author's theory (A., 1925, ii, 812) are discussed.

S. K. TWEEDY.

Photochemical and thermal decomposition of ozone. R. O. GRIFFITH and A. MCKEOWN (Trans. Faraday Soc., 1926, **21**, 597—602, and Z. physikal. Chem., 1926, **120**, 236—244).—See A., 1925, ii, 1080.

Mechanism of the ozone–chlorine reaction. A. J. ALLMAND (Trans. Faraday Soc., 1926, **21**, 603—605, and Z. physikal. Chem., 1926, **120**, 245—249).—See A., 1925, ii, 1079.

Photolysis of methylene-blue sensitised by zinc oxide. E. BAUR (Trans. Faraday Soc., 1926, **21**, 627—629, and Z. physikal. Chem., 1926, **120**, 278—281).—See A., 1925, ii, 1082.

Dissociation theory and photochemical thresholds. E. J. BOWEN (Trans. Faraday Soc., 1926, **21**, 543—546, and Z. physikal. Chem., 1926, **120**, 157—162).—See A., 1925, ii, 1074.

Mechanism of photochemical reactions. M. BODENSTEIN (Trans. Faraday Soc., 1926, **21**, 525—535, and Z. physikal. Chem., 1926, **120**, 129—143).—See A., 1925, ii, 1075.

Influence of radiation on chemical reactions. L. S. ORNSTEIN (Trans. Faraday Soc., 1926, **21**, 504—507, and Z. physikal. Chem., 1926, **120**, 98—102).—See A., 1925, ii, 1077.

Radiation theory of chemical reaction. J. RICE (Trans. Faraday Soc., 1926, **21**, 494—503, and Z. physikal. Chem., 1926, **120**, 83—97).—See A., 1925, ii, 1076.

Transformation of atoms into radiation. O. STERN (Trans. Faraday Soc., 1926, **21**, 477—478, and Z. physikal. Chem., 1926, **120**, 60—62).—See A., 1925, ii, 1021.

Relation between quantum sensitivity and intensity of radiation. C. WINTHER (Trans. Faraday Soc., 1926, **21**, 459—462, and Z. physikal. Chem., 1926, **120**, 32—37).—See A., 1925, ii, 1074.

Law and mechanism of unimolecular reaction. S. C. ROY (Trans. Faraday Soc., 1926, **21**, 512—513, and Z. physikal. Chem., 1926, **120**, 109—112).—See this vol., 483.

Mechanism of photochemical reactions. N. R. DHAR and B. K. MUKERJI (Trans. Faraday Soc., 1926, **21**, 645—650, and Z. physikal. Chem., 1926, **120**, 302—310).—See A., 1925, ii, 1079.

Becquerel effect on copper oxide electrodes. W. J. D. VAN DIJCK (Trans. Faraday Soc., 1926, **21**, 630—636, and Z. physikal. Chem., 1926, **120**, 282—290).—See A., 1925, ii, 1083.

Absorption of light by solutions of electrolytes. H. VON HALBAN (Trans. Faraday Soc., 1926, **21**, 620—626, and Z. physikal. Chem., 1926, **120**, 268—277).—See A., 1925, ii, 1083.

Effect of infra-red radiation on the combustion of gaseous mixtures containing nitrogen. W. T. DAVID, S. G. RICHARDSON, and W. DAVIES (Proc. Leeds Phil. Soc. [Sci.], 1925, **1**, [1], 37—39; cf. A., 1925, ii, 980).—When the nitrogen of the air in the inflammable gaseous mixtures previously investigated is replaced by argon, oxygen, carbon dioxide, or the combustible gas itself, infra-red radiation appears to have little or no effect on the rate of combustion. It is suggested that during combustion in closed vessels there is a temporary association between molecules of nitrogen (or of nitrogen oxides) and those of the combustible gas which tends to retard combustion. Such an association is partly inhibited when the molecules of combustible gas acquire vibratory energy by absorption of infra-red radiation, with consequent increase in the rate of combustion.

J. S. CARTER.

Photochemical properties of chromates. I. PLOTNIKOV and M. KARSULIN (Z. Physik, 1926, **36**, 277—287).—Photographs of the absorption spectrum of potassium dichromate were taken by a large Hilger spectrograph and the absorption constant was determined for the visible region by a König–Martens type of photometer. Experiments with chromated gelatin and a 90,000-candle power arc lamp produced an insoluble brown strip of gelatin in the region of photochemical activity; the gelatin on the rest of the plate dissolved away in water. Collodion together with ammonium dichromate and cresyl-blue 2BS was found to give a plate that was stable in the dark and changed under the action of light into a red and a red-fluorescent colour. Dichromate absorption of light begins at 595 μμ and extends towards the extreme ultra-violet. The "photochemical absorption" also begins at 595 in the yellow; at 500 in the green, it reaches a maximum, and then decreases to about 240 μμ. Einstein's law was found to be inapplicable. Ultra-microscopical observations were made on many dyes and photomicrographs were taken.

E. B. LUDLAM.

Photochemistry of silver chloride, bromide, and thiocyanate. R. SCHWARZ and K. DIEFFENBACHER (Z. anorg. Chem., 1926, **152**, 91—98; cf. A., 1921, ii, 614; 1923, ii, 815; 1924, ii, 550).—The rate of decomposition by light of silver chloride containing adsorbed anions or cations has been measured by determining the amount of chlorine evolved. Acetate, citrate, tartrate, tetraborate, and sulphate are without significant effect. Copper, lead, barium, and thallium

reduced the decomposition to 33, 32, 68, and 29%, respectively, of that of the silver chloride containing adsorbed silver ions only. In each case, 50 mol. % of the foreign nitrate was added to silver nitrate, and an amount of sodium chloride added less than sufficient to precipitate all the silver. Thallium chloride is isomorphous with the silver salt, and it was found to the extent of 0·6% in the impure silver chloride. The other metals do not form isomorphous chlorides, and only 0·004% of copper was found. The poisoning effect of these cations is ascribed to their preventing the normal increase in grain size, or "ageing," which results in increased sensitivity to light. Adsorbed hydrogen ion accelerates decomposition, and acid is known to assist flocculation. Silver thiocyanate is much less sensitive to light than the chloride or bromide. Darkening is first observable after exposure to 400×10^3 metre-candle-seconds, and darkening after development after 200×10^3 metre-candle-seconds; the corresponding figures for silver bromide containing adsorbed silver are 2080 and 0·6, respectively. When silver bromide, containing adsorbed bromine, without a binding medium, is exposed to light and developed with quinol, the darkening is parallel to the intensity up to 12×10^3 metre-candle-seconds, a definite diminution of the darkening occurs at an intensity of $18{\cdot}7 \times 10^3$, and at 75×10^3 this has become more pronounced, and the darkening is then comparable with that produced by an illumination of 2×10^3 metre-candle-seconds. In the presence of adsorbed silver, solarisation commences at $33{\cdot}3 \times 10^3$ metre-candle-seconds and the darkening is much greater than in the presence of bromine. The primary darkening of silver bromide does not show this phenomenon, which is therefore connected with the development process.

A. GEAKE.

Nature of the action on a photographic plate of sawdust and cholesterol irradiated by a mercury-vapour quartz lamp. N. S. LUCAS (Biochem. J., 1926, **20**, 23—25).—The action on a photographic plate of sawdust after irradiation is due to the production and subsequent gradual emanation of ozone or hydrogen peroxide and not to a secondary radiation.

S. S. ZILVA.

Nature of optical sensitisation and desensitisation. G. KÖGEL and A. STEIGMANN.—See B., 1926, 386.

Decomposition of carbon dioxide under reduced pressure by spark discharge. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1926, **182**, 1026—1028; cf. Jolibois, A., 1925, ii, 1194).—Carbon dioxide at pressures varying between 0·3 and 20 mm. of mercury was subjected to a spark discharge from a condenser of known capacity, the voltage of which was determined before and after the discharge. The degree of dissociation into the monoxide and oxygen was determined from the pressure and compared with the energy supplied by each spark. About 20% of the energy of the first spark was converted into chemical energy, the remainder being dissipated. A limiting dissociation of 90% was attained.

F. G. SOPER.

Reactions of active hydrogen with gases. E. BOEHM and K. F. BONHOEFFER (Z. physikal. Chem., 1926, **119**, 385—399; cf. A., 1925, ii, 839).—Active hydrogen does not react with water vapour, nitrogen, ammonia, or methane. With oxygen, hydrogen peroxide is formed, with carbon dioxide or monoxide traces of formaldehyde, and with chlorine and bromine the corresponding hydrogen halides, which apparently themselves then react to some extent, thus: $H + HX = H_2 + X$. Hydrogen sulphide, hydrogen bromide, hydrogen chloride, and methyl chloride cause de-activation, probably owing to some such reactions as the above, although in this case free halogens have not actually been detected in the products of reaction. Addition of oxygen to the hydrogen before activation increases its reactive power with bromine. Quantities of hydrogen sulphide above 1% repress the Balmer spectrum; smaller quantities have no effect.

R. CUTHILL.

Hydrogen electrode studies of the reactions between solutions of salts of weak metallic bases and sodium acetate, oxalate, and tartrate. Effect of dextrose on zirconium chloride solution. H. T. S. BRITTON (J.C.S., 1926, 269—299; cf. this vol., 247).—Sodium acetate fails, at the ordinary temperature, to precipitate zirconium, thorium, and chromium hydroxides from solutions of their salts, although the p_H values at which precipitation normally occurs are exceeded. Thorium sulphate is exceptional, the basic sulphate being precipitated when the p_H reaches 3·4 (normal precipitation value 3·5), although this redissolves in excess of sodium acetate. In the case of chromium salts the precipitation p_H is not exceeded and no precipitation occurs, but the chromium in solution can be precipitated at any stage by alkali. Under certain conditions the chromium when combined with acetic acid may be made resistant to precipitation by alkali by boiling.

Sodium oxalate precipitates a basic oxalate from zirconium chloride solution, through the incapacity of the second stage of dissociation of oxalic acid to interact with zirconium hydroxide, but the precipitate dissolves in excess of sodium oxalate. No precipitate is formed from solutions of the sulphate except in the presence of traces of another salt such as the chloride or nitrate. No precipitates are formed from salt solutions of slightly stronger bases, although probably very little interaction takes place between the weak bases, such as chromium and aluminium hydroxides, and the hydro-oxalate ions. Observations have been made on complex solutions of chromium hydroxide in oxalic acid and on the double oxalate of chromium and potassium. The titration curve gives no evidence of the existence of a tribasic acid, and to a large extent the colour seems to be due to colloidal chromium hydroxide. Measurements of p_H on the freshly dissolved double salt indicate that changes take place when this is dissolved in water. This is considered to be the cause of the racemisation of Werner's optically active form of the salt. Although the precipitation p_H (4·14) of aluminium hydroxide is exceeded when the sulphate is titrated with sodium oxalate, no precipitation occurs.

The action of sodium tartrate on solutions of salts

of zirconium, thorium, and aluminium is remarkable in that, owing to the failure of much of the tartaric acid to react with the respective bases, increased hydrogen-ion concentrations are produced, and in the case of zirconium and thorium salt solution, basic tartrate precipitates are formed, even though the hydrogen-ion concentrations are considerably higher than those required for the precipitation of the hydroxides. These basic precipitates dissolve in excess of sodium tartrate, and appear to exist unchanged in solution. The behaviour of salts of beryllium, zinc, chromium, and lanthanum was also examined. Complex tartrate solutions which are not precipitated by alkalis appear to contain basic tartrate complexes which are probably colloidal in nature, and are rendered stable by the presence of the hydroxyl groups of the tartrate. Similar increased stability may be brought about by the presence of glycerol or dextrose in solution. Hydrogen electrode titrations of zirconium chloride solutions containing dextrose with sodium hydroxide show that some interaction takes place between the zirconium hydroxide and the dextrose. E. E. WALKER.

Interaction between copper and sulphuric acid. C. W. ROGERS (J.C.S., 1926, 254—269).—At all temperatures between 16° and 270° the completed reaction is $Cu+2H_2SO_4=SO_2+CuSO_4+2H_2O$, representing the end results of at least four different interactions, which have been studied separately: (i) $5Cu+4H_2SO_4=Cu_2S+3CuSO_4+4H_2O$; (ii) $Cu_2S+2H_2SO_4=CuS+CuSO_4+2H_2O+SO_2$; (iii) $CuS+2H_2SO_4=CuSO_4+2H_2O+SO_2+S$; (iv) $S+2H_2SO_4=2H_2O+3SO_2$. The nature of the products formed at any intermediate stage is governed by the relative rates of these various interactions under the particular conditions of temperature and concentration. The temperature range 100—120° is particularly favourable to the formation of sulphides, because at this temperature the rate of interaction between the sulphides and acid is slow compared with the rate of that between acid and copper. At 270°, the rate of disappearance of sulphides is so great that their presence as intermediate products is not readily detected. The crystalline deposit which is formed consists of anhydrous cupric sulphate, this substance being at least dimorphous. At the lower temperatures, the crystals contain inclusions of sulphide and sulphur, which are thus prevented from interacting with the acids. E. E. WALKER.

Hydrolytic action of low-pressure superheated steam on salts of the alkaline-earth metals. P. L. ROBINSON, H. C. SMITH, and H. V. A. BRISCOE (J.C.S., 1926, 836—839).—Quantitative experiments on the hydrolysis of the chlorides, bromides, and carbonates of calcium, strontium, and barium, by steam at atmospheric pressure, have been carried out at temperatures varying from 400° to 980°. Whilst the results obtained from the carbonates are difficult to interpret, the ease of decomposition of any alkaline-earth metal salt is in the order chloride, bromide, whilst for any particular halide it increases in the order barium, strontium, calcium. The sulphates of calcium, strontium, and barium, as well as calcium phosphate, are not hydrolysed under the conditions of the experiments. H. BURTON.

Dissociation of dolomite. C. S. GARNETT (Min. Mag., 1926, **21**, 21—24; cf. A., 1923, ii, 763).—In support of the view that when dolomite is calcined both calcium and magnesium oxides are formed simultaneously by dissociation, it is shown that mixtures of which calcium and magnesium carbonates and magnesium oxide may form part do not set unless there is also calcium oxide present, whilst the setting properties of partly burnt dolomite are well known. W. A. CASPARI.

Hydrofluozirconic acid and the analysis of zirconium fluoride. E. B. R. PRIDEAUX and E. C. ROPER (J.C.S., 1926, 898—903).—Determinations of the zirconia content and total hydrofluoric acid show that samples of zirconium fluoride have the formula ZrF_4, with more or less than $3H_2O$. It is suggested that the *fluoride*, $ZrF_4,1{\cdot}5HF,3{\cdot}74H_2O$, is hydrated hydrofluozirconic acid, $H_2ZrF_6,3H_2O$.
H. BURTON.

Additive compounds of hydrogen chloride and metallic sulphates. II. F. EPHRAIM (Ber., 1926, **59**, [*B*], 790—792; cf. this vol., 36).—The ability to add hydrogen chloride is confined to the sulphates of metals having more than ten outer electrons. The sulphates of the alkali and alkaline-earth metals, of magnesium, beryllium, aluminium, cerium, lanthanum, manganese, iron, cobalt, and nickel do not add hydrogen chloride. Conversely, their chlorides readily evolve hydrogen chloride when covered with concentrated sulphuric acid; this property is not exhibited by the chlorides of the remaining elements with the single exception of thallous chloride.

Stannous sulphate appears to yield a *compound*, $SnSO_4,2HCl$, which is stable below 38·5°. Bismuth sulphate absorbs rather more than 4 mols. of hydrogen chloride at atmospheric temperature; when the product is heated to 110°, at 111°, and 154°, the respective *compounds* $Bi_2(SO_4)_3,4HCl$, $Bi_2(SO_4)_3,2HCl$, and $Bi_2(SO_4)_3,HCl$ are produced. Thallous sulphate appears to give the *compound* $Tl_2SO_4,2HCl$. The behaviour of antimony sulphate towards hydrogen chloride is described. H. WREN.

Basic stannous sulphate. C. M. CARSON (J. Amer. Chem. Soc., 1926, **48**, 906—911).—The precipitates obtained at 100° by the addition of varying amounts of sodium hydroxide solution to stannous sulphate solutions were examined. Within two regions of alkali variation they remain practically constant in composition. The precipitate obtained at low alkali concentrations, $SnSO_4,SnO$, is probably a compound, and the other, $SnSO_4,2SnO,xH_2O$, may also represent a compound (cf. Ditte, Ann. Chim. Phys., 1882, [v], **28**, 145). The analysis of a solid phase may be corrected for the liquid phase it retains on separation, from a knowledge of the weight of the solid phase moist, and then dried at 100°, and of the weight and composition of the residue obtained on evaporating a known weight of the bulk liquid phase.
S. K. TWEEDY.

New example of anomalous mixed crystals. V. CAGLIOTI (Atti R. Accad. Lincei, 1926, [vi], **3**, 332—335).—When precipitated ceric hydroxide, after being collected and washed, is dissolved in dilute hydrochloric acid and the solution treated with the requisite amount of ammonium chloride to give the double salt, $(NH_4)_2CeCl_6$, and with a concentrated aqueous solution of the salt, $(NH_4)_2SnCl_6$, the liquid gives, in successive crystallisations in a desiccator at reduced pressure, (1) the above ammonium ceric chloride, (2) ammonium stannic chloride, and (3) homogeneous, orange-yellow, microscopic cubes, d^{18} 1·536, which consist of mixed crystals of ammonium chloride with either ceric chloride (1·96%) or ammonium ceric chloride (2·71%). T. H. POPE.

Stannous phosphates. K. JABŁCZYŃSKI and W. WIĘCKOVSKI (Z. anorg. Chem., 1926, **152**, 207—212).—*Tertiary stannous phosphate*, $Sn_3(PO_4)_2$, is a white, amorphous powder, $d_4^{17\cdot4}$ 3·823, insoluble in water, but soluble in mineral acids and alkali hydroxides; it is produced by adding a 10% solution of disodium hydrogen phosphate to a cold 10% solution of stannous sulphate containing a little sulphuric acid. *Stannous hydrogen phosphate*, $SnHPO_4$, crystallises in colourless tablets, $d_4^{15\cdot5}$ 3·476, from the solution obtained by dissolving granulated tin in phosphoric acid (d 1·23), or in small, silky crystals by adding water to a solution obtained by dissolving tin in phosphoric acid (d 1·7). *Stannous dihydrogen phosphate*, $Sn(H_2PO_4)_2$, results on heating the previous salt with phosphoric acid at 140° and cooling the solution over phosphoric oxide; it crystallises in the form of highly refractive rhombs, $d_4^{22\cdot8}$ 3·167, which are readily decomposed by water. *Stannous pyrophosphate*, $Sn_2P_2O_7$, is obtained as a white powder, $d_4^{16\cdot4}$ 4·009, when the monohydrogen phosphate is heated at 350—400° in a current of carbon dioxide. *Stannous metaphosphate*, $Sn(PO_3)_2$, is a white, glassy mass, $d_4^{22\cdot8}$ 3·38, formed by heating the dihydrogen phosphate at 390° in a current of carbon dioxide. The stannous phosphates are more readily hydrolysed than the corresponding lead compounds, but otherwise are relatively stable. A. R. POWELL.

Influence of neutral salt on the precipitation of metal sulphides. L. DEDE and T. BECKER (Z. anorg. Chem., 1926, **152**, 185—196).—Addition of alkali or alkaline-earth chlorides to solutions of lead, cadmium, and stannic chlorides and to solutions of molybdic acid in hydrochloric acid decreases the amount of acid required to prevent precipitation of the metal sulphide by hydrogen sulphide. Similar results are obtained on adding alkali perchlorate to lead or cadmium perchlorate solutions and, to a smaller extent, by adding sodium sulphate to a solution of cadmium sulphate. Thus, a 0·001M-solution of cadmium chloride gives no precipitate with hydrogen sulphide in 0·8N-hydrochloric acid in the absence of other salts; in a 2N-solution of potassium chloride, only 0·38N-hydrochloric acid is necessary to prevent precipitation. The corresponding figures for sulphuric acid are 2·89N-acid without sodium sulphate, and 1·89N-acid with 2N-sodium sulphate. The effect of temperature on these limiting values is most marked n the absence of neutral salt; in 3N-sodium sulphate solution, the acidity required to prevent precipitation of cadmium sulphate is not influenced at all by the temperature. A. R. POWELL.

Transfer of excited energy from ozone to hydrogen and nitrogen. A. C. GRUBB (Nature, 1926, **117**, 658).—When a current of hydrogen and nitrogen (approx. 3 : 1 by vol.) was passed over a platinum anode at which ozonised oxygen was being rapidly evolved, much ammonia was formed. It is supposed that ozone emits enough energy on decomposing to activate the hydrogen. A. A. ELDRIDGE.

Factors affecting the fixation of nitrogen as sodium cyanide. E. W. GUERNSEY, J. Y. YEE, J. M. BRAHAM, and M. S. SHERMAN.—See B., 1926, 358.

Oranges and reds of uranium. V. AUGER and J. N. LONGINESCU (Compt. rend., 1926, **182**, 970—972).—The coloured compounds precipitated on the addition of alkali sulphides to a dilute solution of uranyl nitrate have been analysed. Those amounts of sulphides which produced the most intense colours were used, orange and red compounds being obtained with potassium and ammonium sulphides, and a red compound with barium sulphide. The analyses indicate that these compounds are amorphous salts of a thiouranic acid ($H_6U_5S_2O_{16}$ or $H_{10}U_{10}S_4O_{31}$), which plays the part of a quinquevalent and quadrivalent anion, respectively, for the reds of potassium and ammonium, and for the corresponding oranges and the red of barium. J. GRANT.

Cobalt nitrite. L. LE BOUCHER (Anal. Fís. Quím., 1926, **24**, 91—98).—By the action of sodium nitrite on cobalt nitrate in pyridine–water solution at 0° in an atmosphere of hydrogen, a light red *salt* having the composition $Co(NO_2)_2,3C_5H_5N$ is obtained. By crystallisation from pyridine, dark red *crystals* of composition $Co(NO_2)_2,6C_5H_5N$ are obtained. Both compounds are hydrolysed by water. The latter compound is readily oxidised in air, mixed crystals of the nitrate and nitrite being formed. G. W. ROBINSON.

Molybdates of cobaltiammines and molybdatocobaltiammines. B. K. PAUL and P. V. SARKAR (Ann. Chim., 1926, [x], **5**, 199—217).—The following compounds have been prepared: *dimolybdatotetramminecobaltic trimolybdate* ($+6H_2O$); double *salts* (1 : 1, $+3H_2O$, and 5 : 1) of diaquotetramminecobaltic molybdate and dimolybdate; *molybdatotetramminecobaltic molybdate* ($+3H_2O$); *nitratotetramminecobaltic molybdate*; *molybdatotetramminecobaltic nitrate*; *molybdatotetramminecobaltic trimolybdate* ($+4H_2O$); *hexahydroxydodecammine tetracobaltic molybdate*; and the *aquopentammine* compounds:

$[Co(NH_3)_5H_2O]_2(Mo_3O_{10})_3,9H_2O$;
$[Co(NH_3)_5H_2O]_2(MoO_4)_3$;
$[Co(NH_3)_5H_2O]_2[Mo(MoO_4)_6]$.

F. G. SOPER.

Pure neutral distilled water [for biological purposes]. F. BORDAS and F. TOUPLAIN (Ann. Falsif., 1926, **19**, 134—141).—If distilled water is prepared by means of a naked flame in metal vessels, more or less superheating occurs with a corresponding increase of conductivity in the distillate, *e.g.*, an increase from $3\cdot3\times10^{-6}$ to 20×10^{-6} in 3 hrs. when

heated on a sand-bath in a platinum vessel with an upright condenser. This increase of conductivity is reduced by 80% if pyrex glass vessels are used. A water of high conductivity may lose a great part of its conductivity by keeping in a half-filled pyrex glass vessel, and the diminution is much hastened by warming of the water vapour and slow cooling.

D. G. HEWER.

Preparation of pure alkali metals. R. SUHRMANN and K. CLUSIUS (Z. anorg. Chem., 1926, **152**, 52—58).—The presence of hydrogen in metals greatly increases the number of electrons emitted under the action of light. Hydrogen cannot be completely removed from alkali metals, and the pure metals can, therefore, be obtained only by preparing them under conditions which preclude the presence of hydrogen, *e.g.*, by the decomposition of the alkali azides. Pure chlorides are converted successively into the nitrates, oxalates, and carbonates, and azoimide, prepared from sodium azide and sulphuric acid, is passed into the last. Azides prepared by crystallisation from these solutions are spectrally pure and are free from sulphate, chloride, and carbonate. The pure azides are decomposed in a high vacuum by heating in vessels of Jena glass; rubidium and cæsium azides are decomposed in silica tubes. Sodium, potassium, rubidium, and cæsium azides decompose at 275°, 355°, 395°, and 390°, respectively. The metals are distilled off and redistilled in the same apparatus, and the yields are approximately 100, 80, 60, and 90%, respectively. The metals are spectrally pure and completely free from gases. The yields are not quantitative, and the residues contain nitrides; it is also possible that a modified form of nitrogen is formed.

A. GEAKE.

Preparation of disilicon hexachloride. J. B. QUIG and J. A. WILKINSON (J. Amer. Chem. Soc., 1926, **48**, 902—906).—The yield of disilicon hexachloride obtained by passing chlorine over ferrosilicon at 200° (cf. Martin, J.C.S., 1914, **105**, 2836) is increased, up to a certain point, by the addition of silicon tetrachloride to the chlorine, because the final chlorination of the hexachloride to the tetrachloride is thereby retarded. The chlorination of a mixture of iron and silicon yields no silicon chlorides below 300°, showing that ferric chloride neither catalyses the formation of disilicon hexachloride nor lowers the temperature of the reaction.

S. K. TWEEDY.

Germanium and gallium from germanite. W. KEIL (Z. anorg. Chem., 1926, **152**, 101—104).—Germanite is dissolved in sulphuric and nitric acids, the residue is evaporated, dissolved in water, and after adding hydrochloric acid, distilled in a current of chlorine. The germanium tetrachloride distilling over is purified by repeating the distillation. The liquid distillate is freed from chlorine by shaking with mercury and re-distilled. The chloride which remains dissolved in the aqueous layer of the distillate is precipitated as sulphide, and converted through the nitrate into germanium dioxide. Germanium metal is obtained by reducing the dioxide with potassium cyanide and carbon, or preferably by fusing the disulphide with potassium cyanide. Gallium is obtained from the residue after distillation with chlorine. Copper, lead, arsenic, and sulphuric acid are precipitated with hydrogen sulphide and barium chloride, and the filtrate is digested with barium carbonate. The precipitate contains barium carbonate, gallium, and iron. It is dissolved in hydrochloric acid, precipitated with ammonia, redissolved in hydrochloric acid, and the gallium precipitated as ferrocyanide. This is purified by dialysis, fused with potassium hydroxide, and dissolved in water. After removing the iron, any zinc is precipitated as sulphide, the filtrate acidified, and the gallium precipitated as hydroxide with ammonia. On ignition gallium trioxide is obtained.

A. GEAKE.

Plumbic ammonium chloride. A. SEYEWETZ and H. TATU (Bull. Soc. chim., 1926, [iv], **39**, 647—651).—Plumbic ammonium chloride may be economically prepared by adding a slow stream of nitric acid to an agitated suspension of 1 mol. of lead chloride (or sulphate) and 2 mols. of ammonium chloride in four times the theoretical quantity of concentrated hydrochloric acid. The filtered product, freed from acid with alcohol and ether, and heated at 80°, is a yellow powder, insoluble in the common organic solvents, which turns bright red at 70—80° and loses chlorine at 140°. In a 0·08% aqueous solution it forms colloidal lead dioxide, which slowly settles; in this form, it may be used as an active oxidising agent. Solutions between 4% and 22% (saturation) decompose into lead chloride and an oxygenated chlorine compound; with concentrations between 0·08% and 4%, both reactions occur. The second type of decomposition is avoided by dissolving in concentrated hydrochloric acid, but can be favoured by carefully regulating the quantity and concentration of the acid. Phosphoric acid in all concentrations does not hinder the second type of decomposition. It stabilises dilute solutions in which the first type of decomposition occurs, by retarding the flocculation of the oxide, even at concentrations slightly below that at which the formation of the oxide is hindered. Acetic acid behaves similarly to phosphoric acid, although much higher concentrations are necessary. Above 120° in a non-aqueous medium, plumbic ammonium chloride yields nascent chlorine and so may be used as a chlorinating agent (cf. A., 1903, ii, 371).

S. K. TWEEDY.

Caro's reagent. R. H. VALLANCE.—See B., 1926, 318.

Microchemical methods. F. HENRICH (Z. angew. Chem., 1926, **39**, 447—450).—A general account of apparatus and procedures employed in microchemical analysis.

B. W. CLARKE.

Use of porcelain filtering crucibles in gravimetric analysis. L. MOSER and W. MAXYMOWICZ (Chem.-Ztg., 1926, **50**, 326—327).—Porcelain crucibles with a bottom plate of porous, sintered porcelain are very convenient for the weighing of silver chloride after drying at 105°, lead and barium sulphates and chromates, zinc, magnesium, and manganese pyrophosphates and bismuth phosphate after the usual ignition, and cuprous thiocyanate, calcium oxalate, and nickel dimethylglyoxime after drying at 110°. Alkali hydroxides cause a serious loss in weight, but

alkali carbonates are practically without action. The weight of the crucible after drying at 100—110° is always about 0·7—0·9 mg. higher than after heating to redness. The rate of filtering on the vacuum pump is about 3—5 min. for 20 c.c.

A. R. POWELL.

Analysis with the aid of the dropping mercury cathode. J. HEYROVSKÝ (Chem. Listy, 1926, **20**, 122—130).—Polarisation curves of solutions of metals containing traces of more noble metals from the electrochemical point of view show a number of undulations the positions and dimensions of which are characteristic of the metallic impurities present. The method is thus suitable for the detection and, sometimes also, for the determination of small amounts of impurities in metal salts, and may also be used for the study of the solubility of "insoluble" salts, of the amphoteric nature of certain hydroxides, and of the degree of complexity of ions. By the use of the polarograph of Heyrovský and Shikata, it has been shown that the hydroxides of copper, bismuth, cadmium, cobalt, and iron are amphoteric, whilst chromic hydroxide is not. Alkaline solutions of the latter are true colloidal solutions. The limit of sensitiveness of the method is about 10^{-7} g.-equivalent of metal per litre. A. R. POWELL.

Quantitative spectrum analysis. J. ŠEBOR (Chem. Listy, 1926, **20**, 55—63, 174—194).—From a study of the absorption spectra of a large number of solutions of different dyes, a relation has been discovered between the width of the absorption bands and the concentration of the dye, and its use in determining the concentration of an unknown solution is demonstrated. For a solution of definite concentration, the width of the bands, B, depends on the thickness of the coloured layer, d, according to the equation $B=Ae^{\alpha d}$, where A is a constant and α is negative for luminous bands and positive for absorption bands. If c is the concentration of the dye in solution, then $B=Ae^{\alpha d+\gamma}$, where γ is a constant of positive sign for absorption bands.

A. R. POWELL.

Salt errors of indicators caused by standard alkaline buffers themselves. J. W. MCBAIN, O. E. DUBOIS, and K. G. HAY (J. Gen. Physiol., 1926, **9**, 451—465).—Many indicators which give a certain depth of colour with pure sodium hydroxide solutions give the same colour in alkaline buffer solutions which have p_H values differing in extreme cases by as much as two units from the p_H values of the sodium hydroxide solutions. In some cases, addition of more indicator after the maximum colour has been reached causes a diminution of the colour.

H. J. CHANNON.

Meulen-Heslinga halogen determination. L. COHEN (Chem. Weekblad, 1926, **23**, 232—233; cf. Rec. trav. chim., 1923, **42**, 1093).—The difficulties arising from the tendency of the ammonium halides formed to appear as fumes not easily condensible may be overcome by the use of a lightly-compressed moistened wad of asbestos. S. I. LEVY.

Electrometric titration of halides. W. CLARK (J.C.S., 1926, 749—775).—Soluble halides, when titrated electrometrically with silver nitrate, give results identical with those obtained by ordinary titration. The silver electrode used for determining chloride must be so prepared that potential alteration on adding silver nitrate is not more than 8 millivolts. Single halides in solution can be determined also by means of a bimetallic electrode system of silver and amalgamated silver. Results show that 0·2% of chloride in bromide or iodide, and 0·2% of iodide in bromide, can be determined accurately, provided barium, sodium, or ammonium nitrate or sodium acetate is present in the solution. Low percentages of bromide in chloride cannot be determined electrometrically if less than 5% is present, but quantities of 0·5—1% can be determined by distilling the bromine with permanganate, absorbing the bromine in ammonia, and titrating the resulting solution. Mixtures of three halides can be determined accurately. Single silver halides, mixtures of silver chloride and iodide, and silver bromide and iodide can be determined by titrating a cyanide solution of the salts with silver nitrate. For mixtures containing silver chloride, it was found best to reduce the cyanide solution with zinc and determine the liberated halogen ions with silver nitrate in the presence of ammonium nitrate. The method is applied to the analysis of photographic emulsions.

H. BURTON.

Possible error in the calc-spar determination of hydrochloric acid. A. C. D. RIVETT (Chem. News, 1926, **132**, 309—310).—Masson's method (A., 1900, ii, 436) of standardising hydrochloric acid solutions depends for its accuracy on the heating being started while there is still a small amount of acid left to react with any calcium hydrogen carbonate that is formed in the early stages of the action. The best results are obtained by allowing the acid to react with the spar for 1 hr. at the ordinary temperature, heating the solution to boiling, decanting the solution, and washing, drying, and weighing the crystals. Prolonged keeping at the ordinary temperature results in the formation of appreciable quantities of calcium hydrogen carbonate.

A. R. POWELL.

Detection and determination of small quantities of perchlorate in Chile saltpetre and in chlorates. F. L. HAHN.—See B., 1926, 404.

Determination of perchlorate in Chile saltpetre. G. LEIMBACH.—See B., 1926, 404.

Light titrations. I. Starch–iodine reaction. J. FIELD and L. G. M. BAAS-BECKING (J. Gen. Physiol., 1926, **9**, 445—450).—The radiomicrometer has been used to measure the iodine content of starch iodide. H. J. CHANNON.

Rapid volumetric determination of fluoride in simple, complex, and insoluble fluorides. J. H. DE BOER and J. BASART (Z. anorg. Chem., 1926, **126**, 213—220; cf. de Boer, this vol., 40).—Zirconium oxychloride gives a blue lake with sodium alizarinsulphonate in hydrochloric acid solutions, and the colour is discharged by the addition of fluorides. This reaction is made the basis of a method for determining fluorides as follows. The fluoride solu-

tion or insoluble fluoride is treated with 25 c.c. of 10% zirconium oxychloride solution, 50 c.c. of concentrated hydrochloric acid, and 1 c.c. of a 0·03% solution of sodium alizarinsulphonate. A similar solution is prepared without addition of fluoride, and both solutions are diluted to 125 c.c. and titrated with a standard potassium fluoride solution until the same orange tint is obtained in each. The difference between the amounts of fluoride required is a measure of the fluorine in the unknown substance. Sparingly soluble fluorides are brought into solution by digestion with the acid zirconium solution on the water-bath under a reflux air condenser. The method is applicable to fluoborates, fluotitanates, fluosilicates, and fluoaluminates. A. R. POWELL.

Winkler's method for the determination of dissolved oxygen and its use in the presence of oxidisable substances. G. ALSTERBERG (Biochem. Z., 1926, **170**, 30—75).—The methods available for the determination of dissolved oxygen are critically reviewed and that of Winkler is recommended as the safest and simplest. Certain precautions necessary in the preparation of the reagents and their employment are indicated. The modifications which have been introduced to eliminate the interference due to oxidisable impurities are reviewed, and those involving preliminary or parallel treatment with ferricyanide, hypochlorite, permanganate, carbamide, or azoimide are not considered to be of general value. A new method is advanced employing preliminary oxidation of oxidisable substances by means of bromine, followed by removal of excess bromine by salicylic acid. The unmodified method of Winkler is then applied, using phosphoric acid for acidification. The method has been tested in the presence of sulphide, sulphite, thiosulphate, iron, nitrite, cyanides, and organic material.

R. K. CANNAN.

Nitrate determinations [in water and sewage]. G. W. BURKE.—See B., 1926, 389.

Determination of arsenic as elementary arsenic and as magnesium ammonium arsenate hexahydrate. R. FRIDLI (Pharm. Zentr., 1926, **67**, 241—244).—Arsenic in solutions free from gold, mercury, selenium, and tellurium may be determined as the element or as magnesium ammonium arsenate hexahydrate. In the determination as elementary arsenic, a boiling solution of stannous chloride in hydrochloric acid is added to the arsenical solution, and after 15 min. the liquid is boiled gently for 10 min. and kept for 1 day. It is then filtered through specially treated cotton wool, and the precipitate washed successively with hot 5% hydrochloric acid, hot water, alcohol, and ether, dried at the ordinary temperature, and weighed on the filter. For solutions containing more than 10 mg. of arsenic, the results are high, owing to the presence of tin in the precipitate. A table for correcting the weight of the precipitate is given. The method yields good results in the presence of antimony. In the second method, if the arsenic is tervalent, it is slightly acidified with hydrochloric acid, treated with bromine water to a brownish-red colour, and concentrated; the solution is boiled with ammonium chloride solution, ammonia and a solution of magnesium sulphate and ammonium chloride are added successively, and after 24 hrs. the precipitate is collected as in the previous method, washed repeatedly with ammonia, then with alcohol, dried, and weighed.

B. FULLMAN.

Detection of perborates in the presence of borates. L. ROSSI.—See B., 1926, 404.

Analysis of silicates. O. CANTONI.—See B., 1926, 359.

Analysis of silicates. R. SCHWARZ and A. SCHINZINGER.—See B., 1926, 319.

Determination of carbon monoxide in hydrogen. P. SCHUFTAN.—See B., 1926, 405.

Determination of carbon dioxide in carbonates and the evaluation of Ferrum carb. sacchar. F. VON BRUCHHAUSEN (Apoth.-Ztg., 1925, **40**, 938—939; from Chem. Zentr., 1926, I, 186).—The carbonate (0·1 g.) is decomposed in a previously evacuated apparatus, details of which are given, by means of 5% hydrochloric acid, the resulting carbon dioxide being absorbed in a measured excess of 0·2—0·3*N*-barium hydroxide solution, and the excess of barium hydroxide is then determined by titration with 0·1*N*-hydrochloric acid, using phenolphthalein as indicator. Ferrum carb. sacchar. should contain 19·7—20·8% of ferrous carbonate. The amount is usually 16—19%, an old specimen containing only 8·9%.

J. S. CARTER.

Sensitive reagent for potassium and ammonium ions. T. GASPAR Y ARNAL (Anal. Fís. Quím., 1926, **24**, 99—105).—Sodium ferrocyanide in the presence of calcium chloride in 50% ethyl alcohol gives a white precipitate with potassium or ammonium ions, the composition of which corresponds probably with the formula $R_2CaFe(CN)_6$, where R=K or NH_4. The reaction is practically quantitative. The ferrocyanic acid can be liberated and determined by titration with standard permanganate.

G. W. ROBINSON.

Titration of ammonium sulphate by the stearate method. H. ATKINSON.—See B., 1926, 358.

Micro-chemical determination of lead. W. GEILMANN and R. HÖLTJE (Z. anorg. Chem., 1926, **152**, 59—72).—Quantities of lead of the order of 5 mg. and less may be determined by precipitating with known amounts of potassium dichromate or potassium iodate and determining the excess of reagent iodometrically; the error in each case is about ±0·01 mg. of lead. Dissolution of precipitated lead chromate in hydrochloric acid and iodometric determination of the chromic acid leads to irregular results. In impure solutions, the lead may first be precipitated with hydrogen sulphide, the precipitate redissolved in hydrochloric acid, and lead determined by the chromate method; by the iodate method, too low results are obtained owing to a portion of the lead sulphide being oxidised to sulphate. The factor of 0·01*N*-sodium thiosulphate depends on the amount used when this is less than 2 c.c., and it is therefore advisable to take such an excess

of dichromate or iodate that more than this volume of thiosulphate is required for the back titration. The solubility of lead iodate in water at the ordinary temperature is 29±2 mg. per litre. It is greatly diminished by the presence of potassium iodate, and the solubility product is about $0{\cdot}32\times10^{-12}$, corresponding with a solubility in pure water of 24·0 mg. per litre. A. GEAKE.

Iodometric determination of metals [lead, cadmium, and mercury]. E. J. KRAUS (Chem.-Ztg., 1926, **50**, 281).—Lead, cadmium, and mercury may be determined by dissolving the freshly-precipitated sulphide of the metal in hydrochloric acid and iodine and titrating the excess of iodine with thiosulphate. Hydrogen sulphide or ammonium sulphide may be used as the precipitant; the well-washed sulphide together with filter-paper is digested cold with 25 c.c. of concentrated hydrochloric acid and 15 c.c. of 0·5*N*-iodine solution for 15 min., 300 c.c. of water are added, and the excess of iodine is determined with 0·1*N*-thiosulphate. A. R. POWELL.

Fairhall (chromate) method for [determining] minimal amounts of lead in fæcal specimens. ANON. (Ind. Eng. Chem., 1926, **18**, 431—432).—The samples preserved with formaldehyde are ashed, the ash is extracted with hydrochloric acid, and then with tartaric and hydrochloric acids. The combined filtrates are diluted, neutralised with sodium hydroxide, and treated with hydrogen sulphide. The precipitate is completely dissolved in hydrochloric acid containing nitric acid, the liquid evaporated, diluted, and, after adjustment to a suitable hydrogen-ion concentration, twice reprecipitated. The sulphide is dissolved in hot 1 : 1 nitric acid, and the solution evaporated to coagulate sulphur, which is filtered off and washed, the solution then being suitably neutralised and acidified. At the b. p., excess of potassium chromate solution is added, the lead chromate being collected and treated with hydrochloric acid, and the liberated iodine determined volumetrically. The original must be consulted for detailed working instructions. D. G. HEWER.

Gravimetric determination of copper as cuprous iodide. I. M. KOLTHOFF and H. A. KUYLMAN (Chem. Weekblad, 1926, **23**, 185—186).—The method of Winkler (A., 1924, ii, 276) gives discordant results, chiefly by reason of atmospheric oxidation of the precipitate on keeping. In presence of strong acid, and cooling in a stream of carbon dioxide, the method gives very satisfactory results, even in presence of great excess of iron and small quantities of arsenic and antimony; lead interferes, and must be removed before precipitation. The method should be very suitable for the determination of copper in raw pyrites and cinders. S. I. LEVY.

Electrolytic determination of copper in the presence of bismuth. W. MOLDENHAUER (Z. angew. Chem., 1926, **39**, 454).—Copper can be separated completely from bismuth by the electrolysis at 60° of a solution of the metals containing phosphoric acid, and the copper content of the solution determined from the weight of copper deposited is accurate within 2 parts per 1000. B. W. CLARKE.

Determination of mercuric chloride. F. VON BRUCHHAUSEN and E. HANZLIK (Apoth.-Ztg., 1925, **40**, 1115—1116; from Chem. Zentr., 1926, I, 734—735).—Of Rupp's two methods for the determination of mercury in medicinals, the iodometric method is liable to give low results. It is recommended to reduce with sodium arsenite in the presence of sodium hydrogen carbonate, instead of with formaldehyde, and to titrate back with sodio-*p*-toluenesulphonchloroamide. Alternatively, potassium bromate in hydrochloric acid may be used with methyl-orange as indicator. The results are within 0·1—0·4% of theory. A. GEAKE.

Determination of mercuric iodides. J. SANDILANDS.—See B., 1926, 405.

Separation of the metals of group III. G. G. LONGINESCU and (MLLE.) G. CHABORSKI (Bul. Chim., Soc. Româna Stiinte, 1924, **27**, 41—44).—The precipitate is treated with powdered potassium chlorate and concentrated hydrochloric acid in the cold, the excess of acid neutralised by means of solid sodium carbonate, the liquid filtered from any separated sulphur, treated with 20% sodium hydroxide solution, and boiled; after dilution, it is decanted and washed, and zinc and aluminium are identified in the clear liquid in the usual way. On boiling the precipitate with concentrated ammonium carbonate solution, cobalt and nickel pass into solution, and may be identified, after filtration and boiling with sodium hydroxide, in the clear neutralised solution, cobalt as cobaltinitrite, and nickel as hydroxide. The precipitate of iron, chromium, and manganese hydroxides left undissolved by the ammonium carbonate solution is tested for these metals; for chromium by warming a portion with a little sodium hypochlorite solution, for manganese by boiling with excess of the same reagent, and for iron by the ferrocyanide or thiocyanate methods. S. I. LEVY.

Volumetric determination of uranium, vanadium, copper, and iron in uranium ores. A. S. RUSSELL.—See B., 1926, 328.

Air oxidation of titanous sulphate solution. Vanadous sulphate, a new and powerful reducing agent. A. S. RUSSELL (J.C.S., 1926, 497—498).—When titanic sulphate is reduced by zinc amalgam in 4*N*-sulphuric acid solution (A., 1921, ii, 596) and the resulting solution of titanous sulphate kept in a burette exposed to air, its titre remains constant for 12 hrs. Under these conditions, therefore, it can be used for volumetric determinations without the exclusion of air. Vanadous sulphate is an even more powerful reducing agent, but is more readily oxidised by air. It may be prepared in the same way as titanous sulphate. A 0·1*N*-solution in 10*N*-sulphuric acid remains unaltered when kept in a burette exposed to air for 1 hr. E. E. WALKER.

Potentiometric standardisation of titanous chloride solution. E. ZINTL (Z. anorg. Chem., 1926, **152**, 35—38).—Polemical against Kolthoff, Tomiček, and Robinson (this vol., 376). The result, 1% too high, obtained by these authors when titanous chloride was standardised potentiometrically against copper sulphate was probably due to the presence of

oxygen in their solution or in the carbon dioxide. This readily oxidises the cuprous salt. The result, 0·2% too high, obtained by dichromate titration in the presence of a copper salt, was probably due to the same cause. Many determinations have given uniformly sharp end-points by the copper titration method. A. GEAKE.

Phenylarsinic acid as a reagent for the determination of zirconium and thorium. A. C. RICE, H. C. FOGG, and C. JAMES (J. Amer. Chem. Soc., 1926, **48**, 895—902; cf. Palmer and Adams, A., 1922, i, 785).—Zirconium may be quantitatively separated in 10% hydrochloric or sulphuric acid solutions from all elements, except hafnium, in the form of its insoluble phenylarsinate, which yields zirconia on ignition. Double precipitation is necessary in the separation from thorium, uranium, phosphoric acid, and large amounts of ferric iron; hydrogen peroxide must be present when separating from titanium. Thorium phenylarsinate is the only rare-earth salt of this acid insoluble in presence of excess of acetic acid; a method of determining thorium is given and is applied to the analysis of monazite sand. S. K. TWEEDY.

Error introduced by the presence of bismuth in the colorimetric determination of iron in red lead. Colorimetric determination of bismuth. H. HEINRICHS and M. HERTRICH.—See B., 1926, 372.

Use of magnesium as electrode supports in spectral analysis. E. DUREUIL (Compt. rend., 1926, **182**, 1020—1022).—Magnesium electrodes are recommended for the production of both arc and spark spectra, since the magnesium lines between 7000 and 3500 Å. are few and do not mask those of other elements. They are particularly useful in the identification of non-conducting minerals such as zircon, cassiterite, etc., which ordinarily give poor spark spectra. With magnesium electrodes, in a small cavity in the positive of which the mineral is placed, the characteristic lines are clearly defined, owing to the reducing action of the electrode. F. G. SOPER.

Use of arcs and other fluctuating sources in photoelectric photometry. B. KURRELMEYER (Nature, 1926, **117**, 657—658).—An arrangement is described whereby the optical paths to the two cells may be made practically identical. A. A. ELDRIDGE.

Use of light filters in polarimetric measurements. H. SCHULZ (Z. Instrumentenkunde, 1925, **45**, 468—470; from Chem. Zentr., 1926, I, 731).—The tungsten point lamp is suitable for increasing the light entering the eye when light filters are used in polarimetric measurements. The angle of the half-shadow can then be reduced to 0·3°. With small angles, any rotation dispersion produces strong colours even with comparatively sharp filtration in the eye-piece half of the polarimeter, and this makes adjustment to light equality difficult. A. GEAKE.

Stereographic protractor for Laue photographs. A. HUTCHINSON (Min. Mag., 1926, **21**, 10—13).—An instrument in the form of a straight-edge protractor is described for the gnomonic projection of Laue spots photographed at 5 cm. distance. Scale-readings on the shorter portion, when laid off against a spot, give its glancing-angle θ directly, and the corresponding scale-reading on the longer portion gives the gnomonic projection of the plane from which the spot was reflected. W. A. CASPARI.

Microbalance. III. Filtration and determination of very small amounts of material. E. J. HARTUNG (J.C.S., 1926, 840—848).—A detailed account of the determination of inorganic salts such as silver nitrate, potassium chloride, calcium carbonate, in quantities of less than 1 mg., involving filtration of a precipitate as part of the operation. Descriptions of the apparatus used, together with a table of results, are given. The method is accurate to the extent of 1% for quantities of 0·1 mg., and even more accurate for quantities between 0·1 and 1 mg. The sources of error, particularly with regard to the washing of the precipitate, are discussed in detail. H. BURTON.

Automatic siphonic gas circulator. G. M. GREEN (J.C.S., 1926, 500).—An apparatus is described capable of giving a constant circulation of at least 50 c.c. gas per minute. The prime mover is a siphon which produces an intermittent pressure. This in turn gives an oscillating motion to a column of mercury in a U-tube, the dry arm of which is connected with a pair of mercury seal valves so arranged as to give a unidirectional flow of gas. E. E. WALKER.

Laboratory mixing machine for solids. R. H. HIXON.—See B., 1926, 303.

M. p. apparatus. J. R. HOSKING and W. F. SHORT (J.S.C.I., 1926, **45**, 89—90T).—The apparatus consists of a hard glass tube in which the thermometer and attached capillary tube are heated in a current of air aspirated from a hot copper spiral. It can be used over a wide range of temperatures, up to 360° and above. Rise of temperature can be regulated to any desired speed, and cooling takes place rapidly.

Automatic apparatus for determining the m. p. of organic compounds. R. B. MACMULLIN (J. Amer. Chem. Soc., 1926, **48**, 439—442).—An elaboration of Dubosc's apparatus (Rev. prod. chim., 1925, **28**, 115). The material to be examined is made to form a coating on a small platinum sphere sealed into a glass tube, thereby insulating the platinum from mercury which is placed above the substance. The mercury and platinum are connected to an electric bell circuit, and immersed in a mercury-bath containing a self-registering maximum thermometer, heated electrically. When the substance melts, contact is established between the mercury and the platinum, the bell rings, and the same circuit operates a relay which switches off the heating circuit, the maximum temperature recorded thus being that of the m. p. of the substance. A safety cut-off is arranged by inserting a second platinum contact, coated with a substance of m. p. about 250°, *e.g.*, dibenzoylethylenediamine, in the bath. F. G. WILLSON.

Extraction apparatus. C. BRÜGMANN (Chem.-Ztg., 1926, **50**, 248—249).—The material to be

extracted is contained in a bottle with a narrow neck provided with a hollow cylindrical fitting of brass or glass, closed at the top and connected with a reflux condenser and to a small boiler containing the extracting solvent. The apparatus carries a hollow stirring rod, to which is sealed a small cylindrical container connecting with the interior of the rod by two small holes; the condensed vapour of the solvent flows back into this container and thence down the rod, and is delivered to the material in the bottle by small holes in the lower portion of the stirring rod, which is bent at a suitable angle. The apparatus is specially applicable to the extraction of plant tissues etc. B. W. CLARKE.

Modification of the Wagner reaction with liquid air cooling. C. J. MAAN (Chem. Weekblad, 1926, **23**, 231—232).—As the method of cooling by adding liquid air directly to the light petroleum bath is not without risk, a modified apparatus is employed in which liquid air is caused to pass through spiral copper tubes immersed in the light petroleum baths. S. I. LEVY.

Highly sensitive Congo paper. F. W. HORST (Z. angew. Chem., 1926, **39**, 432—433; cf. A., 1925, ii, 1196).—The sensitivity of Congo paper to acid is increased by the use of a neutral paper and a solution of which the dye content approximates in constitution to that of the monosodium salt of the indicator. In practice, this is attained by mixing two solutions, one containing the neutral disodium salt and the other the blue acid dye. A preliminary test of the acidity of the paper then allows the solutions to be mixed in such proportions that the monosodium salt with less disodium salt is produced on the paper, which must be dried, after dyeing, in a neutral atmosphere in the dark. Mineral acids in a concentration of 0·0001*N* are indicated by such papers, whilst with the best papers a reaction is given by 0·00008*N*-acids. At still greater dilutions, the presence of acids is shown by comparing the colour given by 5—15 c.c. of the solution to be tested and a similar volume of distilled water, after the addition of 5—7 drops of a solution containing 0·17 g. of neutral dye and 0·06 g. of acid dye per litre. A colour difference is observable with 0·000016*N*-hydrochloric acid. L. M. CLARK.

Drying small quantities of alcohol. J. J. DIEKMANN (Chem. Weekblad, 1926, **23**, 169—170).—The vapour from the boiling alcohol is caused to pass through a wide tube filled with calcium oxide or barium oxide, according to the alcohol to be dried. This drying tube is connected directly at the top, and through a seal tube at the bottom with a side tube into the top of which is connected a condenser. The drying tube is surrounded by a steam or other heating jacket. The course of the drying is followed by the rise in the b. p. registered by a thermometer passing through the cork of the boiling flask. S. I. LEVY.

History of oxygen. (SIR) P. C. RÂY (J. Indian Chem. Soc., 1926, **3**, 1—22).

Mineralogical Chemistry.

Spectroscopic examination of minerals. II. Beryl containing cæsium. G. O. WILD and R. KLEMM (Centr. Min., A., 1925, 295—296; from Chem. Zentr., 1926, I, 339).—Specimens of beryl of various colours and origins have been examined. Rose-coloured specimens contain gallium and cæsium, the more intense the colour the greater being the cæsium content. Gallium, manganese, and lithium appear to have no influence on the intensity of the colour, cæsium alone being responsible. J. S. CARTER.

Faint coloration of minerals. R. KLEMM and G. O. WILD (Centr. Min., A., 1925, 291—295; from Chem. Zentr., 1926, I, 339; cf. preceding abstract).—The faint colorations of simple substances (sodium chloride, calcium fluoride) are due to the decomposition of some of the constituent molecules into their atoms. This idea is in harmony with the fact that on heating the colour gradually disappears. Coloured minerals such as garnet, felspar, tourmaline, etc., owe their colours to the complexity of their molecules. J. S. CARTER.

Simple stoicheiometric ratio of the average biotite of granite and the relation between the anorthite and biotite contents of granite. P. CHIRVINSKI (Centr. Min., A., 1925, 304—313; from Chem. Zentr., 1926, I, 340).—Average analyses of the biotite in granite indicate that this substance is an equimolecular mixture of muscovite and olivine. Granites etc. contain biotite and anorthite in equimolecular proportions. J. S. CARTER.

Gold and silver in Dartmoor granite. A. BRAMMALL (Min. Mag., 1926, **21**, 14—20).—Specimens of normal tor-granites contain gold up to 2·4, silver up to 54·0 grains per ton. Normal quarry granites contain gold up to 6·3, silver (in two cases) up to 156·8 grains per ton; the silver is found to be mainly concentrated in the biotite. In general, none of these varieties of granite is as rich as Bittleford pegmatite, which shows gold 7·2—218·4, silver 14·4—264·0 grains per ton. Examination of the associated minerals leads to the conclusion that both metals are of primary and not of sedimentary or pneumatolytic origin. W. A. CASPARI.

Native platinum. S. SHEMTSCHUSHNY (Jahrb. Min., A., 1925, II, 52—53; from Chem. Zentr., 1926, I, 42).—The densities of platinum fragments and splinters from the Ural district differ considerably. The grains have no effect on a magnetic needle. A typical analysis of the portion soluble in aqua-regia of a platinum from the River Serlich is: platinum, 87·2%; iridium, 1·31%; rhodium, 0·53%; palladium, 0·54%; copper, 0·55%; nickel, 0·06%; iron, 9·19%. J. S. CARTER.

Petrographic and *X*-ray study of the thermal dissociation of dumortierite. N. L. BOWEN and R. W. G. WYCKOFF (J. Washington Acad. Sci., 1926, **16**, 178—189).—The dissociation of Arizona dumortierite, $8Al_2O_3,6SiO_2,B_2O_3,H_2O$, into mullite, $3Al_2O_3,2SiO_2$, and a little excess material commences at 950°. Water and boric oxide are completely expelled at 1500° in 4·5 hrs., and the products of decomposition at this temperature are mullite and a little free silica. The formation of liquid, which occurs at 1550°, is due to melting at the eutectic between mullite and silica (1545°). The thermal behaviour of dumortierite, which, on account of its high alumina content, is favourably regarded as a basis for refractory bodies, is for all practical purposes that of a material containing only alumina and silica, very probably in the proportion $4Al_2O_3,3SiO_2$, and can be determined direct from the alumina–silica diagram given. Nevada dumortierite, containing 3—4% of muscovite, behaves similarly to the purer Arizona product on heating, whereas a specimen containing 20% of muscovite begins to sinter at a lower temperature, and the amount of liquid formed is greater. The thermal decomposition has also been followed by *X*-ray analysis. J. S. H. DAVIES.

Chemical constitution of the monoclinic pyroxenes and amphiboles. B. GOSSNER (Z. Krist, 1924, **60**, 76—124; cf. following abstract). CHEMICAL ABSTRACTS.

Chemical composition of alkali amphiboles. B. GOSSNER (Z. Krist, 1924, **60**, 302—310; cf. preceding abstract and A., 1925, ii, 821).—The compounds correspond with combinations of certain simple molecules. CHEMICAL ABSTRACTS.

Chemical composition of crossite, arfvedsonite, ænigmatite, rhœnite, and babingtonite. B. GOSSNER (Z. Krist., 1925, **61**, 538—544).—An examination of the relationship of these minerals to members of the amphibole and pyroxene groups. CHEMICAL ABSTRACTS.

Barytes from the Giona mine (Racalmuto). C. RUIZ (Atti R. Accad. Lincei, 1926, [vi], **3**, 342—345).—Measurement of translucent, greyish-white or yellow crystals of barytes from the Giona mine (Girgenti), sometimes showing brown zones attributed to inclusions of bituminous matters, indicated the axial ratios $a:b:c=0{\cdot}81558:1:1{\cdot}31427$; the composition of the mineral is

BaO.	CaO.	SrO.	SO_3.	CO_2.	Loss at 115°.	Total.
55·92	0·20	0·13	43·44	trace	0·13	99·82

T. H. POPE.

Analysis of eudialite from the Chibine Mountains and of a product of its change. G. P. TSCHERNIK (Bull. Acad. Sci. Leningrad, 1925, [vi], 711—720).—A sample of transparent eudialite with a slight lilac-red or blood-red tint gave I on analysis.

	K_2O.	Na_2O.	MgO.	CaO.	MnO.	FeO.	Fe_2O_3.
I.	0·71	12·97	0·02	12·10	1·43	7·21	1·54
II.	0·51	5·95	0·04	11·88	2·20	3·85	15·87

	ZrO_2.	TiO_2.	SiO_2.	Cl.	H_2O.	Total, less O≡Cl.
I.	11·91	1·81	47·63	0·96	1·07	99·15
II.	3·92	3·04	48·90	0·14	3·25	99·52

As a result of various influences, the eudialite undergoes changes in composition, and a sample in which these changes had apparently proceeded to the greatest extent gave II on analysis. T. H. POPE.

Wulfenite and vanadinite from Oudida (Morocco). P. COMUCCI (Atti R. Accad. Lincei, 1926, [vi], **3**, 335—341).—Goniometric measurements are given for a specimen of wulfenite occurring as orange or honey-yellow crystals, but the value obtained for the angle (001) : (012) is not sufficiently constant to permit of the calculation of the axial ratio; analysis gave: MoO_3, 38·87; PbO, 60·91%. The vanadinite described was found as a network of hexagonal crystals unsuitable for measurement; its percentage composition was

PbO.	$PbCl_2$.	V_2O_5.	As_2O_5.	P_2O_5.	Insoluble.	Total.
60·08	10·10	20·34	0·39	0·41	0·22	99·54

T. H. POPE.

Scorodite from the Berezovski mine in the Urals. E. F. TSCHIRVA (Bull. Acad. Sci. Leningrad, 1925, [vi], 731—742).—Crystallographic measurements of scorodite from the Berezovski mine lead to the axial ratios, $a:b:c=0{\cdot}86785:1:0{\cdot}96185$.

T. H. POPE.

Minerals of bentonite and related clays and their physical properties. C. S. Ross and E. V. SHANNON.—See B., 1926, 361.

Waters of Bagni di Roselle (Grosseto). R. NASINI, C. PORLEZZA, and A. DONATI (Annali Chim. Appl., 1926, **16**, 99—126).

Organic Chemistry.

Oxidation of organic substances by copper oxide. A. STEOPOE (Bul. Chim., Soc. Româna Stiinte, 1924, **27**, 11—40).—When precipitated cupric oxide, washed and dried at a temperature not exceeding 120°, is used in the oxidation of paraffin and α-naphthylamine, the action is rapid and uniform throughout the mixture. Reaction commences at 125° with the naphthylamine; at higher temperatures, it may become explosive. Paraffin is oxidised partly to fatty acids, partly more completely; admixture with sodium hydroxide favours, whilst sodium carbonate or barium sulphate suppresses the first stage, at temperatures above 200°. α-Naphthylamine yields indulines, *as*-naphthazine, and insoluble brown condensation products, formation of the latter being due to the high temperature and the action of the metallic copper formed; by nitration of the naphthazine, a *mononitro*-derivative, m. p. 304—308°, as well as the

known dinitronaphthazine, m. p. 330—332°, have been obtained. S. I. LEVY.

Chemical action of α-particles on acetylene. W. MUND and W. KOCH.—See this vol., 481.

α-Naphthylcarbimide as a reagent for alcohols. V. T. BICKEL and H. E. FRENCH.—See this vol., 517.

Oxidisability of organic substances. G. LEJEUNE.—See this vol., 482.

Production of pure absolute alcohol. R. E. LYONS and L. T. SMITH.—See B., 1926, 384.

Preparation of dialkylethinenylcarbinols. L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 421—423).—The following dialkylethinenylcarbinols have been obtained by the methods previously described (Locquin and Wouseng, A., 1924, i, 822): *γδ-Dimethyl-Δ$^{\alpha}$-pentinen-γ-ol* (yield 75%), b. p. 133°/760 mm., d_4^{15} 0·876, n_D^{15} 1·459 (*allophanate*, m. p. 144°); *γ-methyl-Δ$^{\alpha}$-heptinen-γ-ol*, b. p. 63°/12 mm., d_4^{0} 0·860, n_D^{14} 1·439 (*allophanate*, m. p. 126—127°); *γε-dimethyl-Δ$^{\alpha}$-hexinen-γ-ol* (yield 65%), b. p. 148°/750 mm., 51—52°/10 mm., d_4^{12} 0·859, n_D^{12} 1·438 (*allophanate*, m. p. 114°); and *γ-methyl-Δ$^{\alpha}$-octinen-γ-ol*, b. p. 75°/10 mm., d_{15}^{19} 0·863, n_D^{19} 1·443 (*allophanate*, m. p. 120°). R. BRIGHTMAN.

Pinacones. L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 424—426).—Pinacones of the type OH·CMeR·CMe$_2$·OH are obtained in 70—85% yields by the action of 2½—3 mols. of magnesium methyl iodide in ether below 0° on the appropriate hydroxyketone (cf. Locquin and Wouseng, A., 1923, i, 433; Locquin and Leers, *ibid.*, 1924, i, 1043). The following are described: *βγ-dimethylhexane-βγ-diol*, b. p. 96—97°/11 mm., m. p. 38°; *βγε-trimethylhexane-βγ-diol*, b. p. 102°/13 mm., and *βγ-dimethyloctane-βγ-diol*, m. p. 29—30°, b. p. 115°/9 mm. R. BRIGHTMAN.

Mercaptomercuric bases and a mercury derivative of bromoform. G. SACHS and L. BALASSA (Z. anorg. Chem., 1926, **152**, 180—184).—Addition of sodium hydroxide to ethylmercaptomercuric acetate solution results in the liberation of a strongly basic substance which in concentrated solution rapidly decomposes with the formation of a yellow precipitate soluble in chloroform. The corresponding bromoform solution, on cooling, deposits crystals of a bromoform *derivative* of ethylmercaptomercuric oxide, EtS·HgOH,3HgO,4CHBr$_3$. This substance is very unstable and decomposes at 92° with explosion. The bromoform compound evolves ethyl mercaptan on exposure to light and the residue contains a true metallo-organic *compound*, CBr$_3$·HgBr,HgBr$_2$, which can be recrystallised from benzene. Addition of water to an alcoholic solution of this compound precipitates *bromomercuribromoform*, CBr$_3$·HgBr, m. p. 137° (decomp.). A. R. POWELL.

Conversion of fatty acids into hydrocarbons. G. STADNIKOV and E. IVANOVSKI.—See B., 1926, 306.

Partial splitting [by saponification] of mixed-acid glycerides. J. P. TREUB.—See this vol., 481.

Course of substitution reactions with halogenohydrins. I. A. GRÜN and R. LIMPÄCHER (Ber., 1926, **59**, [*B*], 690—695).—The action of potassium stearate on glycerol-α-iodohydrin gives α-monostearin in 60% yield, identical with the product obtained by Fischer, Bergmann, and Bärwind from *iso*propylideneglyceryl stearate (cf. A., 1920, i, 805). Conversion of the substance into its *iso*propylidene derivative can be effected to the extent of 97·1%. Assuming that only those glycerides react with acetone which contain hydroxyl groups in the vicinal position to one another, the compound may be regarded as homogeneous α-monostearin. By-products of the action are a *substance*, $C_{42}H_{82}O_7$, probably [CO$_2$C$_{17}$H$_{35}$·CH$_2$·CH(OH)·CH$_2$]$_2$O, m. p. 70·5—71·3°, stearic acid, and glycide (about 15%). Silver stearate and glycerol-α-iodohydrin at 100°, on the other hand, give glycide in yield reaching 79%, with smaller amounts of monostearin, glycerides, diglycerol esters, and stearic acid. The primary action appears, therefore, to consist in loss of hydrogen iodide from the iodohydrin with production of glycide. When potassium stearate is used, this reaction appears to be at most subordinate; the main change consists in the direct replacement of iodine by the acyloxy-group. H. WREN.

Synthesis of waxes. A. GRÜN, E. ULBRICH, and F. KREZIL (Z. angew. Chem., 1926, **39**, 421—428).—By heating a fatty acid in an iron vessel at 300° or less, the corresponding ketone is obtained (cf. J.C.S., 1911, **99**, 2298). Stearone, palmitone, myristone, laurone, and *tritetracontanone* (*behenone*), m. p. 92°, are thus obtained in excellent yield. When these ketones are heated at 300° with ethyl alcohol and sodium hydroxide, the secondary alcohols, *pentatriacontan-σ-ol*, m. p. 92° (corr.) (*acetyl* derivative, m. p. 58—59°; *benzoyl* derivative, m. p. 55—56°); *hentriacontan-π-ol*, m. p. 85·6° (corr.); *heptacosan-ξ-ol*, m. p. 81·8° (corr.), and *tricosan-μ-ol*, m. p. 75·5° (corr.), are formed in 80—90% yields. The alcohols, when heated to 200° with 1% of β-naphthalenesulphonic acid, lose water to produce mixtures of isomeric olefines in 98—99% yields; since the symmetrical alcohols are the source of these olefines, the isomerism is ascribed to differences in spatial configuration, the *cis*-compound probably having the higher m. p. The following are described, the isomeride of higher m. p. being given first: Δ$^{\rho}$-*pentatriacontene*, m. p. 66·5°; m. p. 45—46°, b. p. 267°/1 mm. (ρσ-*dibromopentatriacontane*, m. p. 63—63·5°; ρσ-*dichloropentatriacontane*, m. p. 47°, exceptionally stable to alkali); Δ$^{\sigma}$-*hentriacontene*, m. p. 45·2—45·4°, b. p. 245—246°/1 mm.; liquid, b. p. 241—242°/2 mm. [οπ-*dibromohentriacontane*, m. p. 43—43·5° (corr.)]; Δ$^{\nu}$-*heptacosene*, m. p. 34·2°; liquid, b. p. 210°, setting to a pulp at −2°, converted into higher-melting form by nitric acid and mercury; oxidation in acetone solution with potassium permanganate gives a mixture of tri- and tetra-decanecarboxylic acids, proving that the double linking is symmetrically placed in the molecule (ν$\bar{\nu}$ξ-*dibromoheptacosane*, m. p. 38·5—39°); Δ$^{\lambda}$-*tricosene*, m. p. 17—18°; liquid, setting to a pulp at −5°; oxidation of the liquid isomeride gives undecanecarboxylic acid and lauric acid [λμ-dibromotricosane,

m. p. 35·5° (corr.)]. Catalytic reduction of pentatriacontene with hydrogen and palladium-black gives *n*-pentatriacontane, m. p. 74·6°, which is also prepared by reducing pentatriacontanone to the alcohol, followed by reduction of the latter with sodium and amyl alcohol. Wax esters are produced on the technical scale by heating mixtures of acids and alcohols in iron vessels or in the presence of molten tin, the ester mixture so formed having the consistency, plasticity, and conchoidal fracture of most waxes. The pure alcohols combine with the chlorides of the higher fatty acids, when heated in an atmosphere of carbon dioxide, to give wax esters in 90—95% yield. The following esters are described : *μ-tricosyl laurate*, m. p. 21·5—22·5°; *μ-tricosyl myristate*, m. p. 25—25·5° (corr.); *μ-tricosyl palmitate*, m. p. 27·5—28° (corr.); *μ-tricosyl stearate*, m. p. 29·5—30·5°; *ξ-heptacosyl laurate*, m. p. 34—35°; *ξ-heptacosyl myristate*, m. p. 37·5—38° (corr.); *ξ-heptacosyl palmitate*, m. p. 41·5—42° (corr.); *ξ-heptacosyl stearate*, m. p. 39·5—40·5° (corr.); *π-hentriacontyl laurate*, m. p. 39·5—40·5°; *π-hentriacontyl myristate*, m. p. 45·5—46·5°; *π-hentriacontyl palmitate*, m. p. 48·5—49·5° (corr.); *π-hentriacontyl stearate*, m. p. 50·5—51° (corr.); *σ-pentatriacontyl laurate*, m. p. 42·5—43·5° (corr.); *σ-pentatriacontyl myristate*, m. p. 49—50° (corr.); *σ-pentatriacontyl palmitate*, m. p. 54—55° (corr.); *σ-pentatriacontyl stearate*, m. p. 56—57° (corr.). The pure esters show less plasticity than the mixture obtained from natural waxes. L. M. Clark.

Synthesis of dihydrochaulmoogric and dihydrohydnocarpic acids. II. C. R. Noller and R. Adams (J. Amer. Chem. Soc., 1926, **48**, 1080—1089; cf. this vol., 47).—Condensation of magnesium *cyclo*pentyl bromide with trimethylene oxide in ether affords *γ*-cyclo*pentylpropyl alcohol*, b. p. 85—86°/6 mm., n_D^{20} 1·4590, d_4^{20} 0·9137 (*phenylurethane*, m. p. 55—55·4°), together with a *liquid*, b. p. 152—157°. Condensation of magnesium *cyclo*pentyl bromide with methyl λ-aldehydododecoate affords *methyl μ-hydroxy-μ-cyclopentyltridecoate*, m. p. 29—29·5°, b. p. 205—210°/4 mm., from which the corresponding *acid*, m. p. 70·5—71°, was obtained by hydrolysis, together with the *methyl* ester, m. p. 38—40° (*phenylurethane*, m. p. 73·5—74°), of *μ-hydroxytridecoic acid*, m. p. 77—77·5°, and the *pinacol* of *methyl λ-aldehydododecoate*, $CO_2Me{\cdot}[CH_2]_{11}{\cdot}CH(OH){\cdot}CH(OH){\cdot}[CH_2]_{11}{\cdot}CO_2Me$, m. p. 58—59·5°, from which the corresponding *acid*, m. p. 59—65°, was obtained on hydrolysis. Magnesium *cyclo*pentylmethyl bromide and methyl θ-aldehydononoate afford similarly the *methyl* ester, b. p. 175—180°/3 mm., of *ι-hydroxy-κ-cyclopentylundecoic acid*, m. p. 60—60·5°. *μ*-cyclo*Pentyltridecoic acid*, m. p. 70—71°, and *κ*-cyclo*pentylundecoic acid*, m. p. 63—63·5°, obtained from the above corresponding hydroxy-esters, are identical with dihydrochaulmoogric and dihydrohydnocarpic acids, respectively. F. G. Willson.

Synthesis of homologues of dihydrochaulmoogric and dihydrohydnocarpic acids containing a *cyclo*hexyl in place of a *cyclo*pentyl group. III. G. S. Hiers with R. Adams (J. Amer. Chem. Soc., 1926, **48**, 1089—1093; cf. preceding abstract).—Treatment of β-*cyclo*hexylethyl alcohol with sulphuric and hydrobromic acids affords *γ*-cyclo*hexylethyl bromide*, b. p. 70—71°/6 mm., n_D^{25} 1·4888, d_{25}^{25} 1·2069. Condensation of magnesium β-*cyclo*hexylethyl bromide with methyl *η*-aldehydo-octoate yields the *methyl* ester, m. p. 35—36°, b. p. 192—198°/4 mm., of θ-*hydroxy-κ*-cyclo*hexylundecoic acid*, m. p. 76—77°, from which *κ*-cyclo*hexylundecoic acid*, m. p. 58—59°, was prepared. Methyl λ-aldehydododecoate (*loc. cit.*) is converted similarly into the *methyl* ester, b. p. 212—217°/4 mm., of *μ-hydroxy-μ*-cyclo*hexyltridecoic acid*, m. p. 72—73°, from which *μ*-cyclo*hexyltridecoic acid*, m. p. 63—64°, was prepared. F. G. Willson.

Conversion of optically active lactic acid into αβ-dihydroxypropane. P. A. Levene and H. L. Haller (J. Biol. Chem., 1926, **67**, 329—332).—Ethyl *l*-lactate, $[\alpha]_D^{20}$ −2·5°, yielded, on reduction with sodium and alcohol, *d*-αβ-dihydroxypropane, $[\alpha]_D^{20}$ +0·6° in alcohol; ethyl *d*-lactate, $[\alpha]_D^{22}$ +10·7°, gave, similarly, *l*-αβ-dihydroxypropane, b. p. 60—70°/1 mm., $[\alpha]_D^{21}$ −1·85° in alcohol; the latter, with phenylcarbimide, gave the *d*-diphenylcarbamate, m. p. 136—140°, $[\alpha]_D^{25}$ +2·8° in alcohol. C. R. Harington.

Structure of pyruvic acid. P. Pascal (Bull. Soc. chim., 1926, [iv], **39**, 396—398).—A comparison of the observed and calculated values for the molecular magnetic rotation of pyruvic acid and its lead and silver salts indicates that the liquid acid at 18° contains about 20% of the enolic form and a 90% solution 38% at the same temperature, whilst the salts possess almost entirely a ketonic structure (cf. Henri and Fromageot, A., 1925, ii, 929). R. Brightman.

Preparation of stearolactone. A. Blumenstock (Monatsh., 1926, **46**, 333—345).—The production, in quantity, of stearolactone by the action of sulphuric acid on either pure or technical oleic acid without heating the sulphonated product (cf. Shukoff and Schestakoff, A., 1908, i, 755) could not be confirmed. Distillation, under reduced pressure in a stream of carbon dioxide, of the product obtained by the action of zinc chloride on pure oleic acid (cf. Benedikt, A., 1890, 763) yielded an oil, b. p. 225—235°/12 mm., which partly solidified on cooling. Fractional crystallisation of this solid product from alcohol yielded four products, viz., of m. p. 75—76°, 48—49°, 64—65°, respectively, and a brown, viscous anhydride which deposited crystals of stearolactone, m. p. 51·2°. The best yields of the latter are obtained by dissolving the crude solid distillate (freed from oil) in alcohol, neutralising with sodium hydrogen carbonate, and extracting with light petroleum. Vacuum distillation and fractional crystallisation of the sulphonated pure oleic acid yielded similar products : (I), m. p. 72—73° (28%), (II), m. p. 48° (9%), (III), m. p. 64—65° (2%), and (IV), the liquid anhydride (17%), which deposited stearolactone on keeping, the yield of the latter being 12% of the weight of the oleic acid, as against 4·5% in the case of the zinc chloride method. F. G. Willson.

Transformation of maleic acid into fumaric acid accelerated by colloidal sulphur. H. Freundlich and G. Schikorr.—See this vol., 481.

Conversion products of dibenzoyl-*d*-tartaric anhydride. F. ZETZSCHE and M. HUBACHER (Helv. Chim. Acta, 1926, **9**, 291—297).—Dibenzoyl-*d*-tartaric anhydride is slowly converted on keeping, more rapidly on boiling with water, into the hydrated acid ($1H_2O$). Precipitation of the ammonium salt with mineral acid gives anhydrous dibenzoyl-*d*-tartaric acid (*magnesium* salt, decomp. at 220°, $[\alpha]_D^{20}$ —104·15° in water; *ammonium* salt, decomp. at 190°, $[\alpha]_D^{15}$ —151·8° in water; *monomethyl* ester, an oil decomposing on vacuum distillation with separation of benzoic acid). Dibenzoyl-*d*-tartaric anhydride reacts with aniline at the ordinary temperature with spontaneous warming, giving the *aniline* salt of *dibenzoyl*-d-*tartranilic acid*, m. p. 152°, $[\alpha]_D^{20}$ —78·24° in absolute alcohol, which is converted by mineral acid into dibenzoyl-*d*-tartranil. The by-product obtained by Vallée (Ann. Chim., 1908, [viii], **15**, 368) in the preparation of the anil from dibenzoyl-*d*-tartaric anhydride and *s*-diphenylcarbamide is shown to be anilidomaleïnanil, which is also produced, together with tartranilide, by interaction of the anhydride and aniline at 170°. Reduction of the anil with zinc dust and acetic acid or with sodium ethoxide gives oxanilide. Aniline dibenzoyl-*d*-tartranilic acid is decomposed by heating it above its m. p. for 1 hr.; aniline is eliminated with production of tartranilide, dibenzoyl-*d*-tartranil, and anilidomaleïnanil.

Attempts to prepare dibenzoyl-*d*-tartaryl chloride from the anhydride were unsuccessful. Reaction with phosphorus pentachloride for 3—4 hrs. at 130° gives a product containing benzoyl chloride. Esterification, after removal of phosphoryl chloride, gives a mixture of ethyl benzoate and ethyl chlorofumarate.

M. CLARK.

Constitution of dithiocarbonic acids and their salts. A. HANTZSCH and W. BUCERIUS (Ber., 1926, **59**, [*B*], 793—813).—Dithioacetic, *p*-methoxydithiobenzoic, and α-dithionaphthoic acids are normal pseudo-acids, since, as unimolecular "hydrogen esters," R·C(:S)·SH, in all non-aqueous solutions they are almost completely identical optically with their alkyl esters. In sufficiently dilute aqueous solution, they are completely identical optically with their alkali salts, since they pass through a series of equilibria entirely into true acids or, more correctly, into their hydroxonium salts, $R{\cdot}CS_2[H_3O]$, by addition of water. The transition is most rapid with acids of high dissociation constant. This is regarded as the "salt-formation constant," and therefore expresses numerically the tendency towards the formation of hydroxonium salts. The values of k for dithiocarbonic acids lie between 10^{-2} and 10^{-3}; they are therefore approximately 100 times as strong as the corresponding carboxylic acids. The optical anomaly of the xanthic acids, *i.e.*, the marked difference from their esters, is explained chemically by an extension of their structural formulæ to the subsidiary valency constitution, S:C$\langle^{SH}_{OR}$. This also explains why they are less readily oxidised than the oxygen-free dithio-acids to disulphides and their tendency towards intramolecular decomposition to alcohol and carbon disulphide. The optical anomaly of the unstable acids increases with increasing tendency towards decomposition. In dilute aqueous solution, they become optically identical with their salts and are then sufficiently stable to permit measurements of the dissociation constant. Decomposition therefore takes place only with the pseudo-acids and not with the true acids or acid ions. The stable dithio-acids, like their esters, are yellowish-red to dark red when molten; in the solid state, they are much paler in colour owing to association of the thiocarbonyl. The acids dissolve in water as hydroxonium salts with the same yellow to orange-yellow colour as their ammonium or alkali salts.

Catalytic decomposition of xanthic acids into alcohols and carbon disulphide in the "most sluggish," oxygen-free media (cf. von Halban, A., 1923, ii, 835) is probably induced only by traces of moisture. Only solvents which contain oxygen are certainly catalytic in action. The least active media, ether and acetone, form additive products by union of the oxygen with the thiocarbonyl. The most active solvents, alcohols and, particularly, water, yield primarily similar additive compounds which pass secondarily into spontaneously decomposable derivatives of orthocarbonic acid, $(SH)_2C(OR'){\cdot}OR^2$. Only in this manner is it possible to explain why methylxanthic acid in ethyl alcohol and ethylxanthic acid in methyl alcohol decompose at almost exactly the same rate, since the same orthocarbonic acid derivative is formed from each, and why the decomposition constants of the two systems lie between those of ethylxanthic acid in ethyl alcohol and methylxanthic acid in methyl alcohol.

The heavy metal salts, which are regarded as internally complex salts, are homopolar pseudo-salts, R·C(:S)·SX, and hence differ from the heteropolar true salts of the alkali and alkaline-earth metals with ionogenic linking, $[R{\cdot}CS_2]X$. As "metal esters," they resemble the pseudo-acids as "hydrogen esters" physically in their solubility and unimolecular constitution in indifferent media, optically in their ester-like absorption, and chemically by the absence of ionic reactions, which are slowly induced by acids or alkalis or by "hydrolysis." The stability (chemical indifference) of these pseudo-salts increases with the stability of the corresponding sulphides. The zinc and nickel salts pass more or less readily by addition of water into true salts, generally of the type $R{\cdot}C\langle S_2\rangle[X(H_2O)_6]$; the change is characterised by alteration in colour, and is analogous to the conversion of pseudo-acids into hydroxonium salts. They are not therefore "internally complex salts," since these are stable towards water. The existence of these aquo-salts is proved by their absorption in the ultra-violet being similar to that of the alkali salts. They are, however, generally so unstable that they can be extracted by ether as pseudo-salts in the same manner as the orange or red pseudo-acids can be removed from the yellow, aqueous solutions of the true acids.

H. WREN.

Constitution of aldehyde and ketone hydrogen sulphite compounds. F. RASCHIG (Ber., 1926, **59**, [*B*], 859—865).—The constitution, $CH_2(OH){\cdot}O{\cdot}SO_2Na$,

assigned to the additive compound of formaldehyde and sodium hydrogen sulphite by Knoevenagel (A., 1904, i, 867), and $CH_2(OH)\cdot O\cdot SONa$ for "rongalite" (cf. Reinking and others, A., 1905, i, 261), are not compatible with the ready production of methyl mercaptan from "rongalite," the stability of "formaldehyde bisulphite" to oxidising agents, its ready reducibility, and its ability to react with phenols yielding undoubted sulphonic acids. The direct attachment of sulphur to carbon in the formaldehyde hydrogen sulphite compound is probable, since it is readily transformed by ammonia into a compound which, with acetic anhydride, affords sulphur dioxide and acetamidomethyl alcohol, and hence must be regarded as aminomethylsulphonic acid. Further "formaldehyde bisulphite" and ethyl acetoacetate in faintly alkaline solution afford ethyl α-sulphomethylacetoacetate, $COMe\cdot CH(CH_2\cdot SO_2H)\cdot CO_2Et$, which is hydrolysed in alkaline solution to β-sulphopropionic acid and in acid solution to γ-ketobutanesulphonic acid. It is shown that the change is not due to initial fission of the "aldehyde bisulphite," with subsequent production of ethyl methyleneacetoacetate and addition of sulphurous acid. "Formaldehyde bisulphite" must therefore definitely be regarded as sodium hydroxymethylsulphonate. The product isolated by Glimm (Diss., Fribourg, 1902) and by Reinking and others was actually potassium methyl sulphate. The attachment of the hydroxy- (or amino-) and sulphonic groups to the same carbon atom confers a peculiar lability on each and is responsible for the ready loss of the latter group as sulphur dioxide. Bucherer's conversion of naphthol (and its derivatives) into naphthylamine by warm ammonium hydrogen sulphite is explained by the initial conversion of naphthol into its ketonic form, reaction of the latter to form the compound $\cdot CH_2\cdot C(OH)\cdot SO_2NH_4$, replacement of the hydroxy- by the amino-group, and loss of sulphurous acid yielding the amine $\cdot CH{:}C(NH_2)\cdot$. H. WREN.

Distillation of aqueous formaldehyde solutions. E. W. BLAIR and R. TAYLOR.—See B., 1926, 339.

Monothio- and dithio-triacetaldehyde. S. W. LEBEDEV and M. PLATONOV (Ber., 1926, **59**, [*B*], 762—767).—*Monothiotriacetaldehyde*, $S<\begin{matrix}CHMe\cdot O\\CHMe\cdot O\end{matrix}>CHMe$, m. p. 53·5—54°, b. p. above 160° (decomp.), is obtained in about 50% yield by passing hydrogen sulphide into a well-stirred solution of acetaldehyde in hydrochloric acid, the aldehyde being always in excess. It is conveniently purified by sublimation. It appears to be identical with Marckwald's monothiodiacetaldehyde. It is oxidised by potassium permanganate in acid solution to the corresponding *sulphone*, m. p. 150—152°. More prolonged action of hydrogen sulphide on acetaldehyde gives *dithiotriacetaldehyde*, $O<\begin{matrix}CHMe\cdot S\\CHMe\cdot S\end{matrix}>CHMe$, m. p. 70—72° (together with trithioacetaldehyde), which is oxidised to the *disulphone*, decomp. 215°. H. WREN.

Glyoxal. H. O. L. FISCHER and C. TAUBE [in part with B. KÜHN] (Ber., 1926, **59**, [*B*], 851—856).—Glyoxal sulphate, $C_2H_2(SO_4)_2$, prepared by the action of fuming sulphuric acid on *s*-tetrachloroethane in the presence of mercury salts (cf. A., 1923, i, 896), when warmed with a mixture of acetic acid and acetic anhydride, gives glyoxal tetra-acetate, m. p. 104—105°, in 70% yield. With the requisite alcohol, it affords *glyoxaltetramethylacetal*, b. p. 160—161°/760 mm., d_4^{23} 1·0103, $n_D^{21\cdot5}$ 1·4023, and glyoxaltetraethylacetal, b. p. 200—201°/760 mm., 90—92°/17 mm., $n_D^{22\cdot5}$ 1·4056. The latter compound yields very pure polymeric glyoxal when hydrolysed with 0·1*N*-sulphuric acid. Direct hydrolysis of glyoxal sulphate by warm water involves considerable production of glycollic acid; if the product is distilled in a vacuum, the *compound* $\begin{matrix}CO-O\\|\\CH_2\cdot O\end{matrix}>CH\cdot CH<\begin{matrix}O\cdot CO\\|\\O\cdot CH_2\end{matrix}$, m. p. 120°, is formed. Aqueous acetone and glyoxal sulphate yield the *compound* $C_{12}H_{18}O_8$, m. p. 206—207°, which has no ketonic properties. Magnesium phenyl bromide converts glyoxal sulphate into *iso*hydrobenzoin in 44% yield (cf. Wren and Still, J.C.S., 1913, **103**, 1770); the corresponding *methyl ether* has m. p. 92—93°. With tertiary bases, glyoxal sulphate gives non-crystalline, additive compounds containing 2 mols. of base to 1 mol. of sulphate. With glacial acetic acid, it affords the *compound* $C_2H_2O_8S_2,C_2H_4O_2$, m. p. 121—122° after softening. *Glyoxalmonophenylhydrazone* has m. p. 108° (decomp.). H. WREN.

Methylglyoxal. II. H. O. L. FISCHER and C. TAUBE (Ber., 1926, **59**, [*B*], 857—858).—Anhydrous, unimolecular methylglyoxal, when prepared by the distillation in a vacuum of polymeric methylglyoxal with phosphoric oxide (cf. A., 1924, i, 1167), frequently contains traces of phosphoric acid which influence its stability; they can be removed by a second distillation. With diazomethane, methylglyoxal gives diacetyl in poor yield. It is converted by magnesium phenyl bromide into methyl*iso*hydrobenzoin (cf. McKenzie and Wren, J.C.S., 1910, **97**, 473). H. WREN.

Dehydration of pinacones. I. R. LOCQUIN and L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 426—432; 433—438).—A more detailed account of work already published (A., 1924, i, 1043). βγγ-Trimethylpentan-δ-one is oxidised by nitric acid to ββ-*dimethylvaleric acid*, b. p. 104—105°/12 mm. (*chloride*, b. p. 148—150°/760 mm.; *amide*, m. p. 129°). R. BRIGHTMAN.

α-Hydroxyketones. L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 423—424).—The dialkylethinenylcarbinols (this vol., 596), on treatment with water in the presence of acid mercuric sulphate (cf. Locquin and Wouseng, A., 1924, i, 822), are converted into α-hydroxyketones. *γδ-Dimethylpentan-γ-ol-β-one* (yield 70%) has b. p. 163—165°/760 mm., 58°/16 mm., d_4^0 0·951 (*semicarbazone*, m. p. 134°); *γ-methylheptan-γ-ol-β-one*, b. p. 74°/10 mm., d_4^0 0·931 (*semicarbazone*, m. p. 152°); *γε-dimethylhexan-γ-ol-β-one* (yield 80%), b. p. 69—70°/12 mm., d_4^0 0·930 (*semicarbazone*, m. p. 154°); and *γ-methyloctan-γ-ol-β-one* (yield 80%), b. p. 85—86°/9 mm., d_4^{11} 0·914 (*semicarbazone*, m. p. 139°). R. BRIGHTMAN.

Residual affinity and co-ordination. XXVI. Quadridentate group in combination with bivalent metals. G. T. MORGAN and J. D. M. SMITH (J.C.S., 1926, 912—921).—Cupric ethylenediaminobisacetylacetone (cf. Combes, A., 1899, 851) behaves as a non-ionised complex (I) containing one bivalent copper atom in combination with one mol. of the bivalent quadridentate radical. It is unsaturated co-ordinatively and combines with one mol. of water, giving the dark green *aquo-cupric ethylenediaminobisacetylacetone*. Similarly, it gives rise to *cupric ethylenediaminobisacetylacetone ethylenediamine hydrate*, which, when exposed over solid sodium hydroxide or calcium chloride, passes into ethylenediamino-dicupric bisethylenediaminobisacetylacetone, $C_2H_4[NH_2 \ldots Cu\{\cdot O_2N_2\}C_{12}H_{18}]_2$. It is concluded that one characteristic co-ordination number of copper is 5, and this is confirmed by the preparation of *quinolinocupric acetylacetone*; similar, but less stable, compounds are obtainable from cupric acetylacetone and ammonia or pyridine. Hexa-aquo-nickel chloride and ethylenediaminobisacetylacetone yield *nickel ethylenediaminobisacetylacetone*, m. p. 200°, which, out of contact with air, boils without decomposition. It is unsaturated and on treating the alcoholic solution with aqueous ammonia gives the unstable *diammino-nickel ethylenediaminobisacetylacetone*, whilst with ethylenediamine hydrate it forms *ethylenediammino-nickel ethylenediaminobisacetylacetone*, $C_2H_4(NH_2)_2{=}Ni\{O_2N_2\}C_{12}H_{18}$. *Palladous ethylenediaminobisacetylacetone*, m. p. 228°, is similarly unsaturated; with chloroform, it yields *dichloroformopalladous ethylenediaminobisacetylacetone*. It appears that the co-ordination numbers of nickel and palladium may rise from 4 to 6. The co-ordination numbers of 5 for copper and 6 for nickel and palladium are discussed in connexion with Smith's scheme of electronic structure. A constitutional formula is ascribed to ethylenediamine hydrate in which the base is regarded as consisting of a cyclic co-ordination complex and a hydroxyl ion. F. M. HAMER.

Production of aldehydes from sugars. G. KLEIN (Biochem. Z., 1926, **169**, 132—138).—Formaldehyde is obtained from pentoses and hexoses by distillation of their pure, neutral, aqueous solutions; rhamnose yields acetaldehyde. Glucosides and polysaccharides show a behaviour similar to that of their constituent sugars when distilled in acid solution and some also when in neutral solution. Of the other compounds investigated, only glycollic acid and glycerol yielded formaldehyde under these conditions. C. RIMINGTON.

Synthesis of derivatives of γ-xylose. W. N. HAWORTH and G. C. WESTGARTH (J.C.S., 1926, 880—887).—Condensation of xylose with methyl alcohol containing hydrogen chloride is complete in the cold after 5—7 days; the *γ-methylxyloside*, b. p. 161·5°/0·03 mm., $[\alpha]_D$ in ethyl alcohol +62·8°, on methylation yields *trimethyl-γ-methylxyloside*, b. p. 110—114°/14 mm., n_D 1·4387, $[\alpha]_D$ in methyl alcohol, +32·0°, which may be hydrolysed to *trimethyl-γ-xylose*, b. p. 110°/0·04 mm., $[\alpha]_D$ +24·7° ⟶ 31·2°. Trimethyl-γ-xylose vigorously reduces permanganate and combines rapidly with acid methyl alcohol. It is oxidised by bromine water to *trimethyl-γ-xylonolactone*, b. p. 105°/0·04 mm., $[\alpha]_D$ in water +74·1° ⟶ 61·4° (period, 21 days), n_D 1·4465. By heating an aqueous solution of trimethyl-β-methylxyloside with hydrobromic acid, followed by addition of bromine water, *trimethyl-δ-xylonolactone* is prepared, b. p. 115—120°/0·05 mm., m. p. 55°, $[\alpha]_D$ in water −3·8° ⟶ +20·8° (period, 8 days). F. M. HAMER.

Constitution of *h*-glucose. H. H. SCHLUBACH and H. VON BOMHARD (Ber., 1926, **59**, [*B*], 845—848; for nomenclature see A., 1925, i, 1243).—Treatment of βγζ-trimethylglucose with methyl-alcoholic hydrogen chloride (cf. Irvine and Hirst, J.C.S., 1922, **121**, 1221) affords a trimethylmethylglucoside mixture of which the minimum specific rotation is lower than that of 2 : 3 : 6-trimethyl-β-methylglucoside (Schlubach and Moog, A., 1923, i, 1063). Displacement of the oxygen bridge must therefore have occurred with formation of the amylene oxide ring. Assuming Fischer's *h*-methylglucoside to contain a similar ring, the tetramethyl-*h*-glucose obtained therefrom must be identical with that derived from the authors' trimethylmethylglucoside; this is found to be the case as far as identity can be established with non-crystalline materials.

The isolation of βγζ-trimethylglucose by the hydrolysis of methylated starch does not afford proof of the presence of the butylene oxide ring in the components of the molecule; if an amylene oxide structure is assumed, the production of βγζ-trimethyl-*h*-glucose would be expected, which, however, under the experimental conditions, would immediately become isomerised to the normal βγζ-trimethylglucose. If Haworth's conception of the amylene oxidic structure of glucose be adopted (A., 1925, i, 1133), *h*-glucose must be considered to contain the butylene oxide ring. H. WREN.

Isomeric lævorotatory acetylchloroglucose. H. H. SCHLUBACH (Ber., 1926, **59**, [*B*], 840—844).—Dextrorotatory acetylchloroglucose has been assigned to the β-series, but, considered according to Hudson's rules (A., 1924, i, 371), it appears to belong to the α-series. It is therefore designated "α-acetylchloroglucose," and its lævorotatory isomeride (cf. Fischer and Armstrong, A., 1901, i, 257, 671; Fischer, *ibid.*, 1911, i, 605) β-acetylchloroglucose.

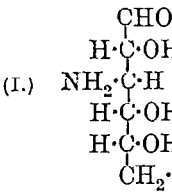
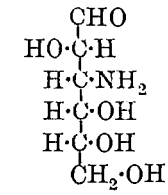
The successive action of aluminium chloride and phosphorus pentachloride on an ice-cold solution of tetra-acetylglucose in chloroform leads almost exclusively to dextrorotatory acetylchloroglucose. *β-Acetylchloroglucose*, m. p. 99—100°, $[\alpha]_D^{17}$ −13·0° in chloroform, −24·0° in carbon tetrachloride, −27·0° in benzene, −13·7° in ether, is prepared under stringent conditions by the action of silver chloride on acetylbromoglucose in presence of boiling ether. It readily becomes isomerised during preparation, but, once isolated, it may be crystallised from pure ether. In carbon tetrachloride, benzene, and ether it is relatively stable, but rapidly exhibits mutarotation in chloroform. H. WREN.

Acetylated monosaccharides. I. II. P. A. LEVENE and H. SOBOTKA (J. Biol. Chem., 1926, **67**, 759—770, 771—779).—I. The molecular rotations of the α-carbon atom (cf. Hudson, A., 1909, i, 135) of various acetyl derivatives of monosaccharides indicate that α- and β-penta-acetylgalactose, in common with penta-acetyl-*d*-mannose, have an amylene oxide structure. The ring formula for monosaccharides implies the existence of a *cis–trans*-isomerism between the α- and β-forms, expressing the different spatial relationships of the hydroxyl group attached to the α-carbon atom on the one hand, and of the residual chain of carbon atoms on the other, with respect to the plane of the ring; *e.g.*, in the *d*-series, the α-forms would possess the *trans*-configuration, since the α-hydroxyl group, and the ε- and ζ-carbon atoms, are on opposite sides of the plane of the ring. The experimental results recorded below indicate a difference between the structure of the tetra-acetylalkylmannosides prepared by acetylation of the mannosides, which possess the amylene oxide structure, and those derived from bromotetra-acetylmannose. Arguments are advanced against the view of Hudson (A., 1924, i, 371) that the halogenoacetyl derivatives of monosaccharides exist ordinarily in the α-form.

II. From penta-acetyl-β-mannose there was obtained *bromotetra-acetylmannose*, $[\alpha]_D$ +122·1° in chloroform; this yielded *methyltetra-acetylmannoside*, m. p. 105°, $[\alpha]_D^{23}$ −31·0° in chloroform, and *ethyltetra-acetylmannoside*, m. p. 81—82°, $[\alpha]_D$ −27·6° in chloroform. Both these compounds, on alkaline hydrolysis, lost three acetyl groups, to give the corresponding monoacetyl derivative. Acetylation of methyl-α-mannoside yielded *methyltetra-acetyl-α-mannoside*, m. p. 62—63°, $[\alpha]_D$ +49·0° in chloroform. By acetylation of the dextrorotatory syrup, resulting from the action of alcoholic hydrogen chloride on mannose, there were obtained two forms of *ethyltetra-acetylmannoside*, one (in small yield), having m. p. 110—113°, $[\alpha]_D$ +1·8° in chloroform, and the other a syrup, $[\alpha]_D$ +42·5° in chloroform. The above three acetylmannosides all lost four acetyl groups on alkaline hydrolysis.

Methyltetra-acetyl-β-galactoside, prepared from bromotetra-acetylgalactose, had m. p. 94°, $[\alpha]_D$ −10·5° in chloroform; *methyltetra-acetyl-α-galactoside*, by acetylation of methyl-α-galactoside, was obtained as a syrup, b. p. 190°/0·8 mm., $[\alpha]_D$ +69·3° in chloroform; both these compounds lost four acetyl groups on alkaline hydrolysis. C. R. HARINGTON.

Acetone sugars. VIII. New aminoglucose. K. FREUDENBERG, O. BURKHART, and E. BRAUN (Ber., 1926, **59**, [*B*], 714—720; cf. Freudenberg and Doser, A., 1925, i, 366; Freudenberg and Smeykal, this vol., 274).—*p*-Toluenesulphonylglucose di*iso*propylidene ether is converted by alcoholic ammonia at 175° into *γ-aminoglucose di*isopropylidene ether, m. p. 92—93°, $[\alpha]_{578}^{18}$ +40·5° in *s*-tetrachloroethane (*benzoyl* derivative, m. p. 142—143°, $[\alpha]_{578}^{18}$ +96·64° in *s*-tetrachloroethane). Removal of the *iso*propylidene groups leads to the production of non-crystalline *γ-aminoglucose* (I), which affords a *benzoyl* derivative, m. p. 128—130°, and *phenylosazone*, decomp. 207° (corr.), $[\alpha]_{578}^{18}$ −58° (±6°) in a mixture of pyridine, water, and methyl alcohol. γ-Aminoglucose di*iso*propylidene ether is converted by methyl-alcoholic hydrogen chloride into *γ-amino-α-methylglucoside hydrochloride*, m. p. about 207°

(I.)  (II.) 

(decomp.), $[\alpha]_{578}^{18}$ −46·6° in water; after hydrolysis by acid, it is oxidised by mercuric oxide to *γ-aminogluconic acid*, m. p. 168° (decomp.), $[\alpha]_{578}^{18}$ +13° in water. *p*-Toluenesulphonylglucose di*iso*propylidene ether and methyl-alcoholic dimethylamine at 160° afford *γ*-dimethylaminoglucose di*iso*propylidene ether, which readily yields the corresponding *methiodide*, $[\alpha]_{578}^{18}$ +49·5° in water. The reaction between ammonia and *p*-toluenesulphonylglucose di*iso*propylidene ether does not proceed very satisfactorily, but better results are not obtained with *γ-2-naphthalenesulphonylglucose di*isopropylidene ether, m. p. 101—102°, $[\alpha]_{578}^{18}$ −69·7° in *s*-tetrachloroethane, or *γ-ethanesulphonylglucose di*isopropylidene ether, m. p. 84—85°, $[\alpha]_{578}^{20}$ −51·58° in *s*-tetrachloroethane. An amine could not be prepared from p-*toluenesulphonyl-α-fructose di*isopropylidene ether, m. p. 97°, $[\alpha]_{578}^{20}$ −159·5° in *s*-tetrachloroethane, or *ethanesulphonyl-α-fructose di*isopropylidene ether, m. p. 100—101°, $[\alpha]_{578}^{20}$ −163·62° in *s*-tetrachloroethane.

p-Toluenesulphonyltriacetylbromoglucose (cf. Freudenberg and Ivers, A., 1922, i, 524) is converted by silver carbonate into *γ-*p-*toluenesulphonyl-βεζ-triacetylglucose*, m. p. 175°, $[\alpha]_{578}^{18}$ +52·8° in acetone.

The amino-group must occupy the γ-position in methyl*epi*glucosamine (Fischer, Bergmann, and Schotte, A., 1920, i, 426), since methylglucoside-β-chlorohydrin and hydrazine give trihydroxypropylpyrazole (cf. Freudenberg and Doser, A., 1923, i, 652). To the free sugar, therefore, the configuration II is assigned (cf. Levene and Meyer, *ibid.*, 445).

H. WREN.

Acetone sugars. IX. Constitution of the *iso*propylidene ethers of rhamnose and mannose. K. FREUDENBERG and A. WOLF (Ber., 1926, **59**, [*B*], 836—840; cf. preceding abstract).—The action of acetone on rhamnose gives rise to *rhamnose* iso*propylidene ether*, b. p. 108—110°/0·5 mm., m. p. 79—80°, $[\alpha]_{578}^{20}$ +17·4° in water (final value), in addition to the compound, m. p. 87—89°, isolated by Fischer. Since rhamnose *iso*propylidene ether is converted by alcoholic dimethylamine at 100° into *dimethylaminorhamnosyl* iso*propylidene ether*, b. p. 82—84°/1 mm., $[\alpha]_{578}^{18}$ −20·2° in water (from which the parent compound is regenerated by dilute acetic acid), the α-hydroxyl group of the parent substance must be intact. Similarly, rhamnose *iso*propylidene ether is transformed by methyl iodide and silver oxide into dimethylrhamnose *iso*propylidene ether, b. p. 65—67°/0·5—1 mm., $[\alpha]_{578}^{16}$ −32·5° in water (cf. Purdie and Young, J.C.S., 1906, **89**, 1194), which is hydrolysed by acids to *ε-methylrhamnose* (*phenyl-*

hydrazone, decomp. 163—164°) instead of to dimethylrhamnose. The ready loss of one methyl group shows it to be in glucosidic union, and hence in the α-position. The butylene oxide structure of rhamnose *iso*propylidene ether is established by the oxidation of the methyl ether thus derived from it into *l*(—)-α-methoxypropionic acid, identified as the *silver* salt and as l(—)-ω-α-*methoxypropoxyacetoveratrone*, m. p. 91°, $[\alpha]^{18}_{5773}$ −38·8° in *s*-tetrachloroethane; the corresponding d-*compound*, m. p. 91°, $[\alpha]^{17}_{5773}$ +38·32° in *s*-tetrachloroethane, and the r-*derivative*, m. p. 74°, are described. Rhamnose itself therefore possesses the butylene oxide structure, since it is improbable that the oxygen bridge should be ruptured by the entry of the *iso*propylidene group. The close similarity of rhamnose and mannose causes the latter to be regarded as a butylene oxide form, although the possibility of an equilibrium between butylene and amylene oxide forms is not excluded. H. WREN.

Constitution of maltose. J. C. IRVINE and I. M. A. BLACK (J.C.S., 1926, 862—875).—Methylation of maltose in two stages by means of methyl sulphate, followed by hydrolysis of heptamethyl-methylmaltoside, gives βγδζ-tetramethylglucose, but the second scission product is βγζ-trimethylglucose, m. p. 113—114°, and not the βγδ-isomeride as stated by Haworth and Leitch (*ibid.*, 1919, **115**, 809). Heptamethyl-methylmaltoside has also been treated with methyl-alcoholic hydrogen chloride, with subsequent hydrolysis, by aqueous hydrogen chloride, of the resulting mixture of tetramethyl- and trimethyl-methylglucosides. A mixture of βγδζ-tetramethylglucose and βγζ-trimethylglucose is also obtained by hydrolysis of heptamethyl-methylmaltoside, n_D 1·4662, obtained by methylation of methylmaltoside ($+H_2O$), m. p. 110—111°, which is prepared by the action of alcoholic ammonia on hepta-acetylmethylmaltoside, m. p. 128—129°. Maltose is converted into octa-acetylmaltose, which, by the action of hydrogen bromide, in presence of acetic acid, ether, and benzene, and subsequent treatment with methyl alcohol and silver carbonate, yields hepta-acetylmethylmaltoside, together with a *by-product*, m. p. 145—146°, $[\alpha]_D$ in chloroform +69·1°. Since βγζ-trimethylglucose is capable of reacting as a γ-sugar, its production does not lead to discrimination between positions δ and ε as the point of union of two glucose residues. Formulæ for maltose and *iso*maltose, and for cellobiose and *iso*cellobiose are suggested. F. M. HAMER.

Constitution of the disaccharides. X. Maltose. C. J. A. COOPER, W. N. HAWORTH, and S. PEAT (J.C.S., 1926, 876—880; cf. *ibid.*, 1919, **115**, 809).—By hydrolysing heptamethyl-methylmaltoside and separating the products by extraction with chloroform, there is isolated, from the chloroform solution, βγδζ-tetramethylglucose, whilst evaporation of the aqueous part yields, not βγδ-trimethylglucose, as previously stated, but βγζ-trimethylglucose, m. p. 110—116°, together with a syrup consisting of the β-form of this sugar. The product of oxidising the trimethylglucose with nitric acid was originally regarded as a trimethylsaccharolactone, but is now considered to have been a mixture of dimethylsaccharolactone and its ethyl ester. Esterification of the oxidation product gives a liquid, b. p. 110—115°/0·03 mm., the titration results of which correspond with those required for dimethylsaccharolactone ethyl ester. F. M. HAMER.

Synthesis of gentiobiose. A. GEORG and A. PICTET (Helv. Chim. Acta, 1926, **9**, 444—445; cf. Helferich, this vol., 386).—The action of concentrated hydrochloric acid on dextrose yields, in addition to *iso*maltose (Fischer, A., 1891, 412), a small quantity of the isomeric gentiobiose. Separation of the disaccharides is effected by acetylation. The amorphous *acetyl* derivative of *iso*maltose, m. p. 72—77°, is less readily soluble in alcohol than β-octa-acetylgentiobiose. Gentiobiosazone has m. p. 163—164° (cf. Haworth and Wylam, J.C.S., 1923, **123**, 3120, m. p. 162—167°; Helferich, *loc. cit.*, m. p. 170—173°). M. CLARK.

Identity of *iso*maltose with gentiobiose. H. BERLIN (J. Amer. Chem. Soc., 1926, **48**, 1107—1111).—The unfermentable portion of the product obtained by the action of concentrated hydrochloric acid on dextrose (cf. Fischer, A., 1891, 412) was acetylated with acetic anhydride and pyridine (cf. Zemplén, A., 1915, i, 119), giving β-gentiobiose octa-acetate (yield 1% of the dextrose). On hydrolysis with methyl-alcoholic sodium methoxide and treatment with phenylhydrazine in presence of glacial acetic acid, gentiobiosephenylosazone, m. p. 179—181°, was obtained, apparently identical with the product designated *iso*maltoseosazone by Fischer (*loc. cit.*). F. G. WILLSON.

Influence of acid character of polynitrophenols and nitronaphthols on their capacity for forming glucosides. E. GLASER and A. C. THALER.—See this vol., 608.

Preparation of diamines and amino-alcohols. N. PUTOCHIN (Ber., 1926, **59**, [*B*], 625—630).—Ethylenediamine is obtained in 95% yield by the hydrolysis of ethylenediphthalimide with cold, aqueous potassium hydroxide followed by distillation of the solution to dryness, addition of water to the residue, and repeated distillation to dryness. Trimethylenediamine and pentamethylenediamine are prepared similarly in almost theoretical yield. Analogous treatment of γ-bromopropyl- and β-bromoethyl-phthalimide affords γ-amino-*n*-propyl alcohol and β-aminoethyl alcohol in 90% and 75—80% yield, respectively.

[With M. A. LISSIZIN.]—ε-Bromo-*n*-amylphthalimide yields *ε-amino-n-amyl alcohol*, b. p. 221—222°, m. p. 27—28°, d^{17}_{16} 0·9488, n^{17}_D 1·4618; the *chloroplatinate* is described. H. WREN.

Reactions between sugars and amino-acids. I. Synthesis of sarcosineglucoside. K. MAURER (Ber., 1926, **59**, [*B*], 827—829).—*Ethyl tetra-acetylglucosylmethylaminoacetate*, $C_{19}H_{29}O_{11}N$, m. p. 87—88°, $[\alpha]^{20}_D$ −5·29° in methyl alcohol, is prepared in 79% yield by the action of acetobromoglucose on sarcosine ester (2 mols.). The corresponding *amide*, $C_6H_{11}O_5{\cdot}NMe{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, has m. p. 169—170° (decomp.) after darkening at 165°, $[\alpha]^{21}_D$ +15·01° in aqueous solution. The glucoside is very readily

hydrolysed by acids or alkalis. Reaction between acetobromoglucose and ethyl aminoacetate does not proceed simply. H. WREN.

Naturally occurring amino-acids. P. KARRER and M. EHRENSTEIN (Helv. Chim. Acta, 1926, **9**, 323—331).—*d*-Lysine yields the *d*-dibenzoyl derivative, m. p. 149—150°, $[\alpha]_D^{20}$ +3·06° in 0·1*N*-sodium hydroxide solution, $[\alpha]_D^{15}$ −8·59° in methyl alcohol, hydrolysed by hydrochloric acid or barium hydroxide to d-ε-*benzoyl-lysine*, m. p. 235°, $[\alpha]_D^{19}$ +20·12° in hydrochloric acid solution. The monobenzoyl derivative reacts with nitrosyl bromide, giving an active *α-bromo-ε-benzamidohexoic acid*, m. p. 128·5—129°, $[\alpha]_D^{18\cdot5}$ −29·15° in absolute alcohol, resolidifying above its m. p. to give the *dl*-compound, m. p. 164—165°. The active bromo-compound is reduced by sodium amalgam to ε-benzamidohexoic acid. *d*-ε-Benzoyllysine yields a *phenylcarbamate*, m. p. 128—130° (decomp.), converted by boiling with 12% hydrochloric acid into the active *hydantoin*, m. p. 145°, $[\alpha]_D^{16}$ −45·84° in absolute alcohol, which is racemised by boiling with stronger hydrochloric acid.

Benzoylation of ornithine from arginine gives the *d*-dibenzoyl derivative, m. p. 185—186°, $[\alpha]_D^{15}$ −1·6° in methyl alcohol. Hydrolysis with barium hydroxide solution (cf. A., 1912, i, 13) gives d-α-*monobenzoylornithine*, m. p. 224—226°, $[\alpha]_D^{20}$ +8·03° in aqueous solution, converted by nitrous acid into α-benzamido-δ-hydroxyvaleric acid, which gives with hydriodic acid in a sealed tube at 120—140° a mixture of active and inactive pyrrolidine-2-carboxylic acids (cf. A., 1905, i, 749) separated through the copper salts. The active proline thus obtained was strongly lævorotatory in aqueous solution, but the quantity of material was insufficient for purification. The constitution was inferred from the presence of all the characteristic properties of proline. M. CLARK.

Aldehydic compounds of amino-acids. M. BERGMANN and L. ZERVAS (Z. physiol. Chem., 1926, **152**, 282—299).—The following alkylideneamino-acids and their salts have been prepared by the authors' methods (A., 1925, i, 890): o-*hydroxybenzylidenehistidine*, *brucine* salt, m. p. 96—102° (decomp.); *benzylidene*-l-*cystine*; o-*hydroxybenzylidene*-l-*cystine*, *barium* salt; o-*hydroxybenzylidene*-dl-*serine*, *quinine*, *cinchonidine*, and *brucine* salts; *benzylidene*- and o-*hydroxybenzylidene*-d-*lysine*; o-*benzylidene*-d-*ornithine*; *benzylidene*-d-*arginine*, m. p. 204—205° after softening at 200°. Free arginine with salicylaldehyde gives *o*-hydroxybenzylidenearginine, but arginine nitrate with sodium hydroxide and salicylaldehyde gives *o*-hydroxybenzylidene-*d*-arginine–sodium nitrate, $(C_{13}H_{18}O_3N_4)_4,NaNO_3$. The determination by means of aldehydic compounds of the amounts of lysine, arginine, and proline in the hydrolysate of glue gave 2·3, 6·43, and 7·44%, respectively. The method is rapid, and may be further simplified if the isolation of arginine only is required. Arginine is converted into ornithine by treating with barium hydroxide, followed immediately by salicylaldehyde, which precipitates the barium salt of *o*-hydroxybenzylideneornithine; with acids, this readily gives pure ornithine. An attempt to use aldehydic compounds for the separation of optically active components was not successful, as the decomposition of the amino-acid–aldehyde–alkaloid complex could not be achieved. P. W. CLUTTERBUCK.

Preparation of *d*-arginine carbonate. A. E. PRATT (J. Biol. Chem., 1926, **67**, 351—356).—After hydrolysis of the protein with hydrochloric acid, the arginine is separated from the solution as the 2 : 4-dinitro-α-naphthol-7-sulphonate (cf. Kossel and Gross, A., 1924, ii, 211); the salt is recrystallised from dilute sulphuric acid, dissolved in hot dilute sulphuric acid, and the sulphonic acid removed by extraction with butyl alcohol. The aqueous solution is treated with barium hydroxide in slight excess, saturated with carbon dioxide, and filtered, the filtrate yielding, on evaporation, 85—90% of the theoretical amount (calculated on the arginine content of the protein) of pure arginine carbonate. C. R. HARINGTON.

Polypeptides, in the synthesis of which glutamic acid is concerned, and their derivatives. E. ABDERHALDEN and E. ROSSNER (Z. physiol. Chem., 1926, **152**, 271—281).—The following substances have been prepared: *diethyl* dl-*bromoisohexoyl*-d-*glutamate*, oil, b. p. 153° in a high vacuum; *ethyl* dl-*leucyl*-d-*glutamic anhydride*, m. p. 214—215°; dl-*leucyl*-d-*glutamic anhydride*, m. p. 203°; *dimethyl* dl-*bromoisohexoyl*-d-*glutamate*, b. p. 133°/high vac.; dl-*leucyl*-d-*glutamamide anhydride*, m. p. 252° (decomp.); *ethyl benzoyl*-d-*glutamate*, m. p. 73—74°, b. p. 290°/high vac.; *methyl benzoyl*-d-*glutamate*, m. p. 76—78·5°, b. p. 220°/vac.; *leucylasparagine anhydride*, m. p. 247°. P. W. CLUTTERBUCK.

Preparation of cyanogen. Preservation of gaseous cyanogen. B. RICCA.—See this vol., 489.

Nickel carbonyl, carbon monoxide, and Grignard reagents. W. L. GILLILAND and A. A. BLANCHARD (J. Amer. Chem. Soc., 1926, **48**, 410—420).—Ethereal magnesium methyl iodide or magnesium phenyl bromide reacts vigorously with nickel carbonyl, with precipitation of metallic nickel and basic magnesium salt, whilst yellow organic products of high b. p. remain dissolved in the ether. Carbon monoxide alone is without action on ethereal magnesium phenyl bromide, but in presence of a trace of nickel carbonyl it is absorbed. At the commencement of the reaction, the rate of absorption of carbon monoxide by the cooled ethereal solution is 20—25 litres per hr. per mol. of Grignard reagent, becoming considerably less when 7—8 litres of the gas are absorbed. If the mixture is then boiled, rapid absorption again takes place in the cooled solution, and this reactivation process can be repeated until a total of 14—16 litres of carbon monoxide have been absorbed per mol. of Grignard reagent. Hydrolysis of the reaction product is accompanied by the evolution of much heat. A trace of phenol is the only organic product remaining in the aqueous layer, whilst the ethereal solution deposits, on keeping, a small quantity of pentaphenylethane, and yields, on evaporation, triphenylmethane, triphenylvinyl alcohol, and tetraphenylethylene, together with a considerable proportion of non-volatile tarry matter, from which, by hot extraction with ether, a brown solid can be isolated. The

primary reactions when excess of the Grignard reagent is present are formulated as follows: $CO + PhMgBr \longrightarrow O{:}CPhMgBr \longrightarrow {:}CPh_2(OMgBr)\cdot MgBr$ (I) $\longrightarrow CPh_3MgBr$ (II) $+ O(MgBr)_2$. In contrast to the products obtained analogously from carbon dioxide, these products are themselves Grignard reagents. Condensation of (I) with carbon monoxide, followed by loss of magnesium oxybromide, would yield diphenylketen, and this, by condensation with magnesium phenyl bromide and subsequent hydrolysis, affords triphenylvinyl alcohol. The synthesis of pentaphenylethane from (II) proceeds analogously. The occurrence of tetraphenylethylene in the product is ascribed to the decomposition of more complex substances, *e.g.*, pentaphenylethane, on distillation.

F. G. WILLSON.

Application of thallium compounds in organic chemistry. III. Alkylations. C. M. FEAR and R. C. MENZIES (J.C.S., 1926, 937—940).—Methyl stearate is formed by boiling thallous stearate and methyl iodide, whilst methyl palmitate and *propyl palmitate*, m. p. 15·3—15·4°, b. p. 209°/22 mm., are prepared analogously. Ethyl ethylacetoacetate has been prepared from ethyl thalloacetoacetate, and *o*-methoxybenzaldehyde from thallous salicylaldehyde, whilst the amorphous *trithallium methylglucoside* yields trimethyl methylglucoside, $[\alpha]_D$ in ethyl alcohol (0·8%) +165·9°. The sparingly soluble tetrathallium tartrate is incompletely methylated by this method after 100 hrs., and an attempt to methylate the thallous compound of *o*-nitrophenol proved unsuccessful.

F. M. HAMER.

Hydrolytic decomposition of the sulphonic acids of the isomeric xylenes in relation to the purification of commercial xylene. N. KISHNER and G. G. VENDELSTEIN (J. Russ. Phys. Chem. Soc., 1925, **57**, 1—12).—In agreement with Crafts (A., 1892, 1134), the authors find that *p*-xylene dissolves in concentrated sulphuric acid (cf. Clarke and Taylor, A., 1923, i, 451), only slight heating taking place. Under similar conditions, *m*-xylene dissolves completely in sulphuric acid, considerable heat being generated. When a mixture of the two xylenes is treated, the proportion of the *para*-compound dissolving with the *meta*-isomeride increases as the temperature rises. With crude xylene, the proportion dissolving in the acid in 30 min. increases from 40% in 92·1% acid to 72·5% in 94·8% acid.

The composition of mixtures of *m*- and *p*-xylenes may be determined by means of the solidifying point, this being, for 100% *para*-compound, 13·5°; 90%, 9·1°; 80%, 4·8°; 70%, −0·4°; 60%, −6·0°; 50%, −12·0°. The presence of *o*-xylene or ethylbenzene does not affect the relation between the proportion of *p*-xylene and the solidifying point.

Sulphonation followed by fractional hydrolysis serves as a means of obtaining pure *m*-xylene from commercial xylene.

T. H. POPE.

Bromination and iodination of organic compounds. E. ZMACZYNSKI (Ber., 1926, **59**, [*B*], 710—711).—Bromination or iodination is effected by mixing the organic compound with a solution of alkali bromide (5 mols.) and alkali bromate (1 mol.) and introduction of gaseous chlorine. Toluene and acetone may be brominated by this method, which ensures the introduction of all the bromine into the organic molecule.

Cyanogen bromide or iodide is economically prepared by treating a solution of sodium or potassium cyanide at 0—5° with successive equivalent quantities of sulphuric acid and bromine or iodine; when reaction is complete, a second equal quantity of alkali cyanide is added, followed by gaseous chlorine until a drop of the solution colours starch–iodide paper blue.

H. WREN.

Coupling action of the Grignard reagent. I. *o*- and *p*-Cyanobenzyl halides. R. C. FUSON (J. Amer. Chem. Soc., 1926, **48**, 830—836).—Treatment of *p*-cyanobenzyl bromide with magnesium ethyl bromide affords an amorphous, greenish-yellow *substance*, softening at 155°, m. p. not below 200°, which contains halogen, but not nitrogen, the reaction between *p*-cyanobenzyl iodide and magnesium ethyl bromide proceeding similarly. *o*-Cyanobenzyl bromide, obtained by the action of bromine on *o*-toluonitrile in absence of solvent, has m. p. 71·5—72·5° (cf. Drory, A., 1891, 1460). It yields *o-cyanobenzyl iodide*, m. p. 76·5—78·5°, when treated with sodium iodide in acetone (cf. Davies and Perkin, J.C.S., 1922, **121**, 2208). Treatment of either *o*-cyanobenzyl bromide or iodide with magnesium ethyl bromide, or of the bromide with magnesium methyl iodide, affords *αβ-di-(o-cyanobenzyl)ethane*, m. p. 138—139·5°, together with, in the first case, a small proportion of a *substance* of high m. p. containing bromine. Treatment of the above cyano-derivative with boiling aqueous 40% potassium hydroxide affords *αβ-diphenylethane-2 : 2′-dicarboxylamide*, m. p. 241—242°, from which, by the action of boiling aqueous-alcoholic potassium hydroxide, *αβ-diphenylethane-2 : 2′-dicarboxylic acid*, m. p. 226—228°, is obtained.

F. G. WILLSON.

Unsymmetrically substituted dinitro- and diamino-derivatives in the stilbene and tolane series. I. Elimination of hydrogen chloride from 3 : 4′-dinitrostilbene dichloride. H. A. HARRISON and H. WOOD (J.C.S., 1926, 577—583).—By heating 3 : 4′-dinitrostilbene dichloride with pyridine, it is converted into α-chloro-4 : 3′-dinitrostilbene. Condensation of *p*-nitrophenylacetic acid and *m*-nitrobenzaldehyde in presence of piperidine at 110—150° gives 3 : 4′-*dinitrostilbene*, m. p. 217° (cf. Cullinane, *ibid.*, 1923, **123**, 2060), together with 3 : 4′-*dinitro-αβ-diphenylethyl alcohol*, m. p. 147—148°, *p*-nitrotoluene, and the *piperidine* salts, m. p. 168—169° and 204—205° (decomp.), of the two stereoisomeric forms of 3 : 4′-*dinitro-α-phenylcinnamic acid*, m. p. 221° and 205·5°, respectively, which on decarboxylation yield the same dinitrostilbene. On heating with pyridine, 3 : 4′-*dinitrostilbene dibromide* loses both bromine atoms. The action of chlorine on a chloroform solution of 3 : 4′-dinitrostilbene gives the α- and β-3 : 4′-*dinitrostilbene dichlorides*, m. p. 207° and 132—138°, respectively. When the mixture of dichlorides is heated with pyridine, the sole product is *α-chloro-4 : 3′-dinitrostilbene*, m. p. 161°, which on decomposition with warm concentrated sulphuric acid, followed by treatment of the product with water,

yields 4-*nitrophenyl* 3-*nitrobenzyl ketone*, m. p. 134° (*semicarbazone*, m. p. 219°), and this with phosphorus pentachloride regenerates the chlorodinitrostilbene. The structure of the ketone has been proved by oxidising 3 : 4′-dinitro-αβ-diphenylethyl alcohol by means of chromic acid to the isomeric 3-*nitrophenyl* 4-*nitrobenzyl ketone*, m. p. 102° (*semicarbazone*, m. p. 230°), which with phosphorus pentachloride forms α-*chloro*-3 : 4′-*dinitrostilbene*, m. p. 162°.

F. M. HAMER.

[Nitro]diphenylene sulphides. C. COURTOT and C. POMONIS (Compt. rend., 1926, **182**, 893—895).—Diphenylene sulphide is oxidised by a mixture of sulphuric and nitric acids to a crystalline *diphenylene sulphinone*, m. p. 188—188·5°, which is readily reduced by magnesium ethyl bromide back to the sulphide, but is not attacked by magnesium phenyl bromide. *Nitrodiphenylene sulphide*, m. p. 183·5—184°, is obtained in 40% yield by adding 1·5 mols. of 90—93% nitric acid to a solution of diphenylene sulphide in acetic acid. On reduction with zinc in boiling ammoniacal alcoholic solution, the corresponding *amino*-derivative, m. p. 131·5—132°, is formed; *acetyl* derivative, m. p. 167—168°. The amine diazotises and couples readily with *R*-salt etc. to give dyes. On adding the nitro-compound slowly to 90% nitric acid at 40°, *dinitrodiphenylene sulphide*, m. p. 324—325° (decomp.), is formed; it is also obtained, in 45% yield, by adding the theoretical quantity of 90% nitric acid to a solution of diphenylene sulphide in 1 part of acetic anhydride and 2 parts of acetic acid. Reduction with tin and acid yields the corresponding *diamine*, m. p. 178° (decomp.); it diazotises and couples readily. The *diacetyl* derivative, m. p. 237—239° (decomp.), when treated with sodium dichromate in acetic acid solution yields *diacetamidodiphenylene sulphide*, m. p. 378°. [Cf. this vol., 620.]

S. K. TWEEDY.

Physical properties of the nitronaphthalenes. L. DESVERGNES (Mon. Sci., 1926, [v], **16**, 73—80).—The m. p., solubilities in water at laboratory temperatures, 50°, and 100°, and in a number of organic solvents at various temperatures up to 50° have been determined for carefully purified specimens of α-nitro-, 1 : 5- and 1 : 8-dinitro-, and 1 : 3 : 8- and 1 : 4 : 5-trinitro-naphthalene. Pyridine forms with 1 : 4 : 5-trinitronaphthalene an insoluble brown compound.

S. I. LEVY.

The π of [minimal concentration of acid for] sulphonation. C. COURTOT and J. BONNET (Compt. rend., 1926, **182**, 855—857).—Benzene, toluene, chlorobenzene, and naphthalene are monosulphonated in good yield by adding the theoretical quantity of sulphur trioxide to the substance in chloroform solution at 0° to −10°. When, for the disulphonation of naphthalene, 3 mols. of sulphur trioxide to 1 mol. of naphthalene are employed, an additive *compound* of naphthalenedisulphonic acid (1 mol.) and sulphur trioxide (2 mols.) separates. The additive compound is broken down into naphthalenedisulphonic acid and sulphuric acid by the addition of ice water. The formation of this additive compound limits the yield of naphthalenedisulphonic acid to 50% of theory, if the product is worked up immediately, but the compound, on keeping, gives up sulphuric anhydride to the sulphuric acid monohydrate present, and after 24 hrs. the yield rises to 65%.

L. F. HEWITT.

β-Polynitroarylhydroxylamines. III. W. BORSCHE and E. FESKE (Ber., 1926, **59**, [*B*], 683—690; cf. A., 1923, i, 778, 1091).—6-Bromo-2 : 4-dinitroanisole is converted by hydroxylamine in hot, alcoholic solution into 6-*bromo*-2 : 4-*dinitrophenylhydroxylamine*, m. p. 93° (decomp.) (*dibenzoyl* derivative, m. p. 143—144°), which is transformed by dilute, aqueous ammonia into 6-bromo-2 : 4-dinitroaniline, m. p. 153°. The hydroxylamino-compound is reduced by ammonium sulphide to 6-*bromo*-4-*nitro*-1 : 2-*diaminobenzene*, m. p. 203—205°, which does not react with benzil, but is converted by phenanthraquinone into *bromonitrophenanthraphenazine*, m. p. 245°. It is oxidised by chromic acid in acetic acid solution to 6-*bromo*-2 : 4-*dinitro*-1-*nitrosobenzene*, m. p. 99°, and by nitric acid to 6-*bromo*-1 : 2 : 4-*trinitrobenzene*, m. p. 101°. 3 : 5-*Dinitro*-o-*tolylhydroxylamine*, m. p. 110°, is prepared from 3 : 5-*dinitro*-2-*phenoxytoluene*, m. p. 108·5°, or, preferably, from the corresponding methyl ether. It yields the following compounds: 3 : 5-*dinitro*-2-*acetoxyaminotoluene*, m. p. 214°; 3 : 5-*dinitro*-2-*benzoxyaminotoluene*, m. p. 121·5°, and the corresponding *dibenzoyl* compound, m. p. 178°; 3 : 5-*dinitro*-2-*methoxyaminotoluene*, m. p. 85°; 3 : 5-*dinitro*-o-*toluidine*, m. p. 214° (prepared by use of aqueous ammonia or by aniline in ether); 5-nitro-2 : 3-diaminotoluene, m. p. 175° (*diacetyl* derivative, m. p. 236°; 7-*nitro*-2 : 3-*diphenyl*-5-*methylquinoxaline*, m. p. 193°); 3 : 5-*dinitro*-2-*nitrosotoluene*, m. p. 133° (decomp.); 2 : 3 : 5-trinitrotoluene, m. p. 97°. 3 : 5-*Dinitro*-p-*tolylhydroxylamine*, m. p. 87°, is obtained with greater difficulty than analogous compounds; its *dibenzoyl* derivative, m. p. 175·5°, is described. 3 : 5-*Dinitro*-2-*hydroxylaminoanisole* could not be obtained homogeneous from 3 : 5-dinitroveratrole, m. p. 99°, or 3 : 5-*dinitro*-2-*phenoxyanisole*, m. p. 123°; the only characteristic compound which could be obtained from the crude product was 3 : 5-dinitro-2-aminoanisole, m. p. 177°. 2 : 4 : 6-*Trinitro*-m-*tolylhydroxylamine*, m. p. 99° (decomp.) (*acetyl* derivative, m. p. 122°), is oxidised by nitric acid to 2 : 3 : 4 : 6-*tetranitrotoluene*, m. p. 135°.

H. WREN.

β-Polynitroarylhydroxylamines. IV. 4 : 6-Dinitro-1 : 3-dihydroxylaminobenzene. W. BORSCHE and E. FESKE (Ber., 1926, **59**, [*B*], 815—821; cf. A., 1923, i, 778, 1091; this vol., 390).—4 : 6-Dinitroresorcinol dimethyl ether is converted by hydroxylamine in boiling alcoholic solution into β-4 : 6-*dinitro*-3-*methoxyphenylhydroxylamine*, m. p. 103° (decomp.) (? 130°); the *benzoyl* derivative, m. p. 131°, and *methyl ether*, m. p. 135° (decomp.), are described. Somewhat unexpectedly, the compound is converted by ammoniacal ammonium acetate solution into the *ammonium* salt, $2C_7H_7O_6N_3,NH_3$, m. p. 113° (decomp.), and by aniline into the *compound* $C_{13}H_{14}O_6N_4$, m. p. 116°. With hydrazine, it gives the *substance* $C_7H_7O_6N_3,N_2H_4$, m. p. 170°, which passes

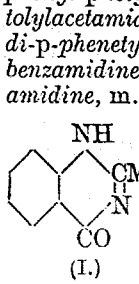
in boiling alcoholic solution into β-4 : 6-*dinitro*-3-*hydrazinophenylhydroxylamine*, m. p. 214° (decomp.). β-4 : 6-Dinitro-3-methoxyphenylhydroxylamine is reduced by ammonium sulphide to 2-*nitro*-4 : 5-*diaminoanisole*, m. p. 184°; it is oxidised by chromic acid in acetic acid to 2 : 4-*dinitro*-5-*nitrosoanisole*, m. p. 158°, and by nitric acid (*d* 1·52) to 2 : 4 : 5-trinitroanisole, m. p. 104°.

β-4 : 6-*Dinitro*-3-*phenoxyphenylhydroxylamine* is the main product of the action of hydrazine (2 mols.) on 4 : 6-dinitroresorcinol dimethyl ether; it forms unstable yellow needles, m. p. 116° (decomp.), and stable red needles, m. p. 108°. The *acetyl* derivative, m. p. 149°, unstable *ammonium* salt, m. p. 114° (decomp.), and *hydrazine* salt, $C_{12}H_9O_6N_3,N_2H_4$, decomp. 193°, are described; the last compound passes in boiling alcoholic solution into β-4 : 6-dinitro-3-hydrazinophenylhydroxylamine (see above). 2 : 4 : 5 : 2′ : 4′-*Pentanitrodiphenyl ether*, m. p. 186·5°, is obtained by treating β-4 : 6-dinitro-3-phenoxyphenylhydroxylamine with nitric acid (*d* 1·52) at 100°.

Treatment of dinitroresorcinol diphenyl ether with two successive quantities of hydroxylamine in boiling alcoholic solution affords 4 : 6-*dinitro*-1 : 3-*dihydroxylaminobenzene*, red plates, m. p. 172° (decomp.), or brownish-yellow needles, ($+1H_2O$), decomp. 184° (*diacetyl* derivative, m. p. 171°). Attempts to obtain the corresponding dinitroso-compound were unsuccessful, but 1 : 2 : 4 : 5-*tetranitrobenzene*, m. p. 188°, is prepared by oxidation with nitric acid (*d* 1·52).

Dinitrophloroglucinol triphenyl ether (cf. Borsche and Trautner, this vol., 390) exists in two *forms*, m. p. 107° and 87°, respectively. Attempts to convert it into dinitrotrihydroxylaminobenzene were unsuccessful. It is transformed by nitric acid (*d* 1·52) into *dinitrophloroglucinol tri-dinitrophenyl ether*, m. p. 279°. H. WREN.

***N*-Alkylated amidines.** M. SEN and J. N. RÂY (J.C.S., 1926, 646—648).—By heating a primary or secondary amine together with an acylamine and phosphorus trichloride at 110—120°, the following *N*-substituted amidines have been prepared: *phenyl*-m-*tolylacetamidine*, m. p. 103° (from acetanilide and *m*-toluidine, or from acet-*m*-toluidide and aniline); *phenyl*-p-*tolylacetamidine*, m. p. 90°; *phenyl*-o-*tolylacetamidine*, m. p. 138°; *phenyl*-p-*nitrophenylacetamidine*, m. p. 189° (from acetanilide and *p*-nitroaniline, or from *p*-nitroacetanilide and aniline); *phenyl*-p-*phenetylacetamidine*, m. p. 102°; *triphenylacetamidine*, m. p. 92°; o-*tolyl*-m-*tolylacetamidine*, m. p. 101°; *di*-p-*tolylacetamidine*, m. p. 120°; m-*nitrophenyl*-p-*tolylacetamidine*, m. p. 134°; and *diphenyl*-p-*tolylacetamidine*, $NPh_2{\cdot}CMe{:}N{\cdot}C_6H_4Me$, m. p. 122°; *di*-p-*phenetylacetamidine*, m. p. 117°; *phenyl*-o-*tolylbenzamidine*, m. p. 107°; p-*bromophenyl*-o-*tolylacetamidine*, m. p. 122°; *phenyl*-m-*tolylmethylacetamidine*, $NPhMe{\cdot}CMe{:}N{\cdot}C_6H_4Me$ (*picrate*, m. p. 157°). On making alkaline the product of reaction of acetanilide and phenylhydrazine, ammonia is evolved, giving diphenylacetamidine. On heating acetanilide and urethane in xylene solution with phosphoric oxide, a cyclic *amidine* (I) results. F. M. HAMER.



(I.)

***p*-Phenoxycarbamides and thiocarbamides derived from *p*-phenoxyaniline. Effect of the phenoxy-group on taste.** N. A. LANGE and W. R. REED (J. Amer. Chem. Soc., 1926, **48**, 1069—1074).—*p*-Nitrodiphenyl ether, m. p. 56—57°, b. p. 225—230°/30 mm., obtained in 33% yield by adding a mixture of nitric and acetic acids slowly to a boiling solution of diphenyl ether in acetic acid, yields, on reduction with tin and hydrochloric acid, *p*-aminodiphenyl ether, m. p. 82°, b. p. 315—320°/30 mm. (*hydrochloride*, m. p. 222°), and this is converted, by the action of aqueous potassium cyanate and phenylcarbimide, respectively, into p-*phenoxyphenylcarbamide*, m. p. 178°, and α-p-*phenoxyphenyl*-β-*phenylcarbamide*, m. p. 201°, both of which are tasteless. α-p-*Phenoxyphenyl*-β-p-*tolylcarbamide*, m. p. 204°, and α-p-*phenoxyphenyl*-β-α-*naphthylcarbamide*, m. p. 216°, both tasteless, are obtained similarly. Treatment of *p*-aminodiphenyl ether hydrochloride with aqueous potassium thiocyanate affords p-*phenoxyphenylthiocarbamide*, m. p. 184°, slightly bitter, through the intermediate formation of a *product*, m. p. 136°, which is probably the thiocyanate of the amino-ether. Treatment of the ether with phenylthiocarbimide affords α-p-*phenoxyphenyl*-β-*phenylthiocarbamide*, m. p. 140°, slightly bitter, whilst carbon disulphide, alcohol, and alkali yield similarly s-*di*-o-*phenoxyphenylthiocarbamide*, m. p. 172°, tasteless. The effect of the phenoxy-group is thus to decrease both the sweet taste of "dulcin" and the bitter taste of the thion group. F. G. WILLSON.

Relative speeds of removal of nitric acid from systems containing certain aromatic compounds. H. RYAN and M. GLYNN (Proc. Roy. Irish Acad., 1926, **B**, **37**, 78—83).—The relative speed of removal of nitric acid from solutions of equimolecular quantities of the acid and typical aromatic compounds in carbon tetrachloride has been determined at 60°. The removal of nitric acid is almost instantaneous with diphenylamine and diphenylnitrosoamine. With the former a green substance, m. p. 98° (decomp.), probably *p*-nitrosodiphenylnitrosoamine, was formed, the main product, however, being a brown solid, decomp. about 260°. Stilbene reacts very quickly at first, but afterwards more slowly, the rate of disappearance of the nitric acid after the first 2 hrs. being practically the same as in the case of phenyl benzyl ether. In the latter case, only half the nitric acid disappears in the first hr., as against 75% in the former case. With diphenyl ether, the reaction is much slower, only about half the nitric acid being removed in 12 hrs. *o*-Tolylurethane reacts less readily than phenyl benzyl ether, but considerably more rapidly than diphenyl ether, and yields 4-nitro-*o*-tolylurethane. With diphenylurethane and *o*-tolylethylurethane, the rate of disappearance of nitric acid is extremely slow and the reaction is incomplete even after 7 days. R. BRIGHTMAN.

Action of nitric acid and of nitrogen peroxide on triphenylamine. H. RYAN and A. MARKEY (Proc. Roy. Irish Acad., 1926, **B**, **37**, 71—77; cf. A., 1919, i, 481, 482; 1923, i, 321). The main product of the action of nitrogen peroxide in carbon tetrachloride on triphenylamine is *tetranitrotriphenylamine*,

m. p. above 280°, together with a substance, m. p. 192°, probably a mixture of a dinitrotriphenylamine with a more highly nitrated derivative. Since the above tetranitrotriphenylamine is the main product of the action of nitric acid in carbon tetrachloride on *p*-nitrotriphenylamine, m. p. 139—140°, from *p*-nitrodiphenylamine and iodobenzene, one of the nitro-groups must occupy a *para*-position. Nitration in carbon tetrachloride solution at the ordinary temperature with fuming nitric acid yields the above tetranitro-derivative with a little of the substance, m. p. 192°, and a *hexanitrotriphenylamine*, m. p. 271—273°, the proportion of the last increasing with the proportion of nitric acid and the time of reaction. In acetic acid solution, nitration is slower and, in addition to the tetra- and hexa-nitro-derivatives, and a yellowish-brown substance, probably an impure dinitrotriphenylamine, a *trinitrotriphenylamine*, m. p. 218·5—219·5°, isomeric with the trinitro-derivative described by Heydrich (A., 1885, 1213), is also formed. The *p*-nitrotriphenylamine is identical with Herz's mononitro-derivative (A., 1890, 1409). Attempts to obtain *o*-nitro- and *op*-dinitro-triphenylamine by a similar method failed, *o*-iodonitrobenzene and diphenylamine under the above conditions giving *oo*-dinitrodiphenyl, m. p. 125°. R. BRIGHTMAN.

Amino-oxidation. X. Oxidation of aliphatic amines and amino-acids. S. GOLDSCHMIDT and W. BEUSCHEL (Annalen, 1926, **447**, 197—210).—Direct proof of the mechanism suggested by the author for the oxidation of primary amines (A., 1924, i, 337) has now been obtained. The amines are oxidised by potassium permanganate in dry acetone at 0° in presence of fused sodium sulphate. The product is isolated without heating, and special precautions are taken throughout to exclude water. Treated in this way, diphenylmethylamine yields *benzophenoneimine*, an extremely unstable oil, decomposing even at −20° with formation of benzophenone and ammonia; 9-aminofluorene yields fluorenoneimine (Kliegl, A., 1910, i, 733), and alanine ethyl ester is partly converted into an imine which breaks up in moist air, giving ethyl pyruvate and ammonia. In the case of ethyl phenylaminoacetate, the imino-ester first formed condenses almost entirely with the starting product, forming, first, a *compound*, $C_{21}H_{22}O_3N_2$, m. p. 135°, of uncertain constitution, and, secondly, *ethyl* 2 : 5-*diphenyl*-4-*glyoxalidone*-2-*carboxylate*, $\begin{matrix}\text{CHPh·NH}\\ \text{CO—NH}\end{matrix}>\text{CPh·CO}_2\text{·Et}$, m. p. 148°. This yields, on hydrolysis with sodium hydroxide, first 2 : 5-*diphenyl*-4-*glyoxalidone*-2-*carboxylic acid*, m. p. 181° (decomp.), and then a mixture of ammonia, phenylaminoacetic acid, and benzoylformic acid. Crude samples of 9-aminofluorene decompose on exposure to the air, forming a yellow *compound*, $(C_{26}H_{18}N)_2$ or $(C_{26}H_{16}N)_2$, m. p. 215°. In hot benzene solution it gives a green colour, which disappears on cooling or treatment with diphenyltrinitrophenylhydrazyl, phenylhydrazine, or bromine, and must be due to formation of a free radical. H. E. F. NOTTON.

Optical study of benzyl and indanyl bases. C. COURTOT and P. PETITCOLAS (Bull. Soc. chim., 1926, [iv], **39**, 452—469).—Treatment of benzylaniline and its homologues with benzyl or indanyl chloride yields tertiary amines. Refractometric measurements on these bases show that, as in the cases previously studied (A., 1925, ii, 274), the indanyl and, to a lesser extent, the benzyl group cause exaltation of the molecular refraction, whilst, in *o*-toluidine derivatives, the *o*-methyl group has a depressant effect. Examination of the absorption curves shows a parallel effect, the indanyl being more chromogenic than the benzyl, whilst the *o*-methyl group is, in general, bathochromic, although not to the extent noticed by Ley and Pfeiffer in the dimethylaniline derivatives (A., 1921, i, 335). The following new or corrected constants are recorded: benzylaniline, m. p. 39°, b. p. 171·5°/10 mm., d_4^{65} 1·0298, n_D^{65} 1·59562; benzyl-*o*-toluidine, m. p. 60°, b. p. 176°/10 mm., d_4^{65} 1·01416, n_D^{65} 1·58611; benzyl-*m*-toluidine, b. p. 179·5°/10 mm., d_4^{65} 1·00833, n_D^{65} 1·58451; benzyl-*p*-toluidine, b. p. 181°/10 mm., d_4^{65} 1·00641, n_D^{65} 1·58324; dibenzylaniline, m. p. 69·5°, b. p. 226°/10 mm., d_4^{80} 1·04436, n_D^{80} 1·60647; *dibenzyl-o-toluidine*, m. p. 42°, b. p. 223°/10 mm., d_4^{65} 1·02347, n_D^{65} 1·58324; dibenzyl-*m*-toluidine, m. p. 78°, b. p. 229°/11 mm., d_4^{80} 1·0265, n_D^{80} 1·59603; dibenzyl-*p*-toluidine, m. p. 56°, b. p. 233°/11 mm., d_4^{65} 1·03721, n_D^{65} 1·60109; *benzylindanylaniline*, m. p. 75°, b. p. 255°/16 mm., d_4^{80} 1·06321, n_D^{80} 1·61108; *benzylindanyl-o-toluidine*, m. p. 95°, b. p. 253—255°/14 mm., d_4^{80} 1·04157, n_D^{80} 1·58774; *benzylindanyl-m-toluidine*, m. p. 57·5°, b. p. 261—262°/16 mm., d_4^{80} 1·0486, n_D^{80} 1·60412; *benzylindanyl-p-toluidine*, m. p. 76°, b. p. 264—266°/16 mm., d_4^{80} 1·0493, n_D^{80} 1·60348. H. E. F. NOTTON.

Coloured derivatives of tetraphenylmethane. VII. Attempted synthesis of carbazine derivatives of naphthalene. F. KEHRMANN and F. BRUNNER (Helv. Chim. Acta, 1926, **9**, 221—222; A., 1921, i, 600).—The toluenesulphonic ester of 2 : 4-dinitro-α-naphthol condenses with *o*-aminotriphenylmethane, giving *o-benzhydrylphenyl*-2 : 4-*dinitronaphthylamine*, $C_{10}H_5(NO_2)_2\text{·NH·}C_6H_4\text{·CHPh}_2$, m. p. 220° (decomp.). The alcoholic solution becomes purple on addition of concentrated alkali, but no metallic derivative was isolated. Ring-closure with elimination of nitrous acid could not be effected. Reduction with stannous chloride gives a *tin double salt*, from which the *hydrochloride* and the base, *o-benzhydrylphenyl*-2 : 4-*diaminonaphthylamine* m. p. 125—130°, giving blue fluorescence in alcohol (*acetyl* derivative prepared), are obtained. M. CLARK.

Benzidine derivatives of thiocarbamide. L. PINTO (Bull. Soc. chim., 1926, [iv], **39**, 470—473).—Acetylbenzidine, obtained as a by-product in the preparation of diacetylbenzidine, on treatment with carbon disulphide in alcoholic solution yields s-*di*-4′-*acetamidodiphenylylthiocarbamide*, m. p. above 360°, from which s-*di*-4′-*aminodiphenylylthiocarbamide*, $CS(NH\text{·}C_6H_4\text{·}C_6H_4\text{·}NH_2)_2$, m. p. 70°, is obtained on hydrolysis with 10% hydrochloric acid. On tetrazotisation, the new base yields substantive cotton dyes of the benzidine type; coupled with 1-amino-8-naphthol-3 : 6-disulphonic acid, it yields a dark blue *dye*, with β-naphthol a red *dye*, and with phenylmethylpyrazolonesulphonic acid a pale yellow *dye*. R. BRIGHTMAN.

Constitution of Hansa-yellow G [M.L.B.] and other yellow pigment colours. F. M. ROWE, A. H. BURR, and S. G. CORBISHLEY.—See B., 1926, 310.

Composition of some products used for the production of insoluble azo colours.—F. M. ROWE and E. LEVIN.—See B., 1926, 310.

Manufacture of trisazo dyes. FARBENFABR. VORM. F. BAYER UND CO.—See B., 1926, 311.

Polyazo dyes. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1926, 312.

s-Di-α-phenylethylhydrazine and related compounds. W. A. SCHULZE and H. L. LOCHTE (J. Amer. Chem. Soc., 1926, **48**, 1030—1035).—Acetophenoneazine, from acetophenone and hydrazine hydrochloride in aqueous-alcoholic solution (cf. Curtius and Thun, A., 1891, 1355), is unaffected by aluminium amalgam in boiling alcoholic solution, but can be reduced catalytically (cf. Lochte, Bailey, and Noyes, A., 1922, i, 329), when freshly prepared, with formation of *s-di-α-phenylethylhydrazine hydrochloride*, m. p. 188°, in 60—70% yield. Treatment of the latter with aqueous alkalis affords the free *base*, b. p. 110—115°/30 mm. with some decomposition into βγ-diphenylbutane. The *nitroso*-derivative, liquid, was prepared. Treatment of the base with phenylcarbimide affords 1 : 2-*di*-α-*phenylethyl*-4-*phenylsemicarbazide*, NH(CHMePh)·N(CHMePh)·CO·NHPh, m. p. 108°, which, when heated at 155° with carbamide, is converted into 1 : 2-*di*-α-*phenylethyl*-4-*phenylurazole*, $CHMePh\cdot\overset{\Big|}{N}\cdot CO\cdot NPh\cdot CO\cdot\overset{\Big|}{N}\cdot CHMePh$, m. p. 105·5°. Oxidation of *s*-di-α-phenylethylhydrazine with alkaline hydrogen peroxide affords a *product*, $C_{16}H_{18}N_2$, m. p. 74°, which is reconverted into the original substituted hydrazine on reduction with aluminium amalgam in alcohol, and affords βγ-diphenylbutane in good yield when distilled under reduced pressure. Hydrolysis of the oxidation product with aqueous hydrochloric acid affords primary *α-phenylethylhydrazine* (*oxalate*, m. p. 172°; *dibenzoyl* derivative, m. p. 193°), which decomposes when liberated from its salts. The reactions of the above oxidation product indicate that it has probably the azo structure, but is readily transformed into the isomeric hydrazone. F. G. WILLSON.

Geometrical stereoisomerism in the *cyclo*hexane series. V. 2-*cyclo*Hexyl*cyclo*hexanols. P. BEDOS (Bull. Soc. chim., 1926, [iv], **39**, 473—487).—The additive compound of *cyclo*hexene oxide and magnesium *cyclo*hexyl chloride (cf. this vol., 164) gives on heating to 200°, and subsequent decomposition with water, a 27% yield of cis-2-cyclo*hexyl*cyclo*hexanol*, b. p. 134—136°/13 mm., d_{18}^{18} 0·971, n_D^{18} 1·4914 (*phenylurethane*, m. p. 122°). trans-2-cyclo*Hexyl*cyclo*hexanol*, m. p. 0—10°, b. p. 136—138°/13 mm., d_{18}^{18} 0·9956, n_D^{18} 1·509 (*phenylurethane*, m. p. 114°), is formed on refluxing *cyclo*hexanol with potassium. Since the compound described by Wallach as *cyclo*hexyl*cyclo*hexanol (A., 1911, i, 473) is different from either of the above, his work has been repeated. Catalytic hydrogenation of 2-*cyclo*hexenyl*cyclo*hexanol gives a mixture of both isomerides, b. p. 140—144° (phenylurethane, m. p. 111—112°), and a similar mixture is obtained on reducing 2-*cyclo*hexyl*cyclo*hexanone. The latter compound, whether prepared by oxidation of any of the above *cyclo*hexyl*cyclo*hexanols, or by hydrogenation of *cyclo*hexylidene*cyclo*hexanone, has always b. p. 128—130°/12 mm., d_{21}^{21} 0·969, n_D^{21} 1·48404 (*semicarbazone*, m. p. 180—181°), and is different from the substance described by Wallach. H. E. F. NOTTON.

Influence of the acid character of the polynitrophenols and nitronaphthols on their capacity for forming glucosides. E. GLASER and A. C. THALER (Arch. Pharm., 1926, **264**, 228—237; cf. A., 1923, i, 694; 1924, i, 797).—2 : 4-*Dinitrophenoltetra-acetylglucoside*, m. p. 169°, $[\alpha]_D^{19}$ +36·8° (in chloroform), is obtained by the action of an aqueous alkaline solution of the phenol on tetra-acetylbromoglucose in acetone. When treated with ammonia in methyl alcohol, it breaks down completely (cf. the tribromo-analogue, Fischer and Strauss, A., 1912, i, 884). 2 : 5-Dinitrophenol interacts with "acetobromoglucose" more rapidly than its isomeride, giving 2 : 5-*dinitrophenoltetra-acetylglucoside*, m. p. 149°, $[\alpha]_D^{19}$ +36·7° (in chloroform). This compound also breaks down on hydrolysis. Picric acid will not interact with "acetobromoglucose." 4-Nitro-α-naphthol, however, yields *4-nitro-α-naphtholtetra-acetylglucoside*, m. p. 150—151°, $[\alpha]_D^{19}$ −66° (in chloroform), which is hydrolysed to *4-nitro-α-naphtholglucoside*, $C_{10}H_6O_2N\cdot O\cdot C_6H_{11}O_5+H_2O$, m. p. 214—215° (decomp.), $[\alpha]_D^{18}$ −73° (in alcohol); the yield is poor. This compound, being sparingly soluble in water, is not attacked by emulsin; it is, however, considered to be a β-glucoside. W. A. SILVESTER.

Migration of the methyl group in Fries' transformation. K. VON AUWERS, H. BUNDESMANN, and F. WIENERS (Annalen, 1926, **447**, 162—196).—The conversion of phenolic acetates into *o*- and *p*-hydroxyacetophenones by heating with aluminium chloride (cf. Fries and Finck, A., 1909, i, 42) is accompanied, in the case of certain polyalkyl phenols, by migration of a methyl group. The following phenyl acetates yield normal products, viz., 2 : 4-dimethyl-, 3 : 4-dimethyl-, 4-methyl-2-ethyl-, 3 : 5-dimethyl-, 3 : 4 : 5-trimethyl-, and 2 : 3 : 4-trimethyl-. On the other hand, 2 : 5-dimethyl-, 5-methyl-2-ethyl-, 2 : 4 : 5-trimethyl-, 2 : 3 : 5-trimethyl-, and 2 : 4 : 6-trimethyl-phenyl acetates yield 2 : 4-dimethyl-, 4-methyl-2-ethyl-, and, in the last three cases, 2 : 3 : 4-trimethyl-6-acetophenols, respectively. Wandering of a methyl group takes place only when the acetyl group migrates to the *o*-position, and then, with one exception, only when the 2- and 5-positions contain alkyl groups. *m*-Alkylphenols give a large proportion of *p*-hydroxyketone, the amount being decreased by raising the reaction temperature. The suggestion of Skraup and Poller (A., 1925, i, 143) that Fries' reaction consists of hydrolysis followed by resubstitution is shown to be improbable. The authors' views on the mechanism of the Beckmann transformation (*ibid.*, 265) are confirmed by further instances. The following acetophenoneoximes give no amine on treatment with 17% hydrochloric acid: 2-hydroxy-4 : 5-dimethyl-, 2-hydroxy-

3 : 5-dimethyl-, and 2-hydroxy-3 : 4 : 5-trimethyl-. The 2-hydroxy-3 : 5-dimethyl compound gives 80% and the 4-hydroxy-2 : 5-dimethyl and 2-hydroxy-4 : 5 : 6-trimethyl compounds give 100% of amine.

The following compounds are described incidentally: 4-o-*xylenyl acetate*, m. p. 22—22·5°, b. p. 235°; 2-*hydroxy*-4 : 5-*dimethylacetophenone*, m. p. 71° (*semicarbazone*, m. p. 292—295°; *oxime*, m. p. 136—137°; *methyl ether*, m. p. 55—56°, and its *semicarbazone*, m. p. 204—205°); 3 : 4-*dimethyl*-6-*ethylphenol*, m. p. 51—52° (*phenylurethane*, m. p. 113°); 4-*ethyl*-m-*cresol*, m. p. 43—44° (*phenylurethane*, m. p. 127—128°); 4-*hydroxy*-2-*methyl*-5-*ethylbenzaldehyde*, m. p. 110° (*semicarbazone*, m. p. 204—206°); 2-*hydroxy*-3 : 5-*dimethylacetophenone*, m. p. 53—54° (*oxime*, m. p. 139·5—141°; *semicarbazone*, m. p. 257°; *methyl ether*, b. p. 120°/13 mm.); 5-*ethyl*-4-m-*xylenol*, b. p. 227—228° (*phenylurethane*, m. p. 113·5°); 2-*hydroxy*-3-*methylacetophenonesemicarbazone*, m. p. 242°; 3-*ethyl*-o-*cresol*, b. p. 212—214° (*phenylurethane*, m. p. 150—151°); 4-*hydroxy*-3-*methyl*-5-*ethylbenzaldehyde*, m. p. 94—95°; 4-*hydroxy*-2 : 5-*dimethylacetophenone*, m. p. 130—131° (*methyl ether*, m. p. 79—80°, and its *semicarbazone*, m. p. 206°; *oxime*, m. p. 155—156°); 6-*benzamido*-3-p-*xylenol*, m. p. 249°; 5-*ψ-cumyl acetate*, m. p. 34—34·5°, b. p. 245—246°; 2-*hydroxy*-3 : 5 : 6-*trimethylacetophenone*, b. p. 145—146°/11 mm., d_4^{20} 1·085, $n_\alpha^{17\cdot4}$ 1·55473 (*semicarbazone*, m. p. 232°; *oxime*, m. p. 163—164°); 1 : 3 : 4 : 6-*tetramethylbenzoxazole*, m. p. 64°; o-*acetamido*-*ψ-cumenol*, m. p. 162—163°; 2 : 4 : 5-*trimethyl*-6-*ethylphenol*, m. p. 65—66°; 2-*hydroxy*-3 : 4 : 5-*trimethylacetophenone*, m. p. 42—43°, b. p. 275—276°/760 mm., 142—144°/11 mm., $d_4^{99\cdot3}$ 1·0261, $n_\alpha^{99\cdot3}$ 1·52569 (*semicarbazone*, m. p. 290°; *oxime*, m. p. 161°); 3 : 4 : 6-*trimethylcoumaran*-2-*one*, m. p. 115—117°; 5-*ψ-cumyl chloroacetate*, m. p. 56—57°, b. p. 149—152°/12 mm.; 2-*hydroxy*-4 : 5 : 6-*trimethylacetophenone*, m. p. 83—84°, b. p. 163—166°/13 mm. (*semicarbazone*, m. p. 210°; *oxime*, m. p. 143°); 2-*benzamido*-3 : 4 : 5-*trimethylphenyl benzoate*, m. p. 171—172°; 2-*hydroxy*-3 : 6-*dimethylbenzaldoxime*, m. p. 124—125°; 2 : 3 : 5-*trimethylphenyl* (iso-*ψ-cumyl*) *acetate*, b. p. 241°; 2 : 4 : 6-*trimethylphenyl* (*mesityl*) *acetate*, b. p. 236°; 3-*methyl*-6-*ethylphenyl acetate*, b. p. 232°; 2-*hydroxy*-5-*methyl*-3-*ethylacetophenone*, b. p. 153°/30 mm. (*semicarbazone*, m. p. 238—239°; p-*nitrophenylhydrazone*, m. p. 176°); 4-*hydroxy*-2-*methyl*-5-*ethylacetophenone*, m. p. 117—118°; 4-*methyl*-6-*ethylphenyl acetate*, b. p. 231—233°; 2-*benzamido*-3 : 4-*dimethylphenol*, m. p. 195—196°; 1-*phenyl*-4 : 5-*dimethylbenzoxazole*, m. p. 164—165°; 2-*benzamido*-4 : 6-*dimethylphenol*, m. p. 187—188° (*benzoate*, m. p. 154—155°); 1-*phenyl*-4 : 6-*dimethylbenzoxazole*, m. p. 99—100°, and 1-*phenyl*-3 : 5-*dimethylbenzoxazole*, m. p. 133—134°.

H. E. F. Notton.

Synthesis of the simplest homologue of urushiol. S. Kawai (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **3**, 263—274).—Condensation of pyrocatechol with allyl bromide in acetone solution in presence of potassium carbonate yields pyrocatechol diallyl ether, b. p. 106—107°/5 mm., 87°/0·1 mm., d_4^{17} 1·0898, n_D^{14} 1·53688, and pyrocatechol monoallyl ether, b. p. 81·2—82·8°/4·5 mm., d_4^{16} 1·0813, n_D^{15} 1·54580; the latter condenses with *p*-nitrobenzyl chloride, yielding *pyrocatechol* p-*nitrobenzyl allyl ether*, m. p. 74°. When heated, the monoallyl ether undergoes a Claisen rearrangement, yielding a mixture of 2 : 3- and 3 : 4-*dihydroxyallylbenzene*, the identities of which were confirmed by methylation and oxidation. The diallyl ether on heating also undergoes molecular rearrangement, yielding a mixture of diallylpyrocatechols, from which, after methylation and oxidation, 1 : 2-*dimethoxyterephthalic acid*, m. p. 214—215°, was isolated and compared with the product synthesised by von Hemmelmayr's method. The dihydroxyallylbenzenes resemble urushiol in forming films in presence of an oxidising catalyst, and in giving coloured particles with aqueous alkalis in ether solution. S. I. Levy.

Acetic esters of *p*-aminophenol. L. Galatis (Ber., 1926, **59**, [*B*], 848—850).—*O*-Acetyl derivatives of aminophenols are conveniently prepared by acetylation of the corresponding benzylidene derivatives and treatment of the compounds thus prepared in benzene solution with dilute mineral acid. *Benzylidene*-p-*aminophenyl acetate*, m. p. 92°, p-*aminophenyl acetate*, m. p. 75° (normal *sulphate*), p-*hydroxybenzylidene*-p-*aminophenyl acetate*, m. p. 181—182° (corr.), and p-*hydroxybenzylidene*-p-*aminophenol*, m. p. 208° (corr.), are described. H. Wren.

New dye intermediates [amino-derivatives of diphenyl ether]. M. T. Bogert and R. L. Evans. —See B., 1926, 354.

Ethylating [aromatic] amines [with ethyl sulphate]. A. R. Cade, Assr. to Carbide and Carbon Chemicals Corp.—See B., 1926, 355.

Oxidation of 4-acetamido-α-naphthol. F. Ullmann (Helv. Chim. Acta, 1926, **9**, 442—443).—Oxidation of an acetic acid solution of 4-acetamido-α-naphthol with sodium dichromate, ferric chloride, or nitric acid gives di-α-naphthaquinone (A., 1897, i, 193) in good yield. M. Clark.

***p*-Alkoxylated benzhydrylamines.** C. Torres (Anal. Fís. Quím., 1926, **24**, 82—90).—p-*Ethoxybenzhydrylamine* was prepared by reduction of *p*-ethoxybenzophenoneoxime with sodium amalgam in alcohol acidified with acetic acid. Its *hydrochloride* has m. p. 229°. The following substituted benzhydrylamines were prepared similarly from the corresponding ketoximes: p-n-*propoxybenzophenone*, m. p. 65—66° (*oxime*, m. p. 104—105°), gives p-n-*propoxybenzhydrylamine* (*hydrochloride*, m. p. 220—221°); p-n-*butoxybenzophenone*, b. p. 235—245°, m. p. 38—39° (*oxime*, m. p. 94—95°), gives p-n-*butoxybenzhydrylamine* (*hydrochloride*, m. p. 213—214°); p-iso*amyloxybenzophenone*, b. p. 225—240° (*oxime*, m. p. 93—94°), gives p-iso*amyloxybenzhydrylamine* (*hydrochloride*, m. p. 224—225°), and p-*phenoxybenzophenone*, m. p. 70—71° (*oxime*, m. p. 124°), p-*phenoxybenzhydrylamine* (*hydrochloride*, m. p. 218—219°). *Ethyl* p-*benzoylphenoxyacetate*, $Bz\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot OEt$, has m. p. 84—85°; p-*benzoylphenoxyacetic acid*, m. p. 154—155°; *oxime*, m. p. 78—79°; *ethyl* p-ω-*aminobenzylphenoxyacetate*, $CHPh(NH_2)\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2Et$; its *hydrochloride*, m. p. 183—184°. αβ-*Diphenylethylamine hydrochloride*, m. p. 251—252°, was

obtained from *phenyl benzyl ketone*, m. p. 57°, b. p. 220—221°, 177°/12 mm.; *oxime*, m. p. 97—98°. α-p-*Methoxyphenyl*-β-*phenylethylamine hydrochloride* has m. p. 234—235°; α-p-*ethoxyphenyl*-β-*phenylethylamine hydrochloride*, m. p. 203—204°; p-*ethoxyphenyl benzyl ketone*, m. p. 105—106°; *oxime*, m. p. 89—90°. *p*-Ethoxybenzhydrylamine was resolved into its optical isomerides by means of α-bromocamphorsulphonic acid. The *d*-isomeride has $[\alpha]_D$ +3° 38′; the *l*-isomeride has $[\alpha]_D$ − 3° 99′.

G. W. ROBINSON.

Preparation of chlorothiolbenzene and its homologues. H. LECHER and F. HOLSCHNEIDER.—See B., 1926, 386.

Phenylated derivatives of *oo*′-ditolyl. A. E. TSCHITSCHIBABIN and P. G. SSERGEJEV (Ber., 1926, **59**, [*B*], 654—660).—Methyl (or ethyl) diphenate is converted by an excess of magnesium phenyl bromide into 2 : 2′-*di*(*hydroxydiphenylmethyl*)*diphenyl*, $HO{\cdot}CPh_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH$, m. p. 252° (the *compound* +EtOH is described); the yield is not good. The glycol is reduced by hydrogen iodide in glacial acetic acid to 2 : 2′-*dibenzhydryldiphenyl*, m. p. 236—237·5°, and converted by acetyl chloride in chloroform or hydrogen bromide in glacial acetic acid into the anhydride, $\begin{matrix}C_6H_4{\cdot}CPh_2\\ C_6H_4{\cdot}CPh_2\end{matrix}\!>\!O$, m. p. 290—292° (cf. Schlenk and Brauns, A., 1915, i, 517). The glycol is also obtained in poor yield from 2 : 2′-dibenzoyldiphenyl, m. p. 172—173° (Werner and Grob, A., 1904, i, 864, record m. p. 166—167°); the main product of the action appears to be the *ketol*, $HO{\cdot}CPh_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}COPh$, m. p. 193—194° (also +EtOH and +$CHCl_3$), which, however, does not react further with magnesium phenyl bromide and does not give the usual reactions for ketones. In addition, *ms*-dihydroxydiphenyldihydrophenanthrene, m. p. 202—204° (cf. Werner and Grob, *loc. cit.*), is produced. The best method of preparing the glycol is by the action of magnesium phenyl bromide on the anhydride or, preferably, the chloride of diphenic acid.

H. WREN.

Elimination of the amino-group of tertiary amino-alcohols. III. Preparation of optically active ketones. A. MCKENZIE, R. ROGER, and G. O. WILLS (J.C.S., 1926, 779—791; cf. *ibid.*, 1923, **123**, 79; 1924, **125**, 844, 2105; 1925, **127**, 283).—Previous work has shown that certain tertiary amino-alcohols yield invariably ketones on treatment with nitrous acid. These results, which cannot be interpreted on the basis of the intermediate formation of the glycol followed by dehydration, are explained in terms of "semipinacolinic deamination," involving the migration of a hydrocarbon residue. Thus, the conversion of *l*-β-amino-αα-diphenyl-*n*-propyl alcohol into *d*-methyldeoxybenzoin on deamination by nitrous acid is explained as follows:

$$CPh_2(OH){\cdot}CHMe{\cdot}NH_2 \longrightarrow CPh_2(OH){\cdot}CHMe{\cdot}N(OH){:}N$$
$$\longrightarrow \underset{O}{\overset{+}{CPh_2}}{\cdot}\underset{+}{CHMe} \longrightarrow Ph{\cdot}CO{\cdot}CHPhMe.$$

Since optical activity is not destroyed as a result of this molecular rearrangement, it is suggested that a positive electric charge plays the part of a group in retaining asymmetry (cf. A., 1921, i, 15; 1922, i, 924, 818; 1923, i, 663; J.C.S., 1925, **127**, 2552; Walden, Naturwiss., 1925, 331) and that, since there is no evidence as to whether *d*-methyldeoxybenzoin has the same configuration as the *d*-alanine from which it is prepared, an intramolecular Walden inversion may have been effected. To account for the non-formation of the stable diphenylpropylene oxide, it is assumed that both the charges in the above scheme are positive. On similar lines, *d*- and *l*-benzyldeoxybenzoin have been prepared from the amino-alcohols derived from *d*- and *l*-phenylalanine. The optically active ketones obtained are readily and completely racemised when a trace of alcoholic potassium hydroxide is added to their ethyl-alcoholic solutions. The catalytic racemisation thus effected by potassium ethoxide is due to the migration of a hydrogen atom, which develops mobility and migrational tendency only after an additive complex with potassium ethoxide has first been formed.

Ethyl *d*-alanine hydrochloride on treatment with magnesium phenyl bromide yields l-β-*amino*-αα-*diphenyl*-n-*propyl alcohol*, m. p. 101·5—102·5°, $[\alpha]_D^{16}$ −82·3°, which, on deamination with aqueous sodium nitrite in 25% acetic acid, furnishes *d*-methyldeoxybenzoin, m. p. 34—35°, $[\alpha]_{6563}^{17}$ +158°. The solutions exhibit no auto-racemisation after keeping for 24 hrs. at the ordinary temperature. *d*-β-Amino-αα-diphenyl-β-benzylethyl alcohol, derived from *d*-phenylalanine, $[\alpha]_D^{16}$ +35·0° (d-*camphorsulphonate*, $[\alpha]_D^{18·5}$ +18·3° in aqueous solution), furnishes on deamination *l*-benzyldeoxybenzoin, m. p. 121—121·5°, $[\alpha]_D^{16·5}$ −242° in chloroform. *l*-Phenylalanine (l-*camphorsulphonate*, m. p. 109—110°, $[\alpha]_D^{18·5}$ −18·3° in aqueous solution) in a similar manner yields l-β-*amino*-αα-*diphenyl*-β-*benzylethyl alcohol*, which, on deamination, gives rise to *d*-benzyldeoxybenzoin, m. p. 121—121·5°, $[\alpha]_D^{16}$ +241° in chloroform. The latter compound furnishes d-αβ-*diphenyl*-αβ-*dibenzylethyl alcohol*, m. p. 167—168°, $[\alpha]_D^{17}$ +155° in chloroform, on treatment with magnesium benzyl chloride, whilst ethyl *r*-alanine hydrochloride and ethyl *r*-phenylaminoacetate hydrochloride on similar treatment yield r-β-*amino*-αα-*dibenzyl*-n-*propyl alcohol*, m. p. 93·5—94·5°, and *r*-β-amino-αα-dibenzyl-β-phenylethyl alcohol, m. p. 125—126°, respectively. The latter deaminates to form benzyl αβ-diphenylethyl ketone, m. p. 74—75°, which does not depress the m. p. of the product obtained by dehydrating α-phenyl-ββ-dibenzylethylene glycol. The results of the catalytic racemisation of *l*-benzoin, *d*-methyldeoxybenzoin, and *d*-benzyldeoxybenzoin by ethyl-alcoholic potassium hydroxide are given.

J. S. H. DAVIES.

Thymolsulphonephthalein, the intermediate acid, 4′-hydroxy-3′-*iso*propyl-6′-methylbenzophenone-2-sulphonic acid, and some of their derivatives. W. R. ORNDORFF and R. T. K. CORNWELL (J. Amer. Chem. Soc., 1926, **48**, 981—993).—Condensation of *o*-sulphobenzoyl chloride with thymol at 100—110° affords chiefly *dithymyl* o-*sulphobenzoate*, m. p. 102—103°, with only about 10—15% of thymolsulphonephthalein, whilst at higher tem-

peratures much tar is formed. Dithymyl *o*-sulphobenzoate is not converted into thymolsulphonephthalein when warmed with an equivalent of aluminium chloride or stannic chloride (cf. Csányi, A., 1920, i, 54). Thymolsulphonephthalein is obtained in 55% yield by heating *o*-sulphobenzoic anhydride, thymol, and fused zinc chloride at 105—110° for 30 hrs. The thymolsulphonephthalein separates in small green crystals, the filtrate from which yields *4'-hydroxy-6'-methyl-3'-isopropylbenzophenone-2-sulphonic acid* ($+2H_2O$) [*ammonium* salt; *barium* salt ($+6H_2O$); *dibenzoate*, m. p. 119—120°]. This acid decomposes slowly at 150° (also at 135° in presence of zinc chloride) with formation of thymolsulphonephthalein, *o*-sulphobenzoic anhydride, and water. It reacts with thymol in presence of zinc chloride at 85°, with formation of the sulphonephthalein. When fused with potassium hydroxide, it yields *p*-thymotic acid (cf. Kobek, A., 1884, 56). The existence of the above salts and of the diacyl derivative indicates the existence of ketone and lactone tautomerides. Thymolsulphonephthalein crystallises with 1 mol. of water. It begins to lose water at 59°, turns red and shrinks at 195°, and melts, with slight carbonisation, at 200—220°. As thymolbenzein is basic, anhydrous thymolsulphonephthalein has either the inner carbonium or inner oxonium structure, the hydrated material being probably a solid solution of the inner salt and the quinonoid hydrate (cf. Orndorff and Sherwood, A., 1923, i, 340; Orndorff and Vose, *ibid.*, 1924, i, 1190). The inner salt structure is supported by the fact that the anhydrous material combines with ammonia to form a purple *triammonium* salt, but not with dry hydrogen chloride, thus showing analogy with taurine. The formation of a colourless *diacetate*, m. p. 171—172°, and *dibenzoate*, m. p. 194—195°, indicates the existence of a lactoid tautomeride, but this could not be isolated. A colourless *dimethyl ether* is obtained by boiling thymolsulphonephthalein with methyl alcohol in presence of hydrochloric acid. It is converted into the purple quinonoid *tautomeride*, m. p. 201—202°, at 180°, the reverse change taking place when the latter is kept in contact with methyl alcohol. The following derivatives of the quinonoid form are described: *monoammonium* salt, red; zinc salt ($+5H_2O$), orange-red; *monosodium* salt, ($+1$EtOAc), orange-red, or anhydrous, brown; *disodium* salt ($+2$EtOH), dark blue; and *aniline* salt, brown, m. p. indefinite. A dark green *dianilino*-derivative was also obtained. When boiled with water and zinc dust until decolorised, thymolsulphonephthalein affords *thymolsulphonephthalin* ($+3\frac{1}{2}H_2O$), m. p. 134—135°, as the *zinc* salt ($+8H_2O$). The former is readily converted into the sulphonephthalein by atmospheric oxygen.

Dibromothymolsulphonephthalein (cf. Clark and Lubs, A., 1916, ii, 44, 571) is precipitated from alkaline solution as the *dihydrate*, dark purple, and this is converted into the colourless form when heated in a stream of carbon dioxide. The colourless *diacetate*, m. p. 222—223°, is described. Both thymolsulphonephthalein and the dibromo-derivative require the addition of 1 mol. of alkali before the colour change in the alkaline range from yellow to blue takes place (cf. Lubs and Acree, A., 1917, ii, 97). F. G. Willson.

Crystalline salts of abietic acid. I. Crystalline sodium abietate and its use in the determination of abietic acid in resins. G. Dupont, L. Desalbres, and A. Bernette (Bull. Soc. chim., 1926, [iv], **39**, 488—492).—If one-fourth of the sodium hydroxide requisite for complete neutralisation is added to an alcoholic solution of abietic acid, the compound $C_{20}H_{29}O_2Na,3C_{20}H_{30}O_2$, m. p. 170—175°, $[\alpha]_{Hg\ yellow}$ −80° ($c = 2{\cdot}5\%$), crystallises out on keeping. Neither the primary resin acids, *e.g.*, pimaric and alepic, nor the intermediate acids, such as alepabietic, give a precipitate under these conditions, but the latter may contaminate the abietate if deposited from a solution containing both. The method has been applied to show that abietic acid, as such, is not present in resins, and to determine the optimum conditions for obtaining abietic acid from them by isomerisation with hydrochloric acid. Bordeaux colophony, when treated in boiling alcoholic solution with 3% of its weight of dilute (1 : 4) hydrochloric acid for 12 min., yields 75% of crystalline sodium salt, corresponding with 73·8% of abietic acid, whilst the resin of the Aleppo pine yields 86%.

The results confirm the authors' opinion that Bordeaux colophony contains about 9% of *d*-pimaric acid, which cannot be isomerised into abietic acid.

H. E. F. Notton.

Crystalline salts of abietic acid. II. G. Dupont and L. Desalbres (Bull. Soc. chim., 1926, [iv], **39**, 492—495).—The well-defined abietates of the following metals have been obtained in alcoholic solution: normal *ammonium*, m. p. 110°, $[\alpha]_{HgY}$ −90°; normal *methylamine*, m. p. 110°; normal *ethylamine*, m. p. 102°, $[\alpha]_{HgY}$ −95·7°; acid *calcium*, $(2C_{20}H_{30}O_2,C_{20}H_{29}O_2)_2Ca$, m. p. 190° (decomp.); acid *strontium*, $(2C_{20}H_{30}O_2,C_{20}H_{29}O_2)_2Sr$, m. p. 155°; normal *barium*, m. p. 200° (decomp.); normal *zinc*, m. p. 190°; normal *lead*, m. p. 150° (decomp.); acid *copper*, $(C_{20}H_{30}O_2,C_{20}H_{29}O_2)_2Cu$; and *nickel* salt. The absence of water and presence of an excess of abietic acid restrict hydrolysis and favour the formation of crystalline salts (cf. A., 1895, i, 384).

H. E. F. Notton.

***p*-Nitrobenzoyl esters of β-phenylethyl, γ-phenylpropyl, and δ-phenylbutyl alcohols.** W. R. Kirner (J. Amer. Chem. Soc., 1926, **48**, 1111—1112; cf. A., 1924, i, 273).—The following are described: *β-phenylethyl*, m. p. 62—63°; *γ-phenylpropyl*, m. p. 45—46°, and *δ-phenylbutyl* p-*nitrobenzoate*, m. p. 18—20°. F. G. Willson.

Nitration of benzamidines. R. Forsyth, V. K. Nimkar, and F. L. Pyman (J.C.S., 1926, 800—808).—Nitration of benzamidine (*nitrate*, m. p. 128°) yields almost wholly *m*-nitrobenzamidine (hydrochloride, m. p. 251°). Similarly, benzenyltrimethylamidine (*nitrate*, m. p. 195—196°) forms more than 80% of *m*-nitrobenzenyltrimethylamidine [*hydriodide*, m. p. 243—246° (decomp.)]. 2-Phenyl-4 : 5-dihydroglyoxaline, m. p. 102—103°, furnishes on nitration 2-*m*-nitrophenyl-4 : 5-dihydroglyoxaline in a yield of more than 80% (*hydrochloride*, $C_9H_9O_2N_3,HCl,H_2O$, m. p. 249—251° when anhydrous, *hydriodide*, m. p. 207—209°, *picrate*, m. p. 224—225°), which forms

m-nitrobenzoic acid on oxidation with alkaline permanganate. 4 : 5-*Dibromo*-2-*phenylglyoxaline*, m. p. 141° (decomp.) (*hydrochloride*, m. p. 235—237°, *picrate*, m. p. 170—172°), obtained by brominating the base in chloroform solution, on nitration yields chiefly 4 : 5-*dibromo*-2-p-*nitrophenylglyoxaline*, $C_9H_5O_2N_3Br_2,2H_2O$, m. p. 220—222°, together with a little 4 : 5-*dibromo*-2-o(or m)-*nitrophenylglyoxaline*, m. p. 181—182°. The former yields *p*-nitrobenzoic acid on oxidation with alkaline permanganate, 4(5)-*Bromo*-2-*phenylglyoxaline*, m. p. 206—207° [*hydrochloride*, $C_9H_7N_2Br,HCl,H_2O$, m. p. 118—119° when anhydrous, *picrate*, m. p. (air dried) 164—165°], obtained by reducing the dibromo-compound with sodium sulphite, forms 4(5)-*bromo*-2-p-*nitrophenylglyoxaline*, m. p. 222—223°, as the sole nitration product isolated. It separates from acetic acid with 1 mol. of acetic acid of crystallisation, and on oxidation with alkaline permanganate furnishes *p*-nitrobenzoic acid. It is concluded that the amidinium ion has a *m*-directive influence, whilst the glyoxaline nucleus exerts an *op*-directive influence similar to that of the phenyl group in diphenyl. The exceptional *m*-nitration of 2-phenylglyoxaline-4 : 5-dicarboxylic acid is an outcome of its true amidine character, owing to the absence of salt formation.

J. S. H. DAVIES.

Action of inorganic iodides on αβ-dibromo-compounds. II. General character of the reaction and the influence of substituents. C. F. VAN DUIN (Rec. trav. chim., 1926, **45**, 345—362).—The study of the reaction velocity between metallic iodides and αβ-dibromo-compounds at 25° (cf. A., 1924, i, 702) has been extended to a large number of the latter, containing bromine in varying degrees of reactivity, and the general character of the reaction thus established. Contrary to the conclusions of Biilmann (A., 1917, i, 378), the reaction is a termolecular one. The acetyl, phenyl, carbomethoxy-, carbethoxy-, and carboxyl groups increase the velocity of the reaction, the magnitude of the effect decreasing in the order given. Bromine atoms have a retarding influence. A carboxyl on both α- and β-carbon atoms more or less neutralise each other's effects. In the case of the dibromosuccinic acids, the reaction velocity is much greater with the *meso* than with the racemic compound. The following corrections are made, all m. p. being corrected : αβ-dibromo-3 : 4-methylenedioxyphenylpropionic acid, m. p. 151—152° (Feuerstein and Heimann, A., 1901, i, 465, give 143—144°); ethyl ester, m. p. 89—90° (Baude and Reychler, A., 1899, i, 142, give 84°); piperonylideneacetone, m. p. 108°; dibromide, m. p. 125° (Rousset, A., 1895, i, 601, gives 96·5° and 76°, respectively); *veratrylideneacetone*, m. p. 84—85° (*dibromide*, m. p. 98°), is obtained by the condensation of veratraldehyde and acetone, the compound obtained by Francesconi and Cusmano (A., 1908, i, 801), m. p. 168°, probably being diveratrylideneacetone. Contrary to the results of Hell (A., 1904, i, 241), the interaction of anisaldehyde and magnesium benzyl chloride results in the formation of the carbinol, which is only converted into *p*-methoxystilbene by heating under atmospheric pressure. The action of potassium iodide on *iso*eugenyl ethyl ether dibromide yields *diisoeugenyl ethyl ether*, m. p. 127·5—128°.

J. W. BAKER.

Organic peroxides. X. Classification of reactions of acyl peroxides. XI. Action of benzoyl peroxide on *cyclo*hexane. H. GELISSEN and P. H. HERMANS (Ber., 1926, **59**, [*B*], 662—666).—The reactions of organic peroxides are classified as follows : (1) $R{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}R \longrightarrow 2CO_2+R{\cdot}R$ (cf. Fichter, A., 1918, i, 369); (2) (involving participation of the solvent) $R{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}R+HR' \longrightarrow R{\cdot}CO_2H+R{\cdot}R'+CO_2$ or $R{\cdot}CO_2R'+RH+CO_2$ (cf. Gelissen and Hermans, A., 1925, i, 379, 545); (3) $R{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}R+2H \longrightarrow 2R{\cdot}CO_2H$ (cf. Wieland, A., 1921, i, 889); (4) $R{\cdot}CO{\cdot}O{\cdot}O{\cdot}CO{\cdot}R+H{\cdot}OH \longrightarrow R{\cdot}CO{\cdot}O{\cdot}OH+R{\cdot}CO_2H$ (cf. Böeseken and Gelissen, A., 1925, i, 30).

Benzoyl peroxide reacts with boiling *cyclo*hexane according to the R·H scheme, yielding carbon dioxide, benzene, benzoic acid, and phenyl*cyclo*hexane; *p*-phenylbenzoic acid is also produced together with considerable amounts of resin. H. WREN.

Instability of the sodium salt of benzoyl hydroperoxide. A. J. GELARIE and F. R. GREENBAUM.—See B., 1926, 384.

2-Aminonaphthoic acid and its nuclear substitution products. FARBW. VORM MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 354.

Preparation of acetylsalicylic acid. DEUTSCHE GASGLÜHLICHT-AUER-GES.—See B., 1926, 385.

Preparation of *o*-phthalaldehydic acid. R. C. FUSON (J. Amer. Chem. Soc., 1926, **48**, 1093—1096).—Naphthalene is oxidised by alkaline permanganate, and the product is converted by warming with aniline into the aniline derivative of phthalonic acid, m. p. 165° (cf. Gilliard, Monnet, et Cartier, D.R.-P. 97241). This decomposes, when boiled with dry xylene, with quantitative formation of *o*-carboxybenzylideneaniline, which, when boiled with aqueous hydrochloric acid, affords *o*-phthalaldehydic acid, m. p. 96·5—97°.

Bromination of *o*-toluonitrile at 180—200° affords *o-cyanobenzylidene bromide*, m. p. 62—63°, in poor yield, which gives *o*-phthalaldehydic acid on hydrolysis with 70% sulphuric acid. F. G. WILLSON.

Isomerism of 9-substituted fluorenes. A. KLIEGL, A. WÜNSCH, and R. WEIGELE (Ber., 1926, **59**, [*B*], 631—641).—Diphenyleneglycollic acid is readily converted by cold acetic anhydride into *acetoxydiphenyleneacetic acid*, m. p. about 190° (decomp.) (the *compound*, $2C_{16}H_{12}O_4,C_7H_8$, is described) (cf. Schmidt and Bauer, A., 1906, i, 25). Negative results were obtained in attempts to prepare fluorenyl benzoate, m. p. 161°, according to the method of Schmidt and Stützel (A., 1910, i, 29); fluorenyl alcohol is readily benzoylated in an indifferent solvent, *e.g.*, pyridine, but then affords the benzoate, m. p. 101—102°, described by Staudinger and Gaule (A., 1916, i, 853). Analyses and determinations of mol. wt. of the β-isomeride of 9-acetoxyfluorene (Schmidt and Mezger, A., 1907, i, 43) indicate the formula $C_{29}H_{20}O_4$. It is hydrolysed by alkali hydroxide to fluorenyl alcohol, acetic and diphenylene-

glycollic acids, converted by glacial acetic and hydrobromic acids into 9-bromofluorene and diphenyleneglycollic acid, and transformed by ethyl alcohol at 200°, not into the α-compound as described by Schmidt and Mezger (*loc. cit.*), but into fluorenyl alcohol, ethyl acetate, carbon dioxide, and 9-*ethoxyfluorene*, m. p. 54° (obtained also from 9-chlorofluorene and alcoholic silver nitrate). It is therefore regarded as *fluorenyl acetoxydiphenyleneacetate*. This is confirmed by synthesis of the compound by the action of silver or sodium acetate on *fluorenyl chlorodiphenyleneacetate*, m. p. 209·5—210° (obtained from fluorenyl alcohol and chlorodiphenyleneacetyl chloride in the presence of pyridine). Alternatively, acetoxydiphenyleneacetic acid is heated in a solvent, b. p. above 100°, whereby it loses acetic acid with formation of the *acid ester*, $C_{12}H_8{:}C(OAc)\cdot CO\cdot O\cdot C(CO_2H){:}C_{12}H_8$, m. p. 207—209° (decomp.), which when heated above 130° in acetic anhydride, nitrobenzene, or aniline affords carbon dioxide and fluorenyl acetoxydiphenyleneacetate; if aniline is used, 9-anilinofluorene (cf. Staudinger and Gaule, *loc. cit.*) is also produced. With acetic anhydride in presence of acetic acid, re-formation of acetoxydiphenyleneacetic acid predominates.

The β-9-aminofluorene of Schmidt and Stützel (A., 1908, i, 415) appears to be the 9-aminofluorene *salt* of fluorenyl-9-carbamic acid, $C_{12}H_8{:}CH\cdot NH\cdot CO\cdot O\cdot NH_3\cdot CH{:}C_{12}H_8$, since it is produced when 9-aminofluorene is exposed to air or treated with carbon dioxide in dry ethereal solution (cf. Kuhn and Jacob, A., 1925, i, 1260, 1404). The existence of Kuhn and Jacob's γ-9-aminofluorene could not be confirmed. H. WREN.

Mixed ketones derived from the α-mononitrile of camphoric acid. F. SALMON-LEGAGNEUR (Compt. rend., 1926, **182**, 790—792).—The condensation of magnesium phenyl bromide with the methyl ester of the α-mononitrile of camphoric acid gives rise to a ketone-amide. To prove the constitution of this compound, benzene was condensed with the chlorides of both the α- and β-mononitrile of camphoric acid. In the case of the α-nitrile the condensation product was a nitrile, probably 3-*cyano*-1-*phenyl*-1 : 2 : 2-*trimethyl*cyclo*pentane*, b. p. 153—155°/3·5 mm., $[\alpha]_D^{14}$ +21° 12′ in absolute alcohol; with the β-nitrile, the ketone-nitrile corresponding with the ketone-amide in question was obtained. This compound must thus be 3-benzoyl-1 : 2 : 2-trimethyl*cyclo*pentane-1-carboxylamide.

B. W. ANDERSON.

Configuration of β-truxinic acid. XII. R. STOERMER and H. LACHMANN (Ber., 1926, **59**, [*B*], 642—649).—The internally compensated structure of β-truxinic acid (cf. Stoermer and Bachér, A., 1922, i, 830) is confirmed by introducing a substituent into one carboxyl group, whereby the molecule becomes asymmetric and capable of resolution into its optical antipodes. Removal of the substituent or introduction of it into the second carboxyl group restores the symmetry of the molecule with consequent disappearance of optical activity. β-Truxinic acid has therefore the configuration I or II (see *ibid.*, 831).

β-Truxinic acid is readily converted by acetic anhydride at 110—120° into β-truxinic anhydride, m. p. 116°, which with ethyl alcohol affords *ethyl hydrogen* β-*truxinate*, m. p. 133° (*calcium* salt; *amide*, m. p. 141°); *methyl hydrogen* β-*truxinate*, m. p. 164°, and iso*propyl hydrogen* β-*truxinate*, m. p. 84°, are described. β-*Truxinethylamic acid* has m. p. 168° (decomp.). β-Truxinanilic acid, m. p. 210° (decomp.) when rapidly heated, yields sparingly soluble *sodium*, *barium*, and *potassium* salts; it is hydrolysed by treatment with nitrous fumes in acetic acid solution, followed by decomposition of the *nitroso*-derivative, m. p. 170—175°, with potassium hydroxide. β-*Truxinmethylanilic acid*, m. p. 188—188·5°, and its *sodium* salt are described. Attempts to resolve the above compounds by cinchonine, strychnine, brucine, or morphine were unsuccessful. On the other hand, β-truxinic anhydride is converted by *l*-menthol into a mixture which is separated by crystallisation from alcohol into l-*menthyl hydrogen* d-β-*truxinate*, m. p. 208°, $[\alpha]_D^{20}$ −20·88° in acetone (*ammonium* and *sodium* salts), and l-*menthyl hydrogen* l-β-*truxinate*, m. p. 149°, $[\alpha]_D^{20}$ −37·34° in acetone (*ammonium* and *sodium* salts), which are readily hydrolysed to β-truxinic acid. To obtain optically active derivatives of β-truxinic acid which do not contain an optically active alkyl group, *l*-menthyl hydrogen *d*-β-truxinate is converted through the chloride into l-*menthyl* d-β-*truxinanilate*, m. p. 171°, $[\alpha]_D^{20}$ −63° in acetone, which, when hydrolysed, yields inactive β-truxinanilic acid. Since the structure of the acid renders catalytic racemisation improbable, it is assumed that the inactivation is due to intermediate formation of β-truxinanil. This possibility is excluded when l-*menthyl* l-β-*truxinmethylanilate*, m. p. 108—109°, $[\alpha]_D^{21}$ −22·89° in acetone, is used, and the product of the action is l-β-*truxinmethylanilic acid*, m. p. 167—168° when rapidly heated, $[\alpha]_D^{21}$ +15·98° in acetone. Since this acid and its lævorotatory and racemic isomerides are converted through the chlorides into the same, optically inactive β-*truxindimethylanilide*, m. p. 180°, the internally compensated nature of β-truxinic acid is established. H. WREN.

Ether of a ketone hydrate. J. BOUGAULT (Compt. rend., 1926, **182**, 786—788).—The lactone (formula I, this vol., 518) is also obtained by treating the amide-acid (formula I, *ibid.*, 167, 404) with hydrogen chloride. The acid alcohol (formula II, *ibid.*, 518), m. p. 142°, when heated with acetic anhydride, gives the lactone and also, by molecular rearrangement, the anhydride of benzyl-β-phenylethylsuccinic acid, $CO_2H\cdot CH(CH_2Ph)\cdot CH(CH_2\cdot CH_2Ph)\cdot CO_2H$; the latter change is also effected by boiling with dilute hydrochloric acid. B. W. ANDERSON.

Isomeric benzaldehydephenylhydrazones. S. BODFORSS (Ber., 1926, **59**, [*B*], 666—670).—The action of technical benzylidene chloride on phenylhydrazine in alcoholic solution affords tetraphenyldihydrotetrazine, $CPh\begin{matrix}<\\>\end{matrix}\begin{matrix}N\cdot NPh\\NPh\cdot N\end{matrix}\begin{matrix}>\\<\end{matrix}CPh$, m. p. 201—201·5°, α-benzaldehydephenylhydrazone, and *γ-benzaldehydephenylhydrazone*, orange-red, m. p. 154—155°. The isomerides are distinguished from one another by their varying solubility in alcohol, colour,

and by the absence of phototropy from the γ-substance. Chemically they behave similarly, but, in spite of identity of mol. wt., they are not regarded as *cis–trans*-isomerides. Benzylidene chloride and semicarbazide appear to yield exclusively the known benzaldehydesemicarbazone, m. p. 214°. The origin of the tetrazine derivative is obscure; it is not obtained when pure benzylidene chloride is used, and is possibly due to the presence of benzotrichloride in the technical material. With cold benzotrichloride, however, phenylhydrazine yields benzaldehydephenylhydrazone and phenylhydrazine hydrochloride; in hot, alcoholic solution, formazylbenzene, m. p. 173°, and a compound, m. p. 179—180°, are produced.

H. WREN.

Preparation of aldehydes by oxidation of primary acid hydrazides. L. KALB and O. GROSS (Ber., 1926, **59**, [*B*], 727—737).—Oxidation of primary acid hydrazides occurs according to the schemes: (i) $R{\cdot}CO{\cdot}NH{\cdot}NH_2+O_2=R{\cdot}CO_2H+H_2O+N_2$; (ii) $2R{\cdot}CO{\cdot}NH{\cdot}NH_2+O_2=R{\cdot}CO{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}R+2H_2O+N_2$; (iii*a*) $R{\cdot}CO{\cdot}NH{\cdot}NH_2+O=R{\cdot}CHO+H_2O+N_2$, and (iii*b*) $R{\cdot}CHO+R{\cdot}CO{\cdot}NH{\cdot}NH_2=R{\cdot}CH{:}N{\cdot}NH{\cdot}CO{\cdot}R+H_2O$ (cf. Curtius and Melsbach, A., 1910, i, 508; Darapsky, *ibid.*, 1908, i, 106). With mild oxidising agents in alkaline solution, reaction (iii*a*) preponderates, the maximum yield of aldehydes being 64%. Benzoyl-, β-naphthoyl-, *p*-methoxybenzoyl-, and trimethoxybenzoyl-hydrazides give the highest yields. Substituents in the benzene nucleus (particularly *o* and *p*) depress the yield of aldehyde. The *o*-nitro- and *p*-hydroxy-groups completely inhibit aldehyde production, but this can be countered by alkylation of the latter. Aliphatic acid hydrazides do not yield aldehydes. The main by-products are carboxylic acids, which do not appear to be produced by oxidation of intermediate aldehydes. Arylidenearoylhydrazines are usually produced; secondary hydrazides are less common. The following substances do not appear to have been described previously: o-*chlorobenzoylhydrazine*, m. p. 109—110°; o-*bromobenzaldehyde*-p′-*nitrophenylhydrazone*, m. p. 240—241°; m-*bromobenzylidene*-m′-*bromobenzoylhydrazine*, m. p. 164—165°; o-*methoxybenzoylhydrazine*, m. p. 80—81° [*hydrochloride*, m. p. 194—195° (decomp.)]; o-*methoxybenzylidene*-o′-*methoxybenzoylhydrazine*, m. p. 147—148°; o-*methoxybenzaldehyde*-p′-*nitrophenylhydrazone*, m. p. 206—208° (slight decomp.); 4-*hydroxy*-3-*methoxybenzoylhydrazine*, m. p. 211—212°; 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydibenzoylhydrazine*, m. p. 263° (decomp.); 3 : 4 : 5-*trimethoxybenzoylhydrazine*, m. p. 158—159°; 3 : 4 : 5-*trimethoxybenzylidene*-3′ : 4′ : 5′-*trimethoxybenzoylhydrazine*, m. p. 232—233°; 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethoxydibenzoylhydrazine*, m. p. 177°; *ethyl* 2-*nitro*-5-*aminobenzoate*, m. p. 107·5°; 2-*nitro*-5-*aminobenzoylhydrazine*; *isophthalaldehydebisphenylhydrazone*, m. p. 247·5°; *diphenoyldihydrazide*, m. p. 215—216° [*dibenzylidene* derivative (also +1EtOH), m. p. 178°]; *diphenoylmonohydrazide*, $CO_2H{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}NH_2$, m. p. 164° (decomp.), converted by boiling water into the corresponding secondary *hydrazide*, m. p. 250° (decomp.); *dicinchonoylhydrazine*, m. p. 179°.

p-Tolenylhydrazidine is oxidised by potassium ferricyanide in alkaline solution to the corresponding triazole with simultaneous formation of *p*-toluonitrile; probably *p*-tolualdehyde or its imide is intermediately formed.

H. WREN.

Method for dehydrogenating alcohols. F. ZETZSCHE and P. ZALA (Helv. Chim. Acta, 1926, **9**, 288—291).—An earlier method for the preparation of aldehydes and ketones by catalytic dehydrogenation of alcohols (cf. A., 1921, ii, 393, 631) is improved by substitution of combined oxygen for the free gas. Optimum yields are obtained when copper oxide is allowed to react with equimolecular proportions of the alcohol, quinoline, and dinitrobenzene at a temperature which is seldom below 170°. Benzyl alcohol, at 200—205°, gives a 93% yield of benzaldehyde, and from six other alcohols in a series of ten the yield of aldehyde or ketone is 75% or above. *o*-Chlorobenzaldehyde gives a p-*nitrophenylhydrazone*, decomp. 237—238°. Condensation *products* of cinnamaldehyde and *iso*butaldehyde with barium naphthionate are described.

Similar dehydrogenations of tetrahydronaphthalene and decahydronaphthalene give 19% and 15% of naphthalene, respectively.

M. CLARK.

Phenylacetaldehyde. C. J. ENKLAAR (Chem. Weekblad, 1926, **23**, 174—175).—A specimen of phenylacetaldehyde kept in the dark for 6 months was found to have polymerised to the extent of nearly one-half. Kept under water at 0—5° for 1 month, the oil continued to polymerise, but part was obtained as a crystalline solid, m. p. 33—34°; this reacted immediately with the Grignard reagent, and is thus the monomeric form. The *p*-nitrophenylhydrazone was prepared and analysed, but the figures obtained were not concordant.

S. I. LEVY.

Friedel–Crafts reaction with keten. W. PLOEG (Rev. trav. chim., 1926, **45**, 342—344; cf. Alphen, A., 1925, i, 1149; Hurd, this vol., 70).—When keten and hydrogen chloride are passed into a cooled solution of veratrole in carbon disulphide, and aluminium chloride is added to the reaction mixture, which is well stirred, 3 : 4-dimethoxyphenyl methyl ketone is produced. It was identified as its p-*nitrophenylhydrazone*, m. p. 227°, by comparison with a synthetic specimen. The *phenylhydrazone*, m. p. 131°, *semicarbazone*, m. p. 218°, and *azine*, m. p. 203°, are described.

J. W. BAKER.

Carbon rings. I. Constitution of civetone (zibetone). L. RUZICKA (Helv. Chim. Acta, 1926, **9**, 230—248).—Sack's method (A., 1915, i, 692, 888) for the isolation of civetone from civet is improved by distillation of the latter in a high vacuum before or after hydrolysis with alcoholic sodium hydroxide solution. Extraction of an identical product by vacuum distillation alone shows that no isomerisation is caused by the use of alkali. Civet contains 2·5—3·5% of civetone, $C_{17}H_{30}O$, b. p. 158—160°/2 mm., 145°/0·5 mm., d_4^{37} 0·9135, n_D^{37} 1·4820, m_D 78·07 (calc., for a simple, monocyclic, unsaturated ketone, 78·05) (p-*nitrophenylhydrazone*, m. p. 125°). The ketone instantaneously reacts with bromine in carbon disulphide solution and with aqueous alkaline permanganate, and an aqueous-alcoholic solution is reduced by hydrogen in presence of colloidal

palladium, without loss of the characteristic odour, giving *dihydrocivetone*, m. p. 63—64°, b. p. 145°/0·3 mm. (*semicarbazone*, m. p. 191°). The dihydro-compound decolorises bromine with evolution of hydrogen bromide and condenses with benzaldehyde to the *keto-alcohol*, $C_{17}H_{31}O{\cdot}CHPh{\cdot}OH$, m. p. 113—114°, from which the *benzylidene* derivative, $C_{17}H_{30}O{:}CHPh$, b. p. 203—208°/0·5 mm., is obtained. A reactive methylene group must therefore adjoin the carbonyl group. The latter is shown to be in the ring, since oxidation of the dihydroketone with chromic acid gives a *dicarboxylic acid*, $C_{15}H_{30}(CO_2H)_2$, m. p. 116—117°, containing the same number of carbon atoms. Moreover, the *oxime* of dihydrocivetone, m. p. 63°, is converted by the Beckmann change into the *compound* $C_{16}H_{32}\langle^{CO}_{NH}$, m. p. 123—124°. Hydrolysis gives the *hydrochloride*, m. p. 153°, of the *amino-acid*, $NH_2{\cdot}C_{16}H_{32}{\cdot}CO_2H$. Treatment of civetone in carbon tetrachloride solution with ozone at −10° yields a colourless *product*, presumably the ozonide-peroxide, which, on decomposition with water, gives a waxy, non-homogeneous residue, oxidised by sodium hypobromite solution to suberic acid together with a smaller amount of azelaic acid. Oxidation of civetone in the cold with a restricted amount of aqueous alkaline permanganate (equivalent to 5 atoms of oxygen) gives a *ketodicarboxylic acid*, $C_{14}H_{26}O(CO_2H)_2$, m. p. 113—116°, containing one carbon atom less (cf. Challenor and Thorpe, J.C.S., 1923, **123**, 2480). The ethylenic linking must accordingly be in the ring, and civetone may be represented as $C_{14}H_{26}O\langle^{CMe}_{CH}$ (I) or $C_{14}H_{26}O\langle^{CH_2}_{CH}\rangle CH$ (II). Treatment of the ketodicarboxylic acid with excess of permanganate yields suberic acid, accompanied by smaller amounts of succinic and adipic acids; with sodium hypobromite solution, suberic, succinic, pimelic, and azelaic acids are formed. It is concluded that civetone contains a 16- or 17-membered ring with the carbonyl group and ethylenic linking far removed from each other. Identification of the dicarboxylic acid obtained by chromic acid oxidation of dihydrocivetone as pentadecane-ao-dicarboxylic acid (cf. Chuit, this vol., 499) excludes formula (I). Civetone therefore contains an unsaturated *cyclo*heptadecane ring. Of the possible structures, $\begin{matrix}CH{\cdot}[CH_2]_7\\ \|\\ CH{\cdot}[CH_2]_7\end{matrix}\rangle CO$ (III) and $\begin{matrix}CH{\cdot}[CH_2]_6\\ \|\\ CH{\cdot}[CH_2]_8\end{matrix}\rangle CO$ (IV), the former is supported by the fact that no sebacic acid is produced on oxidation, and the steady preponderance of suberic acid in the oxidation products can be explained only by the representation of civetone as Δ¹-*cyclo*heptadecenone. The ketodicarboxylic acid is accordingly *η-ketotetradecane-aξ-dicarboxylic acid*, and the amino-acid obtained from the oxime of the dihydroketone is *π-aminohexadecane-α-carboxylic acid*. M. Clark.

Carbon rings. II. Cyclic ketones containing from ten to eighteen carbon atoms in the ring. L. Ruzicka, M. Stoll, and H. Schinz (Helv. Chim. Acta, 1926, **9**, 249—264).—The corresponding cyclic ketones are obtained by vacuum distillation of the thorium salts of the polymethylenedicarboxylic acids (cf. Chuit, this vol., 499) ranging from nonane-αι-dicarboxylic acid to heptadecane-αρ-dicarboxylic acid. The product distils over, in general, at 350—400°. The yield of *cyclo*nonanone (cf. later work) amounts to 1·5% of the theoretical, that of *cyclo*decanone falls to a minimum value of 0·1—0·2%, but for the higher members of the series the yield rises steadily with increasing number of carbon atoms. *cyclo*Heptadecanone is shown to be identical with dihydrocivetone (preceding abstract). The constitution of the ketones is established by chromic acid oxidation to the normal polymethylenedicarboxylic acids containing the same number of carbon atoms and identical with the synthetic products. *cyclo*Decanone and *cyclo*undecanone were not obtained pure. The remaining ketones resemble camphor in appearance and, in the case of the 10—12-ring compounds, in odour also. In the ascending members of the series, as in muscone and civetone, an odour reminiscent of that of cedarwood becomes increasingly evident in a high concentration. In greater dilution, the predominant odour in the 14- and 15-ring compounds is that of muscone, and in the higher members that of civetone. The muscone odour is most pronounced in *cyclo*pentadecanone. The following compounds are described: cyclo*decanone*, b. p. 100—102°/12 mm. (*semicarbazone*, m. p. 200—201°); cyclo*undecanone*, b. p. 110°/12 mm. (*semicarbazone*, m. p. 200°); cyclo*dodecanone*, m. p. 59°, b. p. 126—128°/12 mm. (*semicarbazone*, m. p. 226—227°); cyclo*tridecanone*, m. p. 32°, b. p. 137—139°/12 mm. (*semicarbazone*, m. p. 207—208°); cyclo*tetradecanone*, m. p. 52°, b. p. 155—156°/12 mm. (*semicarbazone*, m. p. 197—198°); cyclo*pentadecanone* (exaltone), m. p. 63°, b. p. 120°/3 mm. (*semicarbazone*, m. p. 187—188°); cyclo*hexadecanone*, m. p. 56°, b. p. 138°/0·5 mm. (*semicarbazone*, m. p. 180°); cyclo*octadecanone*, m. p. 71°, b. p. 157—159°/0·3 mm. (*semicarbazone*, m. p. 184°).

M. Clark.

Carbon rings. III. Preparation of *cyclo*octanone from azelaic acid. L. Ruzicka and W. Brugger (Helv. Chim. Acta, 1926, **9**, 339—354; cf. A., 1893, i, 557; 1898, i, 638; 1899, i, 789).—Decomposition by heat of the thorium salt of azelaic acid gives a product, the less volatile fraction (65—100°/12 mm.) of which affords an 18% yield of *cyclo*octanonesemicarbazone. Admixture of the salt with copper turnings increases this yield to 25%. Oxidation of the ketone gives suberic acid as sole product. *cyclo*Hexanone, in 1% yield, is isolated from the more volatile fraction (100—190°/120 mm.) by treatment with sodium hydrogen sulphite, with which *cyclo*octanone fails to react at the dilution in which it occurs in this fraction. In the absence of pimelic acid from the starting material, the presence of the lower ketone must be ascribed to partial degeneration of the azelaic acid.

Decomposition of the calcium salt may be carried out on a similar scale, using copper vessels after admixture of the material with copper filings. Separation of the ketone mixture obtained is effected by treatment with sodium hydrogen sulphite. The

ketone regenerated from the crystalline product is separated by distillation into a lower-boiling fraction (150—160°), from which *cyclo*hexanone is isolated as the dibenzylidene derivative, and a higher-boiling fraction (160—200°), from which the semicarbazone of methyl heptyl ketone is isolated. The ketone which failed to react with sodium hydrogen sulphite is separated by distillation into a lower-boiling fraction (80—95°/12 mm.), from which the semicarbazone of *cyclo*octanone is obtained, and a higher-boiling fraction (95—110°/12 mm.), from which an unidentified semicarbazone, m. p. 155—157°, is isolated. The total ketone yield as crude semicarbazone amounts to 10% of theory, consisting of 1% of *cyclo*hexanone, 2% of methyl heptyl ketone, 5—6% of *cyclo*octanone, and less than 1% of the unidentified ketone. Oxidation of the crude ketone mixture gives suberic and adipic acids.

Decomposition of the cerium salt of azelaic acid gives a 10% yield of *cyclo*octanone. The zirconium and lead salts give only 2%. M. CLARK.

Irreversible reduction of organic compounds. II. Bimolecular reduction of carbonyl compounds by vanadous and chromous salts. J. B. CONANT and H. B. CUTTER (J. Amer. Chem. Soc., 1926, **48**, 1016—1030; cf. A., 1924, ii, 463).—Chromous chloride, in alcoholic or acid aqueous solution, is without effect, at the ordinary temperature, on aliphatic or aromatic saturated ketones, aliphatic aldehydes, αβ-unsaturated acids and esters, olefinic hydrocarbons, and alcohols with the exception of certain aromatic carbinols, but many αβ-unsaturated ketones and aldehydes, and aromatic aldehydes, are reduced with the formation of bimolecular products (cf. Conant, Small, and Taylor, A., 1925, ii, 874; Hantzsch, *ibid.*, 1922, i, 556).

Reduction of styryl methyl ketone with alcoholic chromous chloride affords δε-diphenyloctane-βη-dione, m. p. 161° (cf. Harries, A., 1896, i, 689). Reduction of phenyl styryl ketone with vanadous sulphate and alcohol or with vanadous chloride and acetone affords similarly αδ-dibenzoyl-βγ-diphenylbutane, m. p. 266° (cf. Harries, A., 1897, i, 549), together with an *isomeride*, m. p. 194°, b. p. about 360°/5 mm. with slight decomp., and a small proportion of a non-crystalline product. Treatment of the isomeride, m. p. 194°, with alcoholic sodium ethoxide affords 1-*benzoyl*-2 : 4 : 5-*triphenyl*-Δ¹-cyclo*pentene*, m. p. 123°, which is reduced to the corresponding *benzoyltriphenyl*cyclo*pentane*, m. p. 148—151°, by zinc dust and acetic acid. Treatment of either of the above isomerides with bromine in acetic acid affords the *compound* $C_{30}H_{22}OBr_2$, yellow, m. p. 171°, together with, in the case of the isomeride of higher m. p., a colourless *dibromide*. Reduction of anisaldehyde with alcoholic chromous chloride affords *iso*hydroanisoin, m. p. 101°. Benzaldehyde yields similarly a viscous oil containing halogen, whilst reduction with vanadous sulphate yields hydrobenzoin and *iso*hydrobenzoin. Reduction of acraldehyde with vanadous sulphate yields divinyl glycol and a viscous, yellow, unsaturated oil, b. p. above 120°/20 mm., from which no definite compound could be isolated. In presence of excess of sulphuric acid and zinc sulphate, the yield of divinyl glycol is much smaller, and an unsaturated oil, b. p. 160—167°, is produced. Redistillation of the latter afforded an oil, $C_{12}H_{18}O_3$, b. p. 166—167°, n_D^{25} 0·14435. Similar reduction of crotonaldehyde affords dipropenyl glycol, an unsaturated oil, b. p. 85—100°/12 mm., n_D^{25} 0·14608, and other unidentified liquid products. Reduction of cinnamaldehyde with vanadous sulphate affords diphenylvinylglycol, together with unidentified liquids.

F. G. WILLSON.

Beckmann's rearrangement. XVI. Catalytic action of reduced copper on oximes. S. YAMAGUCHI (Bull. Chem. Soc. Japan, 1926, **1**, 54—58; cf. this vol., 520).—Oximes are classed into three groups according to the nature of the products formed by the contact action of reduced copper at 200° in an atmosphere of hydrogen. Group 1 contains those (*e.g.*, benzophenoneoxime) that yield mainly aldehydes or ketones (which are transformed into hydrocarbons) and some basic compounds; group 2 comprises benzaldoxime and benzhydroxamic acid, an acid amide being produced which changes into a nitrile and an acid, whilst members of group 3 (*e.g.*, acetophenoneoxime) show an intermediate behaviour. The various products are considered to be formed by the varying catalytic action of copper on the successive thermal reactions: (*a*) Beckmann's transformation, (*b*) conversion into ketone or aldehyde, (*c*) conversion into imine or nitrile. The catalytic action is explained by the formation of an intermediate compound between the copper and the oxime, together with the supposition of a hydride CuH_2. When the copper loses electrons so that the combining force between the hydrocarbon radicals and the carbon atom of the methane nucleus of the oxime is smaller than that between the nitrogen and the carbon atoms (cf. Komatsu and Hiraidzumi, A., 1925, i, 934), the Beckmann transformation occurs (group 2). When the opposite holds, and the metal exerts no appreciable influence on the combining forces, an aldehyde or ketone is formed (group 1). The formation of the subsidiary substances is also explained.

S. K. TWEEDY.

Constitution of a methyl*cyclo*pentenolone [1-methyl-Δ¹-*cyclo*penten-2-ol-3-one] found in crude pyroligneous acid. C. A. ROJAHN and F. RÜHL (Arch. Pharm., 1926, **264**, 211—227).—The compound isolated by Meyerfeld (A., 1912, i, 628) sublimes readily and has m. p. 74—78° (from water). The following are described: *di*(?)-*benzylidene* derivative, m. p. 207—208°; *dianisylidene* derivative, m. p. 216—223°; phenylosazone (*loc. cit.*), m. p. 138—139°; p-*nitrophenylhydrazone*, m. p. 227°; p-*nitrophenylosazone*, m. p. 262—263°; two β-*naphthylosazones* (? stereoisomerides), (i) grey-green, m. p. 214—217°, and (ii) almost colourless, turning red on keeping, m. p. 178—180°. The *disemicarbazone* (cf. Meyerfeld, *loc. cit.*) also separates in two forms, one of m. p. 250° crystallisable from water, the other of m. p. 238° almost insoluble in water. The *dioxime*, m. p. 173—174°, is presumably a stereoisomeride of that (m. p. 145—146°) obtained by Meyerfeld. By interaction with aminoguanidine in dilute nitric acid, an *aminoguanidone nitrate*,

m. p. 207° (decomp.), is produced. The *benzoate* has m. p. 37—41°, b. p. about 210°/20 mm. The acetate (*loc. cit.*) yields an *aminoguanidone nitrate*, m. p. 212—213°, and an unstable *p-nitrophenylhydrazone*, m. p. 200—201°.

The *phenylurethane* of methyl*cyclo*pentenolone, m. p. 140—142°, in alcoholic solution in presence of palladised charcoal takes up 1 mol. of hydrogen, giving a product, m. p. 90—95°. *2-Methoxy-1-methyl-*Δ^1*-cyclopenten-3-one*, prepared by treating the alcohol with methyl sulphate and cold sodium hydroxide, has b. p. 85—92°/17 mm., and is very unstable (*semicarbazone*, m. p. 228—229°; *aminoguanidone nitrate*, m. p. 225°, decomp. 231—232°). When reduced in presence of palladised charcoal, it yields eventually *2-methoxy-1-methyl-*Δ^1*-cyclopentan-3-one-semicarbazone*, m. p. 206—207°.

The methyl*cyclo*pentenolone itself is similarly reduced; *methyl*cyclo*pentanolone*, b. p. 97—98°, is obtained (*acetate*, b. p. 120—130°/44 mm.; *phenylhydrazone*, m. p. 183—184°). When tested by the method of Kaufmann and Hansen-Schmidt (A., 1925, ii, 554), the methyl*cyclo*pentenolone is shown to be entirely enolic.

A critical discussion of the constitution (cf. Staudinger and Ruzicka, A., 1924, i, 747) leads to the conclusion that the compound is *1-methyl-*Δ^1*-cyclopenten-2-ol-3-one*. W. A. SILVESTER.

Phenyl β-alkoxystyryl ketones. C. DUFRAISSE and R. CHAUX (Bull. Soc. chim., 1926, [iv], **39**, 443—451).—ω-Methoxy- and ω-ethoxy-acetophenone, when obtained pure by a modification of Robinson's method (J.C.S., 1923, **123**, 748), have m. p. 7—8°, b. p. 117—118°/13 mm., $n_D^{20\cdot2}$ 1·5338, d_4^{18} 1·096 (semicarbazone, m. p. 126—127°), and m. p. 8—9°, b. p. 124—125°/13 mm., $n_D^{20\cdot9}$ 1·5222, d_4^{18} 1·059, respectively. In the preparation of phenyl β-methoxystyryl ketone (cf. A., 1925, i, 559), a small quantity of a *substance*, m. p. 103—105°, is obtained, which may be the other stereoisomeride. Phenyl αβ-dibromo-α-methoxy-β-phenylethyl ketone (cf. *ibid.*) yields γ-bromo-αγ-diphenylpropane-αβ-dione (A., 1917, i, 343) with hydrobromic acid. αγ-Diphenylpropane-αβ-dione exists in three modifications: (*a*) stable, m. p. 90°; (*b*) labile, m. p. 67°; and (*c*) oily; (*c*) is obtained on heating (*a*) or (*b*) and can be resolidified only after conversion into a metallic derivative. *Phenyl β-ethoxystyryl ketone*, m. p. 34—35°, b. p. 175—176°/2·5 mm., is converted by sodium or potassium hydroxide into β-ethoxystyrene and benzoic acid.

H. E. F. NOTTON.

Oximes of 2 : 4-dinitrobenzil and the Beckmann change. G. BISHOP and O. L. BRADY (J.C.S., 1926, 810—813).—The supposed β-oxime of 2 : 4-dinitrobenzil previously described (*ibid.*, 1922, **121**, 2364) has been found to be a mixture. The reactions of the α- and β-oximes are best explained by adopting the view that the Beckmann change takes place in the *trans*- and not in the *cis*-sense. The α-oxime, when heated with alcohol at 165°, yields *7-nitro-4-keto-3-phenyl-*1 : 2*-benzoxazine*, m. p. 169°, identical with the product obtained by the action of alkali on the impure β-oxime, and previously described as 4-nitrosalicylonitrile (*loc. cit.*, p. 2369). The benzoxazine gives benzonitrile and 4-nitrosalicylic acid on hydrolysis. When treated with sodium ethoxide in alcohol, the α-oxime yields a red compound considered to be *6-nitro-3-keto-2-phenyl-*ψ*-indole-1-oxide*, m. p. 198°, which, when boiled with excess of aqueous alkali, yields benzaldehyde and an amorphous product. β-2 : 4-Dinitrobenzilmonoxime, m. p. 168°, is formed together with the α-oxime, the above benzoxazine, and possibly a fourth oxime, when 2 : 4-dinitrobenzil in cold alcoholic solution is treated with 3 equivalents of hydroxylamine. The products of the Beckmann change are benzoic acid and 2 : 4-dinitrobenzonitrile. When heated with alkali, the β-oxime gives benzoic acid and 4-nitrosalicylonitrile by way of an unstable *iso*oxazole.

J. S. H. DAVIES.

New derivatives of naphthaquinones. R. LANTZ and A. WAHL (Compt. rend., 1926, **182**, 976—978; cf. A., 1925, i, 820, 1159).—*2-Hydroxy-α-naphthaquinone-1-imine-4-anil*, $C_{10}H_5(OH)(:NH):NPh$, is prepared by shaking 1-amino-β-naphthol-4-sulphonic acid or 1-amino-β-naphthol with air or oxygen in the presence of aniline in alkaline solution. The compound is readily hydrolysed by acids, giving 2-hydroxy-α-naphthaquinone-4-anil. Other derivatives of the naphthaquinones may be prepared in an analogous manner, using other primary amines and other naphthalene derivatives. L. F. HEWITT.

1 : 5-Dichloro-9-phenylanthracene. E. DE B. BARNETT and M. A. MATTHEWS (Ber., 1926, **59**, [*B*], 670—679).—1 : 5-Dichloro-9-bromoanthrone is converted by benzene in the presence of aluminium chloride into 1 : 5-*dichloro-9-phenylanthrone*, m. p. 245°. The substance closely resembles 1 : 5-dichloroanthrone, but shows markedly less tendency towards enolisation, whilst its other properties indicate that substitution in the *meso*-position occurs in the anthracene series only if the bridged linking is present. Thus the anthrone is not attacked by a large excess of chlorine in carbon tetrachloride solution with or without addition of iodine, whereas 1 : 5-*dichloro-9-phenylanthranyl acetate*, $C_6H_3Cl<\begin{matrix}CPh\text{—}\\ |\\ C(OAc)\end{matrix}>C_6H_3Cl$, m. p. 167°, is readily converted into 1 : 5 : 9-*trichloro-9-phenylanthrone*, m. p. 195°. Similarly, bromine in carbon disulphide transforms the acetate into 1 : 5-*dichloro-9-bromo-9-phenylanthrone*, m. p. 171°, but does not attack 1 : 5-dichloro-9-phenylanthrone. Concentrated nitric acid converts the acetate into 1 : 5-*dichloro-9-nitro-9-phenylanthrone*, m. p. 140° (decomp.), whereas under rather more drastic conditions it transforms 1 : 5-dichloro-9-phenylanthrone into 1 : 5-*dichloro-9-hydroxy-9-nitrophenylanthrone*, m. p. 270°. Dichlorophenylanthrone is very resistant to potassium dichromate in glacial acetic acid, but is oxidised by chromic acid in boiling pyridine to 1 : 5-*dichloro-9-hydroxy-9-phenylanthrone*, m. p. 224° (obtained also from the acetate and nitric acid in boiling glacial acetic acid). The hydroxyanthrone could not be acetylated, but 1 : 5-*dichloro-9-acetoxy-9-phenylanthrone*, m. p. 254°, is obtained from the 9-bromo-compound, sodium acetate, and glacial acetic acid. 1 : 5-Dichloro-9-phenylanthrone

is readily reduced by zinc dust and concentrated hydrochloric acid to 1 : 5-*dichloro*-9-*phenylanthracene*, m. p. 104° (1 : 5-*dichloro*-10-*bromo*-9-*phenylanthracene*, m. p. 174—175°, is described), which with chlorine affords 1 : 5 : 9 : 10-*tetrachloro*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 175° (decomp.), which passes at 200° into 1 : 5 : 10-*trichloro*-9-*phenylanthracene*, m. p. 96°. With aniline and dimethylaniline, it yields, respectively, 1 : 5-*dichloro*-10-*anilino*-9-*phenylanthracene*, m. p. 194°, and 1 : 5-*dichloro*-10-*dimethylaminophenyl*-9-*phenylanthracene*, m. p. 232°. It is hydrolysed by aqueous acetone in the presence of calcium carbonate to 1 : 5-*dichloro*-9 : 10-*dihydroxy*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 164°, and converted by the respective boiling alcohols into 1 : 5-*dichloro*-9 : 10-*dimethoxy*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 210°, and 1 : 5-*dichloro*-9 : 10-*diethoxy*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 201°; under different conditions, 1 : 5-*dichloro*-10-*ethoxy*-9-*phenylanthracene*, m. p. 124°, is produced. 1 : 5-Dichloro-9-phenylanthracene is converted by nitric acid in glacial acetic acid solution into 1 : 5-*dichloro*-10-*nitro*-9-*acetoxy*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 171° (decomp.), which is transformed by boiling ethyl alcohol in the presence of a little sulphuric acid into 1 : 5-*dichloro*-10-*nitro*-9-*ethoxy*-9-*phenyl*-9 : 10-*dihydroanthracene*, m. p. 200°. H. WREN.

9-Methylene-, 9-methyl-, and 9 : 9-dimethylanthrone. E. DE B. BARNETT and M. A. MATTHEWS (Ber., 1926, **59**, [*B*], 767—770).—9-Methyleneanthrone, prepared by the successive addition of piperidine and 40% formaldehyde to a boiling solution of anthrone in methyl alcohol, is reduced by zinc dust and ammonia to α-9-*anthracyl*-β-9-9 : 10-*dihydroanthracylethane*, m. p. 308°. 9-*Methylanthrone*, m. p. 65°, prepared by boiling 10-methoxy-9-methylanthracene with glacial acetic and hydrochloric acids, is converted by acetic anhydride and pyridine into 9-*methylanthracyl acetate*, m. p. 167°; it is reduced by zinc dust and acetic and hydrochloric acids to 9 : 9′-*dimethyl*-9 : 10-*dihydrodianthracyl*, m. p. above 300°, accompanied by a little 9-methylanthracene, and by zinc dust and ammonia to 9-methylanthracene. Treatment of 9 : 9-dimethylanthrone with zinc in acid solution affords *tetramethyltetrahydrodianthracyl*, m. p. 315°. H. WREN.

Colouring matters of sandalwood. [Constitution of santalin.] H. DIETERLE and W. STEGEMANN (Arch. Pharm., 1926, **264**, 1—32).—Red sandalwood (from *Pterocarpus santalinus*) is shown to contain four colouring matters, viz., santalin, soluble in cold alcohol, insoluble in ether; deoxysantalin, soluble in alcohol and in ether; "*colouring matter A*," insoluble in cold alcohol and in ether, soluble in hot alcohol; "*colouring matter B*," insoluble in hot alcohol, but dissolved by potassium hydroxide solution. The individuality of these compounds is proved by the fact that, after repeated purification, each shows a characteristic absorption spectrum (maxima at λ 502, 495, 490, and 485, respectively).

When purified from "colouring matter A," santalin sinters at 268° (decomp. above 300°). The diacetyl derivative has a mol. wt., determined by Rast's method, which confirms the formula, $C_{15}H_{14}O_5$, attributed to santalin (Merck) by Cain and Simonsen (J.C.S., 1912, **101**, 1061). The conclusions of O'Neill and Perkin (*ibid.*, 1918, **113**, 125) were unsound, these, and earlier, discrepancies having been due to the "santalin" examined being impure.

When the diacetyl derivative is reduced with zinc dust and acetic acid, a *dihydro*-compound, m. p. 183°, is obtained (*diacetyl* derivative, decomp. 270—280°).

Santalin contains a methoxyl group and two hydroxyl groups (Cain and Simonsen, *loc. cit.*), and the above result indicates that it is an anthraquinone derivative. When it is distilled over zinc dust, or reduced with hydriodic acid and red phosphorus, an oily product is obtained, in small yield, which can be oxidised by chromic acid to a yellow substance resembling anthraquinone in general behaviour. When santalin is oxidised, in hot acetic acid solution, by nitric acid, it yields oxalic acid and styphnic acid. When oxidised in alkaline solution with hydrogen peroxide (in presence of cobalt sulphate), it yields another coloured *compound*, $C_{15}H_{10}O_7$ (*sodium* salt, m. p. about 123°). When treated in acetic acid solution with bromine, santalin affords two isomeric *bromo*-derivatives, $C_{15}H_{17}O_7Br_3$, one soluble, the other insoluble in ether; both are debrominated by the action of zinc and acetic acid, yielding compounds resembling that produced by oxidising santalin with hydrogen peroxide. When santalin is fused with potassium hydroxide, no recognisable products are obtained. When oxidised by ozone, it yields oxalic acid and unidentified products; when, however, it is oxidised in alkaline solution by potassium ferricyanide, a product is obtained that consists of an as yet unidentified colouring matter, together with homopterocarpin, m. p. 83·5°, identical with that obtained by extracting sandalwood, mixed with slaked lime, with ether.

It is concluded that santalin is a methoxy-derivative of 1 : 3-dihydroxy-5 : 6 : 7 : 8-tetrahydroanthraquinone, but it is not possible to locate the position of the methoxyl group. W. A. SILVESTER.

Condensation products [dyes] of the anthraquinone series. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 311.

Dyes of the dibenzanthrone series. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 311.

Hydroxyanthraquinones. J. THOMAS, H. W. HEREWARD, and SCOTTISH DYES, LTD.—See B., 1926, 312.

1 : 2 : 3 : 4-Tetrahydroxyanthraquinone. FARBENFABR. VORM. F. BAYER UND CO.—See B., 1926, 312.

Strophanthin. IX. Crystalline Kombe strophanthin. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1926, **67**, 609—620).—After shaking crystalline Kombe strophanthin (A., 1924, i, 67) with a mixture of chloroform and water, there was obtained from the chloroform solution a substance identical with the cymarin of Windaus and Hermanns (A., 1915, i, 703). The anhydrous substance had m. p. 204—205°, $[\alpha]_D^{20}$ +37·8° in chloroform; on hydrolysis, it yielded 97% of the theoretical amount of cymarose; it gave a *monoacetyl* derivative, m. p.

160—161°. The formation of the latter compound indicates that, in strophanthin, the probable point of union of the sugar to strophanthidin is the γ-hydroxyl group of the latter. The aqueous solution yielded a second glucoside, *Kombe strophanthin-B*, $C_{36}H_{54}O_{14}$,1·65H_2O, m. p. 176°; on hydrolysis, it yielded strophanthidin and a sugar which gave no pentose reactions and did not yield a crystalline osazone after further hydrolysis, but gave the reactions of cymarose; it was therefore probably a disaccharide of the latter with a hexose. The glucoside gave a *tetra-acetyl* derivative, m. p. 167°. The mother-liquor from the glucoside yielded a further amorphous residue of mixed glucosides. "Crystalline Kombe strophanthin" is therefore a complex mixture, probably not of constant composition. C. R. HARINGTON.

Essential oil of *Daucus carota*, L. Y. ASAHINA and T. TSUKAMOTO.—See B., 1926, 339.

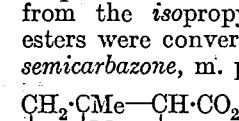
Aliphatic terpenes and their derivatives. V. C. J. ENKLAAR (Rec. trav. chim., 1926, 45, 337—341).—The constitution, that of βζ-dimethyl-$\Delta^{\alpha\eta}$-octatriene, previously assigned to ocimene (cf. A., 1917, i, 111), has been confirmed by microchemical oxidation of the hydrocarbon with potassium permanganate under varying conditions, and microchemical analysis of the crystalline barium or lead salts of the acids so obtained. J. W. BAKER.

Hydration of nopinene. G. AUSTERWEIL (Bull. Soc. chim., 1926, [iv], 39, 690—698).—Nopinene readily takes up the elements of water or acid on treatment with mineral or organic acids; the position of addition depends on the temperature and on the acid used. With cold, more or less dilute mineral acids an ether salt is formed; thus with 45% sulphuric acid at 15—20° nopinene, $C_9H_{13}{\cdot}CH_2$, yields the hydrogen sulphate of pinene hydrate, $C_9H_{13}{\cdot}CMe{\cdot}O{\cdot}SO_3H$. The *sodium* salt rapidly resinifies in air in the presence of alkali, and is readily hydrolysed to pinene hydrate; the latter substance gives all the reactions described by Wallach for homonopinol, and on warming with dilute sulphuric acid is converted into terpineol. Cold 5% sulphuric acid slowly converts it into terpineol and then into terpin hydrate. On heating, or with very concentrated acids, still containing water, the bridge linking of nopinene is broken. Organic acids do not react with nopinene in the cold. With salicylic acid (2 mols.) at 160°, nopinene yields 35—36% of bornyl esters and 15% of a mixture of terpenes containing pinene, limonene, and terpinene. With weaker acids, such as benzoic and abietic acids, and at temperatures up to 145°, the yield of bornyl esters decreases and the yield of pinene increases. With still less acidic substances like phenols, and in the absence of water and with a temperature maximum of 145—150°, pinene is the sole product and only traces of bornyl or fenchyl esters are formed. Very feebly acidic phenols, such as methyl salicylate, are without action. With abietic acid, the isomerisation is complete in 20 hrs. at 175° (yield of pinene, 97·6%); only traces of bornyl esters are formed, but some camphene is produced. This is of importance in the distillation of turpentine, since even at 145—150° the nopinene is converted into pinene at the rate of about 2% per hr. In the presence of catalysts, such as boroacetic anhydride, addition at the bridge-linkings is promoted. Thus with acetic acid (2 mols.) about 44—45% of bornyl acetate is formed, together with increased amounts of terpenyl esters, the same effect being observed with benzoic acid. Pinene under the same conditions gives a yield of bornyl esters about 10—12% lower. R. BRIGHTMAN.

Homologues of the camphor group. IV. Methyltricyclene in relation to the dehydration of methylfenchyl alcohol. S. S. NAMETKIN and L. J. BRUNSOVA (J. Russ. Phys. Chem. Soc., 1925, **57**, 80—86).—The authors have prepared methyltricyclene, b. p. 168—168·5°/762 mm., m. p. 110·5—111°, by oxidising 6-*methylcamphor* (cf. Bredt, A., 1919, i, 125) *hydrazone*, m. p. 103—105°, b. p. 153—154°/42 mm., by means of mercuric oxide, and find it to be different from the α-methylcamphene, b. p. 170·5—171°/764 mm., m. p. 41—43°, formed on dehydration of methylfenchyl alcohol or methylborneol (cf. Zelinski and Zelikov, A., 1902, i, 3). The formation of α-methylcamphene from methylfenchyl alcohol proceeds normally (cf. Bouveault and Blanc, A., 1905, i, 222; Moycho and Zienkowski, *ibid.*, 654), whereas its formation from methylborneol involves pinacolin rearrangement. The supposed methyltricyclene or *pericyclo*homocamphane obtained by Bredt by dehydration of these alcohols by heating them with acetic anhydride at 110° (cf. A., 1918, i, 383) consists of a mixture of α-methylcamphene with another hydrocarbon of higher b. p., possibly methyltricyclene or β-methylcamphene.

6-*Methylcamphorazine*, $C_{11}H_{18}{:}N{\cdot}N{:}C_{11}H_{18}$, has m. p. 131—133°. T. H. POPE.

Camphor group. II. Formation of a new camphorcarboxylic acid from camphane-2-carboxylic esters. Y. MURAYAMA and S. TANAKA (J. Pharm. Soc. Japan, 1926, No. 527, 1—4; cf. *ibid.*, 1925, No. 524, 882).—Silver camphane-2-carboxylate was converted into the methyl (b. p. 106—112°/4 mm.), ethyl (b. p. 110—115°/7 mm.), and *iso*propyl esters (b. p. 155—157°/3 mm.), which were oxidised by chromic anhydride in acetic acid solution to esters of *epi*camphorcarboxylic acid and isolated as *semicarbazones*; that from the methyl ester has m. p. 215°, from the ethyl ester, m. p. 213—214°, and from the *iso*propyl ester, m. p. 195—197°. The esters were converted into epi*camphorcarboxylic acid semicarbazone*, m. p. 231°, by treating with excess of alcoholic potassium hydroxide, and then into epi*camphorcarboxylic acid* (annexed formula), m. p. 185°, $[\alpha]_D$ 0, by boiling with 30% hydrochloric acid. K. KASHIMA.



Lupeylene, a new, crystalline triterpene. K. A. VESTERBERG and H. D. NOJD (Ber., 1926, 59, [*B*], 660—661).—Lupeol, to which the composition $C_{30}H_{50}O$ is assigned, is transformed by phosphorus pentachloride into *lupeylene*, m. p. 173—174°. The relationship of the hydrocarbon to the lupeylene, m. p. 212°, of Jungfleisch and Leroux (A., 1907, i, 783) is not established. H. WREN.

Esters of furfuroic acid. J. E. ZANETTI and C. O. BECKMANN (J. Amer. Chem. Soc., 1926, **48**, 1067—1069).—The following furfuroates were prepared by heating the respective alcohols with a slight excess of furfuroic acid at 120—135° for 12—25 hrs., during which a slow stream of hydrogen chloride was passed through the mixture: n-*butyl*, b. p. 83—84°/1 mm., d_4^{20} 1·0555; n-*amyl*, b. p. 95—97°/1 mm., d_4^{20} 1·0335; n-*hexyl*, b. p. 105—107°/1 mm., d_4^{20} 1·0170; -*heptyl*, b. p. 116—117°/1 mm., d_4^{20} 1·0005, and n-*octyl furfuroate*, b. p. 126—127°/1 mm., d_4^{20} 0·9885; sec.-*butyl*, b. p. 67—69°/1 mm., d_4^{20} 1·0465; sec.-*amyl*, b. p. 75—77°/1 mm., d_4^{20} 1·039; and sec.-*hexyl furfuroate*, b. p. 86—88°/1 mm., d_4^{20} 1·012. The esters darken when kept, chiefly owing to oxidation.

F. G. WILLSON.

Styrylpyrylium salts. VI. Styryl derivatives of 9-methylxanthylium chloride and 3 : 6-dihydroxy-9-methylxanthylium chloride. H. ATKINSON and I. M. HEILBRON (J.C.S., 1926, 676—684).—9-Methylxanthenol (Decker, A., 1905, i, 667) in ethereal solution condenses with aromatic aldehydes on saturation with dry hydrogen chloride. With benzaldehyde, 9-styrylxanthylium chloride is formed identical with the compound prepared by Ziegler and Ochs (A., 1922, i, 1047). *4′-Hydroxy-9-styrylxanthylium chloride* is similarly prepared from *p*-hydroxybenzaldehyde, bright green needles (+1H·CO_2H). With vanillin, *4′-hydroxy-3′-methoxy-9-styrylxanthylium chloride*, m. p. 135° (+H·CO_2H), results. These salts dissolve in dilute formic acid, giving violet to blue solutions, and on dilution with water yield the corresponding quinonoid anhydro-bases, which, in presence of alkali, are slowly transformed into the colourless carbinols. *4′-Methoxy-9-styrylxanthylium chloride*, prepared by condensation with anisaldehyde, separates in bright green needles soluble in dilute formic acid to a dark violet solution from which water slowly precipitates the colourless carbinol base, quinonoid rearrangement being precluded. *3′ : 4′-Methylenedioxy-9-styrylxanthylium chloride* is similarly prepared from piperonal (*zinc* double salt, +H_2O).

3 : 6-Dihydroxy-9-methylxanthylium chloride (Kehrmann, A., 1910, i, 406) is readily obtained by saturating a mixture of resacetophenone and resorcinol at 140—170° with dry hydrogen chloride. The following substituted 3 : 6-dihydroxy-9-styrylxanthylium chlorides are prepared by saturating a suspension of the 9-methylxanthylium salt in alcohol, together with the appropriate aldehyde, with dry hydrogen chloride, the reaction being completed by boiling under reflux: *3 : 4′ : 6-trihydroxy-9-styrylxanthylium chloride*, m. p. 273—274° (+H_2O); *3 : 6-dihydroxy-4′-methoxy-9-styrylxanthylium chloride*, m. p. 282° (+H_2O); *3 : 4′ : 6-trihydroxy-5′-methoxy-9-styrylxanthylium chloride*, m. p. 244°; *3 : 6-dihydroxy-4′ : 5′-methylenedioxy-9-styrylxanthylium chloride*, m. p. 316°. Unlike the styryl salts having the unsubstituted xanthylium nucleus, these derivatives yield neither quinonoid nor carbinol bases on dilution of the solutions with water or on treatment with alkali. This is accounted for by the stabilising influence of the *m*-hydroxyl group (cf. Walker and Heilbron, A., 1925, i, 693). *p*-Dimethylaminobenzaldehyde, when boiled in alcohol with 3 : 6-dihydroxy-9-methylxanthylium chloride, yields *4′-dimethylamino-3 : 6-dihydroxy-9-styrylxanthylium chloride*, green needles, giving green solutions in alcohol and acetone, changing to red on dilution with water; the salt dissolves in dilute sodium hydroxide with bright scarlet coloration. C. HOLLINS.

Action of the oxides and oxy-acids of nitrogen on β-dinaphthylene oxide. H. RYAN, D. FLOOD, and P. MCNULTZ (Proc. Roy. Irish Acad., 1926, B, **37**, 84—89).—β-Dinaphthylene oxide, m. p. 216° (cf. Eckstein, A., 1905, i, 885), when treated in carbon tetrachloride solution with 1 mol. of nitric acid at the ordinary temperature, yields Hodgkinson and Limpach's nitro-β-dinaphthylene oxide, m. p. 185° (J.C.S., 1891, **59**, 1100). With 2—6 mols. of nitric acid, there is also formed an increasing amount of a *dinitro-β-dinaphthylene oxide*, m. p. 318°, isomeric with Knecht and Unzeitig's compound (A., 1881, 281). With excess of fuming nitric acid alone, a *tetranitro-β-dinaphthylene oxide*, m. p. 342° (decomp.), is formed isomeric with Hodgkinson and Limpach's product, and with the *tetranitro-β-dinaphthylene oxide*, decomp. about 320°, obtained by the action of nitrogen peroxide vapour on solid β-dinaphthylene oxide. In acetic acid solution, nitrogen peroxide yields the dinitro-derivative, m. p. 318°. R. BRIGHTMAN.

Nitrodiphenylene sulphides. C. COURTOT and C. POMONIS.—See this vol., 605.

Diphenylene sulphide. C. COURTOT and C. POMONIS (Compt. rend., 1926, **182**, 931—932; cf. this vol., 605).—The compound described in a previous communication (*loc. cit.*) has the constitution 2 : 2′-diaminodiphenylene sulphide, since its diacetyl derivative when oxidised to the corresponding sulphone, and this latter fused with alkalis, yields 4 : 4′-diamino-3-hydroxydiphenyl, showing that the amino-groups are in the *para*-position with respect to the diphenyl linking. L. F. HEWITT.

Transitions from the indole to the quinoline series. II. G. HELLER [with R. FUCHS, P. JACOBSOHN, M. RASCHIG, and E. SCHÜTZE] (Ber., 1926, **59**, [*B*], 704—710).—The main product of the action of diazomethane on isatin is 2 : 3-dihydroxyquinoline (cf. A., 1919, i, 283); if, however, the solution of the crude product in sodium hydroxide is preserved, a *sodium* salt separates which yields *3 : 4-dihydroxyisoquinoline*, m. p. 189—190° (the constitution is assigned on account of its non-identity with any of the theoretically possible dihydroxyquinolines). 5-Chloroisatin affords *6-chloro-2 : 3-diketotetrahydroquinoline*, m. p. 281—282°, whereas 5-bromoisatin yields *6-bromo-2 : 3-diketotetrahydroquinoline*, m. p. 268°, and apparently an *isomeride*, m. p. about 220° (decomp.) after darkening at 190°. The following compounds are analogously prepared: *6 : 8-dibromo-2 : 3-diketotetrahydroquinoline*, m. p. 242—243° after darkening; *5-chloro-6-bromo-2 : 3-dihydroxyquinoline*, m. p. 259—260° after darkening (*monoacetate*, m. p. 270°); *2 : 3-dihydroxy-8-methylquinoline*, m. p. 253°; *2 : 3-dihydroxy-5 : 6 : 8-trimethylquinoline*, m. p. 259°; *3-hydroxy-2-keto-1-methylquinoline*, m. p. 185—186°; *6-chloro-2 : 3-diketo-1-methyltetrahydroquinoline*, m. p. 196—197°; *2 : 3-diketo-1 : 8-dimethyltetrahydroquinol-*

ine, m. p. 168—168·5°; 6 : 8-*dibromo*-2 : 3-*diketo*-1-*methyltetrahydroquinoline*, m. p. 194—195°.

1 : 4 : 5 : 7-*Tetramethylisatin*, m. p. 199—200°, and β-naphthisatin react sluggishly with diazomethane, the latter substance giving a *compound*, m. p. 254—256°; N-*methyl*-β-*naphthisatin*, m. p. 216—218°, is described.

1 : 7-*Dimethylisatin*, m. p. 171—172°, *acetyl*-4 : 6-*dimethylisatin*, m. p. 151°, and 4 : 6-*dimethyl*-3-*isatoxime*, m. p. 220—221° after darkening at 218°, are incidentally described. H. WREN.

Tautomerism in the thyroxin molecule. C. S. HICKS (J.C.S., 1926, 643—645).—The absorption spectra of acetylthyroxin in 75% alcohol and of thyroxin in acid 75% alcohol both show bands at 2850 and 2925 Å., the third band at 2750 Å. present in the curve for alkaline thyroxin solutions being absent in both cases. It is suggested that thyroxin exists in ketonic form in acid solution, the enolic (physiologically active) form being favoured in alkaline solution. C. HOLLINS.

Syntheses of α-unsubstituted dipyrryl-ethanes [carboxylic acids], and -methanes, and pyrrole-aldehydes; dialdehydes of bimolecular pyrroles. H. FISCHER and P. HALBIG (Annalen, 1926, **447**, 123—139).—Ethyl *s*-di-(4-methyl-2-pyrryl)ethane-3 : 3′ : 5 : 5′-tetracarboxylate (cf. A., 1924, i, 1232) is hydrolysed by sodium hydroxide to the 5 : 5′-*dicarboxylic acid*, m. p. 225° (decomp.), which gives, on heating in a vacuum, *ethyl di*-(4-*methyl*-2-*pyrryl*)-*ethane*-3 : 3′-*dicarboxylate*, m. p. 171°, and a little ethyl 3-methylpyrrole-3-carboxylate. The former is converted by Gattermann's method into *ethyl di*-(5-*aldehydo*-4-*methyl*-2-*pyrryl*)*ethane*-3 : 3′-*dicarboxylate*, m. p. 219° [*phenylhydrazone*, m. p. 248° (decomp.), *oxime*, m. p. 245°], whilst it is reduced by acetic–hydriodic acid at 100° to *di*-(4-*methyl*-2-*pyrryl*)*ethane*, m. p. 135—136°. The latter, unlike the dipyrrylmethanes and blood pigments, is not further broken up under these conditions. Ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate, (A), condenses with ethyl 2 : 4-dimethylpyrrole-3-carboxylate in presence of hydrochloric acid to give ethyl 3 : 5 : 4′-*trimethyl*-2 : 2′-*dipyrrylmethane*-3′ : 4 : 5′-*tricarboxylate*, m. p. 157—158°. *Ethyl* 2 : 4 : 4′-*trimethyl*-3 : 2′-*dipyrrylmethane*-3′ : 5 : 5′-*tricarboxylate*, m. p. 160°, and *ethyl* 2 : 5 : 4′-*trimethyl*-3 : 2′-*dipyrrylmethane*-3′ : 4 : 5′-*tricarboxylate*, m. p. 156—157°, are similarly prepared. *Ethyl* 3 : 5 : 4′-*trimethyl*-2 : 2′-*dipyrrylmethane*-3′ : 4 : 5′-*tricarboxylate*, m. p. 157—158°, is obtained on condensing (A) in methyl alcohol with ethyl 2 : 4-dimethylpyrrole-3-carboxylate, and also by fusing the latter with 3 : 5-dicarbethoxy-4-methyl-2-pyrryl carbinol (see following abstract). *Ethyl di*-(4-*methyl*-2-*pyrryl*)*methane*-3 : 3′ : 5 : 5′-*tetracarboxylate*, m. p. 134°, is obtained (*a*) by treating (A) with hydrobromic acid in methyl alcohol, (*b*) by acting on the ethoxy-derivative of (A) with aluminium chloride and decomposing the resulting *aluminium* compound, $C_{24}H_{34}O_8Cl_2Al_3$, m. p. 153°, with water, and (*c*) by boiling (A) in benzene solution with zinc. It is readily attacked by acetic–hydriodic acid. It yields, on partial hydrolysis, the 5 : 5′-*dicarboxylic acid*, m. p. 254° (decomp.), from which, on heating in a vacuum, *ethyl di*-(4-*methyl*-2-*pyrryl*)*methane*-3 : 3′-*dicarboxylate*, m. p. 173°, is obtained. The latter gives a red, amorphous condensation product, $C_{34}H_{44}O_6N_4$, m. p. above 300°, with dimethylaminobenzaldehyde. It is converted by Gattermann's method into *ethyl di*-(5-*aldehydo*-4-*methyl*-2-*pyrryl*)*methane*-3 : 3′-*dicarboxylate*, m. p. 188° (*diphenylhydrazone*, m. p. 246—247°; *dioxime*, m. p. 221°, darkening at 215°). This affords a porphyrin-like absorption spectrum when treated with cold hydrochloric acid. *Ethyl di*-(4-*methyl*-3-*ethyl*-2-*pyrryl*)*methane*-5 : 5′-*dicarboxylate*, m. p. 126°, is prepared by treating ethyl 4-methyl-3-ethyl-2-bromomethylpyrrole-5-carboxylate with hydrobromic acid in methyl alcohol. Oxidation of (A) with chromic acid gives *ethyl* 2-*aldehydo*-4-*methylpyrrole*-3 : 5-*dicarboxylate*, m. p. 125° (*phenylhydrazone*, m. p. 125°, *oxime*, m. p. 139°, from which the *nitrile*, m. p. 153°, is obtained). The aldehyde is reduced by hydrazine and sodium ethoxide to 2 : 4-dimethylpyrrole (*picrate*, m. p. 88°). 3 : 5-*Dicarbethoxy*-4-*methyl*-2-*pyrrylcarbinyl acetate*, m. p. 114—115°, is obtained on heating (A) with acetic acid and sodium acetate. H. E. F. NOTTON.

Synthesis of α-pyrrole-aldehydes and stable tripyrrylmethanes. H. FISCHER and P. ERNST (Annalen, 1926, **447**, 139—162).—Ethyl 3-bromo-4-methyl-2-bromomethylpyrrole-5-carboxylate, (A) (cf. A., 1924, i, 80, 1232), is conveniently prepared, via *ethyl* 3-*bromo*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 150°, by brominating ethyl 2 : 4-dimethylpyrrole-5-carboxylate. The corresponding carboxylic acid is converted by 2 mols. of bromine into 3 : 3′ : 5′-tribromo-2 : 4 : 4′-trimethyldipyrrylmethene (*loc. cit.*). Application of Gattermann's reaction to the above acid yields 3-*bromo*-2 : 4-*dimethylpyrrole*-5-*aldehyde*, m. p. 166—167° (decomp.) [*phenylhydrazone*, m. p. 99—100° (decomp.); *semicarbazone*, m. p. 223—224° (decomp.)]. This is converted by alcoholic hydrochloric acid into the dye *di*-(3-*bromo*-2 : 4-*dimethylpyrryl*)*methene*, m. p. 187° (decomp.). Treatment of (A) with water does not afford the alcohol, but sodium salts yield the corresponding esters. In this way, 3-*bromo*-5-*carbethoxy*-4-*methyl*-2-*pyrrylcarbinyl acetate*, m. p. 107—109°, *chloroacetate*, m. p. 150—153°, and *formate*, m. p. 146—148° (decomp.), are obtained. The anilide of (A) (*loc. cit.*) is oxidised by permanganate to a *Schiff's base*, m. p. 127—128° (*hydrochloride*, m. p. 216°), which is readily hydrolysed to *ethyl* 4-*bromo*-5-*aldehydo*-3-*methylpyrrole*-2-*carboxylate*, (B), m. p. 134—136° (*phenylhydrazone*, m. p. 144°; *oxime*, m. p. 155—156°; *semicarbazone*, decomp. 260°). Similarly, from the anilide of ethyl 4-methyl-2-bromomethylpyrrole-3 : 5-dicarboxylate are obtained a *Schiff's base*, m. p. 82°, and *ethyl* 2-*aldehydo*-4-*methylpyrrole*-3 : 5-*dicarboxylate*, (C), m. p. 124°, which yields 3-methylpyrrole on distillation with soda-lime. 3-*Carbethoxy*-2-*aldehydo*-4-*methylpyrrole*-5-*carboxylic acid*, m. p. 195° (decomp.), 3-*bromo*-2-*aldehydo*-4-*methylpyrrole*-5-*carboxylic acid*, m. p. indefinite, and 2-*aldehydo*-4-*methylpyrrole*-3 : 5-*dicarboxylic acid*, m. p. above 250°, obtained by hydrolysis of (B) and (C), cannot be decarboxylated by heating in a vacuum. On heating (C) with 2 mols. of ethyl 2 : 4-dimethylpyrrole-3-carboxylate [*di*-(2 : 4-*dimethyl*-

3-*carbethoxypyrryl*)]-4-*methyl*-3:5-*dicarbethoxy*-2-*pyrrylmethane*, m. p. 179°, is produced. The following tripyrrylmethanes are obtained in a similar manner: [*di*-(3-*acetyl*-2:4-*dimethylpyrryl*)]-3:5-*dicarbethoxy*-4-*methyl*-2-*pyrrylmethane*, m. p. 254—255°, [*di*-(5-*carbethoxy*-2:4-*dimethylpyrryl*)]-3:5-*dicarbethoxy*-4-*methyl*-2-*pyrrylmethane*, m. p. 199—200°, and [*di*-(3-*carbethoxy*-2:4-*dimethylpyrryl*)]-3-*bromo*-5-*carbethoxy*-4-*methyl*-2-*pyrrylmethane*, m. p. 227—228°. They are stable substances which are converted into red dyes by potassium dichromate. 3:5-*Dicarbethoxy*-4-*methyl*-2-*pyrrylcarbinol*, m. p. 116°, is formed by catalytic hydrogenation of the aldehyde (C). The notable stability of this compound and its derivatives is due to the presence of the carbethoxyl groups. It condenses with itself or with other trisubstituted pyrroles, giving dipyrrylmethanes identical with those described in the preceding paper. From ethyl 2:4-dimethyl-3-ethylpyrrole-5-carboxylate are successively obtained a *bromo*-derivative, m. p. 128—132° [together with the *hydrobromide*, m. p. 144—146°, of a red dye, $C_{21}H_{28}O_4N_2$, m. p. 132—134° (decomp.)], *ethyl* 4-*methyl*-3-*ethyl*-2-*anilinomethylpyrrole*-5-*carboxylate*, m. p. 144—145°, the *Schiff's base*, m. p. 133° (*hydrochloride*, m. p. 196°, converted by sodium acetate into a *substance*, m. p. 119—120°), and *ethyl* 2-*aldehydo*-4-*methyl*-3-*ethylpyrrole*-5-*carboxylate*, m. p. 90° (*oxime*, m. p. 150°). This last is more unstable than (B) or (C), since when it is heated with ethyl 2:4-dimethylpyrrole-5-carboxylate, the aldehyde group splits off, forming ethyl di-(2:4-dimethyl-2-pyrryl)methene-3:3′-dicarboxylate and ethyl 4-methyl-3-ethylpyrrole-5-carboxylate.

H. E. F. NOTTON.

Compounds of arsenic halides with pyridine. O. DAFERT and Z. A. MELINSKI (Ber., 1926, **59**, [*B*], 788—790).—When solutions of arsenic trichloride and pyridine in light petroleum are mixed, the very hygroscopic *compound*, $AsCl_3,C_5H_5N$, m. p. 145·5°, separates. The *substances* $AsBr_3,2C_5H_5N$, m. p. 195°, and $AsI_3,3C_5H_5N$ are also described. H. WREN.

Quinoline derivatives. IV. Compounds of 2-phenyl-4-methylquinoline. H. JOHN [with V. FISCHL] (Ber., 1926, **59**, [*B*], 722—726; cf. A., 1925, i, 1317).—2-Phenyl-4-methylquinoline is converted by 40% formaldehyde solution at 130° into 2-*phenyl*-4-ββ-*dihydroxy*iso*propylquinoline*, m. p. 163·5° (*hydrochloride*, m. p. 195°; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *tartrate*; *picrate*, m. p. 113°). Oxidation of 2-phenyl-4-ββ-dihydroxy-*iso*propylquinoline yields 2-phenylquinoline-4-carboxylic acid. 6-Methoxy-2-phenyl-4-methylquinoline similarly affords 6-*methoxy*-2-*phenyl*-4-ββ-*dihydroxy*iso*propylquinoline*, m. p. 93° (*hydrochloride*; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *tartrate*; *picrate*). 2-*Phenyl*-4-Δ$^{\alpha}$-*propenylquinoline*, m. p. 54°, is obtained from 2-phenyl-4-methylquinoline and acetaldehyde at 200—210°; the *hydrochloride*, *sulphate*, *nitrate*, additive *compound* with mercuric chloride, *tartrate*, and *picrate*, m. p. 207°, are described. 6-*Methoxy*-2-*phenyl*-4-Δ$^{\alpha}$-*propenylquinoline*, m. p. 123°, yields a *hydrochloride*, *sulphate*, *nitrate*, additive *compound* with mercuric chloride, *tartrate*, and *picrate*. Benzaldehyde and 2-phenyl-4-methylquinoline at 200—210° yield 2-*phenyl*-4-*styrylquinoline*, m. p. 102° (*hydrochloride*; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *tartrate*; *picrate*, m. p. 268°). 6-*Methoxy*-2-*phenyl*-4-*styrylquinoline*, m. p. 140°, yields a *hydrochloride*, *sulphate*, *nitrate*, additive *compound* with mercuric chloride, *tartrate*, and *picrate*. 2-Phenyl-4-methylquinoline could not be condensed with paracetaldehyde, propaldehyde, *iso*butaldehyde, *iso*valeraldehyde, or heptaldehyde below 310°, or with *o*- or *p*-nitrobenzaldehyde, *m*-aminobenzaldehyde, *p*-dimethylaminobenzaldehyde, *p*-tolualdehyde, cumaldehyde, phenylacetaldehyde, cinnamaldehyde, salicylaldehyde, anisaldehyde, vanillin, piperonal, or furfuraldehyde.

H. WREN.

Preparation of 2-phenyl-4-aminoethylquinoline. CHEM. FABR. AUF ACTIEN, VORM. E. SCHERING.—See B., 1926, 385.

Iodination in the carbazole series. S. H. TUCKER (J.C.S., 1926, 546—553).—Iodination of pure carbazole, m. p. 245°, in boiling glacial acetic acid with potassium iodide and excess of potassium iodate gives 3:6(?)-*di*-*iodocarbazole*, m. p. 202—204°, and 3-iodocarbazole, separable by conversion into acetyl or benzoyl derivatives. Classen's method of iodination with iodine and yellow mercuric oxide (D.R.-P. 81929) in alcohol gives the di-iodocarbazole, m. p. 201—204° (Classen, 184°). 3-*Iodo*-9-*acetylcarbazole*, m. p. 145—147°, is prepared from 3-iodocarbazole by acetylation or from 9-acetylcarbazole by iodination. 3-*Iodo*-9-*benzoylcarbazole*, from iodocarbazole or benzoylcarbazole, is dimorphic, m. p. 145—146°. 3:6-*Di*-*iodo*-9-*acetylcarbazole*, m. p. 224—225°, and the corresponding *benzoyl* compound, m. p. 204—205°, are described. 3-Iodo- (m. p. 170—171°) and 3:6-*di*-*iodo*-9-*toluene*-p-*sulphonylcarbazole* (m. p. 257°) are prepared by iodination or by toluenesulphonylation. Iodination of 9-methylcarbazole gives 3-iodo- and 3:6-*di*-*iodo*-9-*methylcarbazole*, m. p. 181—182°; 3-iodo- and 3:6-*di*-*iodo*-9-*ethylcarbazole*, m. p. 152—153°, are obtained from ethylcarbazole. 3-*Iodo*-9-iso*propylcarbazole*, from 3-iodocarbazole, *iso*propyl iodide, and potassium hydroxide, has m. p. 95—97°.

C. HOLLINS.

Manufacture of acridine derivatives [bactericides]. BRIT. DYESTUFFS CORP., W. H. PERKIN, and A. W. BURGER.—See B., 1926, 420.

Abnormal oxime of dehydro-2:2′-dihydroxydi-α-naphthylmethane. O. DISCHENDORFER (Ber., 1926, **59**, [*B*], 774—777).—The oxime of dehydro-2:2′-dihydroxydi-α-naphthylmethane described by Abel (A., 1893, i, 172; cf. Pummerer and Cherbuliez, *ibid.*, 1915, i, 417; Kohn and Ostersetzer, *ibid.*, 1918, i, 501) is identified as di-αβ-naphthacridone. When distilled with zinc dust, it yields di-β-naphthylamine. The conception is confirmed by the observation that *dehydrophenyl*-2:2′-*dihydroxydi*-α-*naphthylmethane*, m. p. 210—211°, in which the hydrogen is not attached to the central carbon atom, affords a normal *oxime*, m. p. 209° (decomp.). H. WREN.

Preparation of parabanic acid. H. BILTZ and G. SCHIEMANN (Ber., 1926, **59**, [*B*], 721—722).—Parabanic acid is obtained in 77—81% yield by the

oxidation of purified uric acid by hydrogen peroxide in boiling aqueous hydrochloric acid solution; the use of crude uric acid is accompanied by much foaming. The crude acid is sufficiently purified by solution in concentrated sulphuric acid and precipitation by water. H. WREN.

Condensation of aldehydes with diphenyl-*iso*thiohydantoin. R. M. HANN and K. S. MARKLEY (J. Washington Acad. Sci., 1926, **16**, 169—175).—The following condensation products were obtained after heating a mixture of diphenyl*iso*thiohydantoin and the appropriate aldehyde with acetic acid and fused sodium acetate. 5-*Benzylidene*-2 : 3-*diphenyl*-iso*thiohydantoin*, m. p. 215—216°; 5-(o-*nitrobenzyl-idene*)-2 : 3-*diphenyl*iso*thiohydantoin*, m. p. 196—197°; 5-*cinnamylidene*-2 : 3-*diphenyl*iso*thiohydantoin*, m. p. 225—226°; 5-*furfurylidene*-2 : 3-*diphenyl*iso-*thiohydantoin*, m. p. 221—222°; 5-*salicylidene*-2 : 3-*diphenyl*iso*thiohydantoin*, m. p. 249—250°; 5-(3' : 5'-*dichlorosalicylidene*)-2:3-*diphenyl*iso*thiohydantoin*, m. p. 234—235°; 5-(3' : 4'-*dihydroxybenzylidene*)-2 : 3-*di-phenyl*iso*thiohydantoin*, not melting below 300°; 5-(4-*hydroxy*-3-*methoxybenzylidene*)-2 : 3-*diphenyl*iso-*thiohydantoin*, m. p. 250—251°; 5-(5'-*chlorovanillyl-idene*)-2 : 3-*diphenyl*iso*thiohydantoin*, m. p. 132—134° (decomp.); 5-(5-*nitrovanillylidene*)-2 : 3-*diphenyl*iso-*thiohydantoin*, m. p. 100—102° (decomp.); 5-(5-*bromo-vanillylidene*)-2 : 3-*diphenyl*iso*thiohydantoin*, decomp. 100°. J. S. CARTER.

Decarboxylation of amino-acids, and preparation of the enol form of 2 : 5-diketopiperazines. E. ABDERHALDEN and F. GEBELEIN (Z. physiol. Chem., 1926, **152**, 125—131).—Tyramine may be prepared in 90% yield by heating tyrosine with diphenylamine at 240°. Glycine and alanine may be decarboxylated in the same way, but the yields are not so good. A number of dipeptides have also been submitted to this treatment. Leucylglycine is transformed, almost quantitatively, into the anhydride, which is obtained, at least in part, in the reactive enol form. α-Amino*iso*butyryl-α-amino*iso*butyric acid, since it has no hydrogen attached to the α-carbon atoms, is incapable of giving the enol form, and is converted completely into the stable anhydride. On the other hand, α-aminobutyryl-α-aminobutyric acid gives, at least in part, the reactive anhydride. Leucylvaline, alanylalanine, and leucyl-leucine behave similarly, giving practically quantitative yields of the corresponding anhydride, which displays in each case reactions attributed to the presence of an enol grouping in the molecule. H. D. KAY.

Action of alkali arsenites on some halogenated organic compounds. I. E. BALABAN (J.C.S., 1926, 569—573).—Attempts to prepare organic arsinic acids by the interaction of potassium arsenite and organic halides were unsuccessful under a variety of conditions. In 4(5)-methyl-5(4)-chloromethylglyoxaline and 5-chloro-1-methyl-2-chloromethylglyoxaline the chloromethyl group is hydrolysed to hydroxymethyl. 5-Chloro-4-nitro-1-methylglyoxaline yields 4-*nitro*-5-*hydroxy*-1-*methylglyoxaline*, m. p. 106° [*potassium* salt ($+\frac{1}{2}H_2O$), decomp. 292°; *sodium* salt, decomp. 320°]. 1-Bromo-2 : 4-dinitrobenzene gives dinitrophenol, m. p. 113—114°, and 8-chlorocaffeine is converted by alcoholic potassium arsenite into 8-hydroxycaffeine, m. p. 335°, and 8-ethoxycaffeine, m. p. 140—142°. Phthalbromomethylimide, $C_6H_4[C_2O_2]N{\cdot}CH_2Br$, with potassium arsenite in acetone, gives ethylenediphthalimide, m. p. 230°.

Phthalimidomethanesulphonic acid, m. p. about 295° ($+2{\cdot}5H_2O$, decomp.; does not melt at 320° after drying at 120°), is obtained in 13% yield by boiling the bromomethylimide with aqueous sodium sulphite solution. It is hydrolysed by hot 20% hydrochloric acid to phthalic acid and ammonium chloride, no aminomethanesulphonic acid being found.

C. HOLLINS.

Isomeric relationships in the pyrazole series. VI. Alkyl derivatives of 5-methylpyrazole-3-carboxylic acid and of 3(5)-methylpyrazole. K. VON AUWERS and H. HOLLMANN (Ber., 1926, **59**, [*B*], 601—607; cf. A., 1925, 1176, 1178, 1180).—Alkylation of ethyl 5-methylpyrazole-3-carboxylate followed by elimination of the carbethoxyl group leads to the production of 1 : 3- and 1 : 5-dialkylpyrazoles (cf. Rojahn, following abstract). Contrary to previous observations, direct alkylation of 3(5)-methylpyrazole gives 1 : 5- as well as 1 : 3-dialkyl derivatives.

Ethyl 5-methylpyrazole-3-carboxylate is converted by sodium ethoxide and ethyl bromide into a mixture of *ethyl* 5-*methyl*-1-*ethylpyrazole*-3-*carboxylate*, b. p. 154°/12 mm., d_4^{20} 1·079, n_{He}^{20} 1·4922, and *ethyl* 3-*methyl*-1-*ethylpyrazole*-5-*carboxylate*, b. p. 101·5°/12 mm., d_4^{20} 1·040, n_{He}^{20} 1·4768 (*picrate*, m. p. 68—69°). 5-*Methyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 136—137°, is converted by bromine in glacial acetic acid solution into 4-*bromo*-5-*methyl*-1-*ethylpyrazole*-3-*carboxylic acid*, m. p. 148·5—149°, which cannot contain a substituent attached to the nitrogen atom in position 2, since it is transformed by methyl alcohol and hydrogen chloride into methyl 4-bromo-5-methyl-1-ethylpyrazole-3-carboxylate, m. p. 65—66°. Similarly, 3-*methyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 141—142°, affords 4-*bromo*-3-*methyl*-1-*ethylpyrazole*-5-*carboxylic acid*, m. p. 159° (*hydrobromide*, m. p. 194°), which contains substituents in both positions vicinal to the carboxyl group, since it cannot be esterified by methyl alcohol and hydrogen chloride. When decarboxylated, 5-methyl-1-ethylpyrazole-3-carboxylic acid yields 5-methyl-1-ethylpyrazole, b. p. 161°, d_4^{20} 0·951, n_{He}^{20} 1·4741, identical with the compound described previously as 3-methyl-1-ethylpyrazole. In a similar manner, 3-methyl-1-ethylpyrazole-5-carboxylic acid gives 3-*methyl*-1-*ethylpyrazole*, b. p. 152°, d_4^{20} 0·936, n_{He}^{20} 1·4675 (*picrate*, m. p. 114·5—115·5°).

Precisely analogous results are obtained by methylation of ethyl 5-methylpyrazole-3-carboxylate by sodium methoxide and methyl iodide, which leads to the production of *methyl* 1 : 5-*dimethylpyrazole*-3-*carboxylate*, b. p. 144°/11 mm., m. p. 71·5—72·5°, and *methyl* 1 : 3-*dimethylpyrazole*-5-*carboxylate*, b. p. 91°/11 mm. The former ester is hydrolysed to 1 : 5-*dimethylpyrazole*-3-*carboxylic acid*, m. p. 175—176°, which affords 4-*bromo*-1 : 5-*dimethylpyrazole*-3-*carboxylic acid*, m. p. 194—195°, yielding a *methyl* ester, m. p. 79°. 1 : 3-*Dimethylpyrazole*-5-*carboxylic acid*, m. p. 207°, and 4-*bromo*-1 : 3-*dimethylpyrazole*-

5-carboxylic acid, m. p. 232°, are described. 1 : 5-Dimethylpyrazole, b. p. 153°, obtained quantitatively from 1 : 5-dimethylpyrazole-3-carboxylic acid, is identical with the substance described previously as 1 : 3-dimethylpyrazole (cf. Jowett and Potter, J.C.S., 1903, **83**, 468). 1 : 3-*Dimethylpyrazole*, b. p. 136°, and its *picrate*, m. p. 137°, are described. 4-*Bromo*-1 : 5-*dimethylpyrazole*, m. p. 38·5—39·5° (*picrate*, m. p. 122—122·5°; *hydrobromide*, m. p. 125—126°), is obtained by decarboxylation of 4-bromo-1 : 5-dimethylpyrazole-3-carboxylic acid or from the above 1 : 5-dimethylpyrazole and bromine in glacial acetic acid. 4-*Bromo*-1 : 3-*dimethylpyrazole*, b. p. 75°/10 mm. (*picrate*, m. p. 116°), is prepared by analogous methods. H. WREN.

Isomeric relationships in the pyrazole series. C. A. ROJAHN (Ber., 1926, **59**, [*B*], 607—611; cf. A., 1922, i, 1183).—Where theoretically possible, alkylation of pyrazolecarboxylic acids invariably gives rise to two isomeric acids (cf. von Auwers and Hollmann, preceding abstract).

[In part with H. E. KÜHLING.]—1 : 5-Dimethylpyrazole-3-carboxylic acid, m.p. 176—178°, is prepared by the action of sodium hydroxide on an aqueous solution of methylhydrazine sulphate and ethyl sodioacetonylglyoxylate. Treatment of 3(5)-methylpyrazole-5(3)-carboxylic acid with methyl sulphate and sodium hydroxide affords a mixture of 1 : 5-dimethylpyrazole-3-carboxylic acid and 1 : 3-dimethylpyrazole-5-carboxylic acid, m. p. 207°, whereas the latter acid appears to be almost exclusively produced when methyl *p*-toluenesulphonate is employed. Decarboxylation of 1 : 5-dimethylpyrazole-3-carboxylic acid affords 1 : 5-dimethylpyrazole, which is oxidised by potassium permanganate to an acid, m. p. 222°, regarded formerly as 1-methylpyrazole-3-carboxylic acid, but now considered to be 1-methylpyrazole-5-carboxylic acid. 4-Methylpyrazole-3(5)-carboxylic acid is transformed by methyl sulphate and sodium hydroxide into a mixture of 1 : 4-*dimethylpyrazole*-3-*carboxylic acid*, m. p. 171°, and 1 : 4-*dimethylpyrazole*-5-*carboxylic acid*, m. p. 171°; either acid is converted when heated into 1 : 4-dimethylpyrrole, identified as the *picrate*, m. p. 165°. Ethyl benzoylacetoacetate, methylhydrazine sulphate, and sodium carbonate give 3-*phenyl*-1 : 5-*dimethylpyrazole*-4-*carboxylic acid*, m. p. 197—198°; this acid, together with 5-*phenyl*-1 : 3-*dimethylpyrazole*-4-*carboxylic acid*, m. p. 176—177°, is also obtained by methylation of the phenylmethylpyrazolecarboxylic acid, m. p. 254°, derived from ethyl benzoylacetoacetate and hydrazine hydrate. 3-*Phenyl*-1 : 5-*dimethylpyrazole picrate*, m. p. 182°, and 5-*phenyl*-1 : 3-*dimethylpyrazole picrate*, m. p. 168—170°, are described. H. WREN.

Isomeric relationships in the pyrazole series. VII. Diphenylmethylpyrazole and certain other pyrazole derivatives. K. VON AUWERS and H. MAUSS (Ber., 1926, **59**, [*B*], 611—624; cf. preceding abstracts).—The substance, m. p. 156°, obtained by the action of phenylhydrazine on styryl methyl ketone, could not be benzoylated, but the ketone is readily converted by *as*-benzoylphenylhydrazine into the as-*benzoylphenylhydrazone*, m. p. 127·5—128·5°, which is hydrolysed by alcoholic potassium hydroxide to the compound, m. p. 156°, and transformed by acetic and hydrochloric acids into 1 : 5-diphenyl-3-methylpyrazoline, m. p. 116°, thus establishing the constitution of the hydrazone (m. p. 156°) and of 1 : 5-diphenyl-3-methylpyrazole, m. p. 63°. The latter compound is also obtained from phenylhydrazine and ethyl benzoylacetoacetate (cf. Knorr and Blank, Ber., 1885, **18**, 311), but, contrary to the observations of the authors, the pyrazoline derived from it has m. p. 115—116° instead of 109°, and is identical with the compound described above.

The observations of Knorr and Blank on the action of phenylhydrazine on ethyl benzylideneacetoacetate are generally confirmed, but the ultimate 1 : 3-diphenyl-5-methylpyrazole has m. p. 77° instead of 47° (see later). Attempts to reduce the pyrazole to 1 : 3-diphenyl-5-methylpyrazoline were not completely successful. 1 : 3-*Diphenyl*-5-*methylpyrazole picrate* has m. p. 108—109°. The primary action of phenylhydrazine on ethyl benzylideneacetoacetate appears, therefore, to consist of addition at the ethylenic linking, giving rise to the compound $OH\cdot CMe{:}C(CO_2Et)\cdot CHPh\cdot NH\cdot NHPh$. This substance, when formed from its components and preserved for a day at the atmospheric temperature in presence or absence of air, affords *ethyl* 1 : 3-*diphenyl*-5-*methylpyrazole*-4-*carboxylate*, m. p. 118—119°, instead of the expected pyrazoline derivative. Benzaldehydephenylhydrazone is formed as by-product which becomes the main product of the reaction if the mixture is heated, the *compound* $NHPh\cdot NH\cdot CHPh\cdot CH_2\cdot C(:N\cdot NHPh)\cdot CH_2\cdot CO_2Et$, m. p. (indef.) 118—128°, appearing to be formed intermediately. In the presence of acid, ethyl benzylideneacetoacetate and phenylhydrazine give the corresponding *hydrazone*, m. p. 149—150°. The phenylhydrazone of benzylideneacetoacetic acid is very unstable and is oxidised by permanganate to benzoic acid, thus establishing its structure. Ring-closure of the hydrazone, m. p. 149—150°, is most conveniently effected by hot glacial acetic acid, whereby the stable *ethyl* 1 : 5-*diphenyl*-3-*methylpyrazoline*-4-*carboxylate*, m. p. 83—84°, is obtained; this is hydrolysed to 1 : 5-*diphenyl*-3-*methylpyrazoline*-4-*carboxylic acid*, m. p. 123—124°, which is decarboxylated to the known 1 : 5-diphenyl-3-methylpyrazoline, m. p. 114—116°.

1 : 5-Diphenylpyrazole-3 : 4-dicarboxylic acid is converted when heated above its m. p. into 1 : 5-*diphenylpyrazole*-4-*carboxylic acid*, m. p. 162—164°, whereas 1 : 3-*diphenylpyrazole*-4-*carboxylic acid*, m. p. 202—203°, is derived similarly from 1 : 3-diphenylpyrazole-4 : 5-dicarboxylic acid. Esterification of the two dicarboxylic acids with methyl alcohol and hydrogen chloride under identical conditions gives a 70—80% yield of the normal ester with the 3 : 4-dicarboxylic acid and a 10% yield with the 4 : 5-dicarboxylic acid.

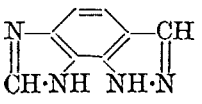
1 : 5-Diphenyl-3-methylpyrazole appears to exist in a second *modification*, m. p. 72°, which represents the stable variety, but is not usually produced. Possibly Knorr and Blank's 1 : 3-diphenyl-5-methylpyrazole, m. p. 47°, is a modification of the substance m. p. 77°.

Ethyl ethylideneacetoacetate, unlike ethyl benzylideneacetoacetate, is converted by phenylhydrazine into a normal hydrazone which yields acetic acid when oxidised by permanganate.

4-Bromo-1 : 3-diphenyl-5-methylpyrazole, m. p. 58—59°, is incidentally described. H. WREN.

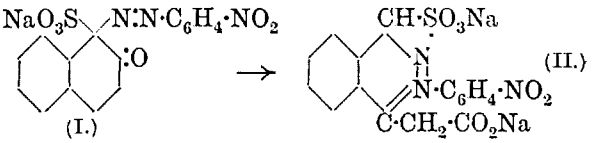
[**Anilino-*o*-nitrophenylacetonitrile.**] A. REISSERT and F. LEMMER (Ber., 1926, **59**, [*B*], 865; cf. this vol., 528).—The previous description of certain indazole derivatives by Heller and Spielmeyer (A., 1925, *i*, 814) has been overlooked. H. WREN.

Comparison of heterocyclic systems with benzene. I. 6 : 7-Indazolequinone-4-sulphonic acid. L. F. FIESER (J. Amer. Chem. Soc., 1926, **48**, 1097—1107).—6-Aminoindazole is obtained in 84% yield by reducing 6-nitroindazole with stannous chloride (cf. Witt, Noelting, and Grandmougin, A., 1891, 312), and affords 6-hydroxyindazole in 74% yield when diazotised and the diazonium sulphate solution boiled in presence of boric acid. When coupled with benzenediazonium chloride, 6-hydroxyindazole affords 6-*hydroxyindazole*-7-*azobenzene*, bright red, m. p. 238°, soluble in alkali, which, on reduction with sodium hyposulphite, affords 7-*amino*-6-*hydroxyindazole*, decomp. about 260° after darkening at about 190° [*monohydrochloride*, $(+H_2O)$; *dihydrochloride*], which is oxidised by atmospheric oxygen or dichromate to 6 : 7-indazolequinone (cf. Fries, A., 1914, i, 584). When treated with concentrated aqueous sodium hydrogen sulphite, the latter is converted into 6 : 7-*dihydroxyindazole*-4-*sulphonic acid*, darkening at 250° (*sodium* salt), and this, on oxidation with sodium nitrite in alcoholic solution, affords sodium 6 : 7-*indazolequinone*-4-*sulphonate*, orange-yellow. Treatment of the latter with aniline in boiling alcohol affords 4-*anilino*-6 : 7-*indazolequinone*, bright red, m. p. 360° (decomp.). Diazotised sulphanilic acid couples with 6-aminoindazole with formation of 6-*aminoindazole*-7-*azobenzene*-4′-*sulphonic acid*, bright red, which, on reduction with stannous chloride, affords 6 : 7-*diaminoindazole monohydrochloride*, rose-coloured. When boiled with formic acid in presence of sodium acetate, the latter yields 6 : 7-*iminazoindazole* (I), m. p. 293°, whilst phenanthraquinone affords similarly 6 : 7-*phenanthrazinoindazole* (1 : 2 : 3 : 12-*indazophenanthrazine*), lemon-yellow, m. p. 364°. The normal reduction potentials of sodium 6 : 7-indazolequinone-4-sulphonate and potassium β-naphthaquinone-4-sulphonate were compared in buffer solutions over a wide range of p_H. The average values obtained, 0·620 and 0·630 volt, respectively, indicate a close relationship between the pyrazole and benzene systems. F. G. WILLSON.



(I.)

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. I. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 4′-nitrobenzene-2-naphthol-1-diazosulphonate. F. M. ROWE, E. LEVIN, A. C. BURNS, J. S. H. DAVIES, and W. TEPPER (J.C.S., 1926, 690—706).—β-Naphthol-1-sulphonic acid condenses with diazonium salts to give stable diazosulphonates (Brit. Pat. 11757/1895, 116360), which are converted by sodium carbonate or sodium hydroxide (1 mol.) into compounds hitherto regarded as diazo-oxides, $SO_3Na{\cdot}C_{10}H_6{\cdot}ON_2Ar$ (Bucherer, A., 1909, i, 193; Wahl and Lantz, *ibid.*, 1923, i, 209), but now considered to be (I). The reaction is limited



(I.) (II.)

to products derived from nitroarylamines or aminoazo-compounds; in other cases, the substance decomposes in the presence of excess of sodium hydroxide, giving the ordinary arylazo-β-naphthol. Derivatives of β-naphthol other than the 1-sulphonic acid do not show the new reaction. Sodium 4′-nitrobenzene-2-naphthol-1-diazosulphonate, obtained by coupling sodium β-naphthol-1-sulphonate with diazotised *p*-nitroaniline, dissolves in sodium carbonate solution and *sodium* 4′-*nitrobenzene*-1-*azo*-β-*naphthaquinone*-1-*sulphonate* [sodium 4′-nitrobenzene-1-azo-2-keto-1 : 2-dihydronaphthalene-1-sulphonate] separates on keeping the solution. When the solution is added at once to excess of aqueous sodium hydroxide, kept over-night, and then acidified, *monosodium* 3-p-*nitrophenyl*-1 : 3-*dihydrophthalazine*-4-*acetate*-1-*sulphonate* (cf. II) is precipitated in 91·5% yield, an intermediate compound being probably first formed by opening of the naphthalene ring (cf. Werner and Piguet, A., 1905, i, 66). The dihydrophthalazine dyes wool a greenish-yellow shade, fugitive to light. When boiled with aqueous hydrochloric or sulphuric acid, it is hydrolysed to 1-*hydroxy*-3-p-*nitrophenyl*-1 : 3-*dihydrophthalazine*-4-*acetic acid*, m. p. 241° [*silver* and *barium* salts described; *methyl* ester, m. p. 153°; *ethyl* ester, m. p. 180° (crystallographic data by H. E. Buckley); *acetate*, m. p. 212°; *anilide*, m. p. 190—192°], which on oxidation with chromic acid gives a *substance*, m. p. 247°. The hydroxy-compound, when reduced with sodium hyposulphite, takes up eight atoms of hydrogen and yields 1-*hydroxy*-3-p-*aminophenyltetrahydrophthalazine*-4-*acetic acid*, m. p. 239° (sodium salt and impure *acetate*, m. p. 266°, described), which is oxidised by chromic acid to a *substance*, m. p. 276°. The tetrahydro-compound is converted by boiling concentrated hydrochloric acid or 25—30% sulphuric acid into 3-p-*aminophenylphthalaz*-4-*one*, m. p. 259° (*hydrochloride*, and *acetyl* derivative, m. p. 348°, prepared), oxidisable to phthalic acid and benzoquinone. Vigorous reduction of the phthalazone with zinc dust and hydrochloric acid gives 4-*amino*-N-*phenylphthalimidine*, m. p. 198° (*sulphate*, *hydrochloride*, *zinc double chloride*, and *acetyl* derivative, m. p. 196°, were prepared), which is converted by diazotisation etc. into *N*-phenylphthalimidine, m. p. 160°, and 4-*hydroxy*-N-*phenylphthalimidine*, m. p. 228° (*methyl ether*, m. p. 134°; *ethyl ether*, m. p. 148°); or by oxidation into phthalimide and benzoquinone.

For purposes of comparison, an *N*-arylimino-derivative of *iso*quinoline was synthesised by the following series of reactions. The δ-lactone of

o-carboxyphenylglyceric acid (Zincke and Scharfenberg, A., 1892, 1232), m. p. 202—203°, is converted by hot concentrated hydrochloric acid into *iso*coumarin-3-carboxylic acid, m. p. 238—239°, which when boiled with *p*-nitrophenylhydrazine yields the p-*nitrophenylhydrazide* of o-*carboxy*-α-*hydroxycinnamic acid*, $NO_2 \cdot C_6H_4 \cdot NH \cdot NH \cdot CO \cdot C_6H_4 \cdot CH{:}C(OH) \cdot CO_2H$, m. p. 189—190° (decomp.). This is cyclised by the action of phosphorus trichloride in hot toluene to N-p-*nitrophenyliminoisocarbostyril*-3-*carboxylic acid*, $C_6H_4 < \begin{matrix} CO \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2 \\ | \\ CH{:}C \cdot CO_2H \end{matrix}$, m. p. 287° (decomp.), which may also be obtained from *iso*coumarin-3-carboxylic acid, *p*-nitrophenylhydrazine, and phosphorus trichloride in boiling toluene. Unlike the 1-hydroxy-3-*p*-nitrophenyl-1 : 3-dihydrophthalazine-4-acetic acid, it is not esterified easily nor convertible into an anilide. It gives on reduction with sodium hyposulphite an *amino-acid*, m. p. 265°, and no trace of *p*-phenylenediamine. C. HOLLINS.

Condensation of salicylamide with aliphatic aldehydes containing a branched carbon chain. V. MOUCKA and C. RÖGL (Ber., 1926, **59**, [*B*], 756—762; cf. Titherley, J.C.S., 1907, **91**, 1429; Keane and Nicholls, *ibid.*, 264; Hicks, *ibid.*, 1910, **97**, 1032).—2-iso*Propyl*-1 : 3-*benzoxazone*, $C_6H_4 < \begin{matrix} CO \cdot NH \\ | \\ O—CHPr^{\beta} \end{matrix}$, m. p. 105·5—106·5°, is prepared by treating a mixture of salicylamide and *iso*butaldehyde with hydrogen chloride. Under similar conditions, *iso*valeraldehyde (b. p. 90—94°) gives 2-iso*butyl*-1 : 3-*benzoxazone*, m. p. 99—99·5°, in 70—75% yield. 2-*iso*Propyl-1 : 3-benzoxazone is converted by sodium hydroxide in aqueous pyridine into syn-iso*butylidenesalicylamide* (cf. I), m. p. 152—160°, which passes at 150—160° into 2-*iso*propyl-1 : 3-benzoxazone. syn-γ-*Methylbutylidenesalicylamide*, m. p. 153—159°, resembles the lower homologue. *iso*Butaldehyde, salicylamide, and sodium acetate at 140—160° afford anti-iso*butylidenesalicylamide* (cf.

(I.) $C_6H_4 < \begin{matrix} CO \cdot N{:}CH \\ | \\ OH \end{matrix}$ (R) $\qquad C_6H_4 < \begin{matrix} CO \cdot N{:}CH \\ | \quad | \\ OH \quad R \end{matrix}$ (II.)

II), m. p. 145—160°; anti-γ-*methylbutylidenesalicylamide*, m. p. about 130° after softening at 120°, is prepared with greater difficulty owing to resinification of the aldehyde. N-iso*Butyrylsalicylamide*, m. p. 110—111°, is prepared from salicylamide and *iso*butyryl chloride or by the oxidation of 2-*iso*propyl-1 : 3-benzoxazone with chromium trioxide in glacial acetic and concentrated sulphuric acids. N-iso*Valerylsalicylamide*, m. p. 126—126·5°, is obtained by similar methods. H. WREN.

Odour and chemical constitution in the benzthiazoles. M. T. BOGERT and A. STULL.—See B., 1926, 384.

Bromination of some 5-substituted 1-phenylbenzthiazoles. R. F. HUNTER (J.C.S., 1926, 537—541).—The close relation between the nitrogen atom and the 5-(*para*)carbon atom in 1-phenylbenzthiazoles, as shown, for example, in the migration of bromine from the nitrogen to the 5-position (Bogert and Abrahamson, A., 1922, i, 576), is further manifested in the influence of substituent groups in that position on the unsaturation of the nitrogen atom (and hence by alternation of affinity on that of the sulphur atom). The depression of unsaturation is greatest for a 5-nitro-group, less for bromo- and least for amino-.

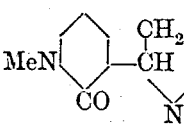
1-Phenylbenzthiazole, m. p. 114°, prepared from benzylideneaniline by Bogert and Abrahamson's method (*loc. cit.*), yields by bromination in chloroform two forms of the *tetrabromide*, m. p. 126° and 153°, respectively (both decomp.). 5-Nitro-1-phenylbenzthiazole, m. p. 188°, obtained by direct nitration, is recovered unchanged after treatment with bromine in acetic acid, but in chloroform gives with difficulty an unstable *dibromide*, m. p. 144° (softens 120°). 5-Bromo-1-phenylbenzthiazole forms a very unstable *tetrabromide*, m. p. 206—208° (decomp.), and a *tribromide*, m. p. 208° (decomp.). From 5-amino-1-phenylbenzthiazole (benzylidene derivative, m. p. 151°), prepared by reduction of the nitro-compound, there are readily obtained a brown *tetrabromide*, m. p. 216°, and a red *tetrabromide*, m. p. 201—211°, both stable. The red isomeride is converted by boiling dilute acetic acid into an impure *dibromo*-substitution product, which softens at 170°. C. HOLLINS.

Halogenation of 2 : 6-dimethylbenzbisthiazole and of 3 : 5-diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole. R. F. HUNTER (J.C.S., 1926, 533—537).—The mutual saturation of the nitrogen atoms in bisbenzthiazole, $C_6H_4 < \begin{matrix} S \\ N \end{matrix} > C \cdot C < \begin{matrix} S \\ N \end{matrix} > C_6H_4$, renders the tetrabromide very unstable (A., 1925, i, 987). In 2 : 6-dimethylbenzbisthiazole (Edge, J.C.S., 1922, **121**, 772), m. p. 105°, this effect is suppressed, but here the result of alternation in affinity in the carbon chain between the two nitrogen atoms is to make one thiazole nucleus much more reactive than the other, as shown in the formation of a moderately stable *hexabromide*, $CMe < \begin{matrix} SBr_2 \\ NBr_2 \end{matrix} > C_6H_2 < \begin{matrix} S \\ NBr_2 \end{matrix} > CMe$, m. p. 117—118° (decomp.), and a monomethiodide (Edge, *loc. cit.*).

3 : 5-Diphenylimino-2 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole, m. p. 136°, prepared by Hugershoff's method (A., 1903, i, 865) from 5-diphenylthiocarbamide, yields an *octabromide*, m. p. 103—105°, which loses bromine and hydrogen bromide on long boiling in acetic acid, giving an impure bromo-substitution derivative, m. p. 200°. It is converted by iodine in acetic acid into a *hexaiodide*, m. p. 122° (decomp.). The formation of these compounds is in accordance with the views already expressed.

C. HOLLINS.

Nicotones. P. KARRER and T. TAKAHASHI (Helv. Chim. Acta, 1926, **9**, 458—461; cf. A., 1925, i, 1084).—The *N*-methylnicotone obtained by treatment of nicotine-*Py*-methiodide (A., 1898, i, 50) with alkaline potassium ferricyanide has the formula appended, since treatment with phosphorus pentachloride yields 2-*chloronicotine*, b. p. 140—145°/75 mm., 108—112°/0·5 mm., $[\alpha]_D^{20}$ —129·7° (in



alcohol —119·2°), oxidised by potassium permanganate to 2-chloropyridine-3-carboxylic acid. *Nicotine*-Py-*ethiodide hydriodide*, m. p. 166°, *nicotine*-Py-*propiodide hydriodide*, m. p. 104—105°, and *nicotine*-Py-*butiodide hydriodide*, m. p. 92—93°, are converted by alkaline ferricyanide into N-*ethylnicotone*, m. p. 110°, b. p. 155—160°/4 mm., $[\alpha]_D^{20}$ in water —54·35°; N-*propylnicotone*, m. p. 95—96°, b. p. 140—145°/3 mm., $[\alpha]_D^{20}$ in water —48·5°, and N-*butylnicotone*, b. p. 155—160°/2 mm., $[\alpha]_D^{20}$ in water —50·78°, respectively. The toxicity for warm-blooded animals of the alkylnicotones is less than that of nicotine. They fail to give the marked increase of blood-pressure characteristic of the last-named substance. M. CLARK.

Derivatives of dihydronicotine. P. KARRER and A. WIDMER (Helv. Chim. Acta, 1926, **9**, 461—463).—Nicotine-*Py*-methiodide reacts with magnesium alkyl compounds to give small yields of *N*-alkyl-2(6)-alkyldihydronicotines. These compounds are unstable in air. They produce in dogs paralysis of the respiratory centre, accompanied by a lowering of the blood pressure, which becomes more marked in ascending members of the series. The following are described: N-*methyl-methyldihydronicotine*, b. p. 99—100°/2 mm.; N-*methyl-ethyldihydronicotine*, b. p. 102—103°/2 mm.; N-*methyl-propyldihydronicotine*, b. p. 112—113°/1 mm.; N-*methyl-butyldihydronicotine*, b. p. 121—122°/2 mm. M. CLARK.

Rotation of quinine and its salts. N. SCHOOREL (Pharm. Weekblad, 1926, **63**, 469—483).—The rotation of quinine reaches a maximum in presence of 2·4 mols. of hydrogen chloride, and the most suitable solution for the examination is one containing 2 millimols. each of the alkaloid, sulphuric acid, and hydrogen chloride. The specified limits of rotation for such a solution are fulfilled by preparations containing 11·5% of hydroquinine, 5·8% of cinchonidine, 1·1% of cinchonine, or 1% of quinidine. It is pointed out in an additional note by P. VAN DER WIELEN that the rotation test is of little help in determining purity of commercial preparations, but that the chromate test, which is much more sensitive, should be specified. S. I. LEVY.

Preparation of codeinone. E. MERCK.—See B., 1926, 386.

Oxyacanthine. J. GADAMER and W. VON BRUCHHAUSEN (Arch. Pharm., 1926, **264**, 193—210).—The results of this incomplete, independent investigation amplify those of Späth and Kolbe (this vol., 82). Repeated analyses fail to determine whether the alkaloid (m. p. 208—209°, $[\alpha]_D^{20}$ +279° in chloroform) has the composition $C_{38}H_{42}O_6N_2$, *i.e.*, double that given by Pommerehne (A., 1896, i, 66), or $C_{37}H_{40}O_6N_2$, assigned to it by Späth and Kolbe. The "doubled" formula is confirmed by cryoscopic and ebullioscopic mol. wt. determinations. It is again proved that three methoxyl groups are present and that one of the remaining oxygen atoms is phenolic. The o-(mono)-*benzoyl* derivative (decomp. 135—140°; $[\alpha]_D$ +90·5°; the *hydrochloride* and *chloroaurate* are described and the *methyl ether* (*hydrochloride*, *hydrobromide*) have been prepared. The function of the remaining two oxygen atoms remains obscure, but it is suggested that they may be present as ether linkings. The two nitrogen atoms, which are present as methylimino-groups, differ in basicity; a *monohydrochloride*, $C_{38}H_{42}O_6N_2$,HCl(?), which yields a *methiodide*, is described. Benzoylation by the Schotten–Baumann method produces an amorphous *dibenzoyl* derivative (decomp. 120—130°; $[\alpha]_D$ +20·6°; *hydrochloride* described); this result suggests that one methylimino-ring is disrupted. Both rings appear to be broken when the alkaloid is treated with boiling acetic anhydride (cf. Pommerehne, *loc. cit.*) for the amorphous *tetra-acetyl* derivative [m. p. 110—112° (decomp.); $[\alpha]_D$ —45°] so obtained is no longer basic. Cold acetic anhydride, on the other hand, yields an oily *mono-* or *di-acetyl* derivative ($[\alpha]_D$ —13·5°) which, from the composition of its *chloroaurate*, is either a diacid base or a mixture. Ethyl chloroformate also causes scission of the *N*-rings, an amorphous, non-basic, feebly *l*-rotatory (?) *di*-N-*carbethoxy*-derivative being formed. The dimethiodide (decomp. 250°) of the alkaloid yields, *via* the methochloride, two *methine* bases, viz., "A," $C_{40}H_{48}O_7N_2$ or $C_{40}H_{50}O_8N_2$, m. p. 212°, $[\alpha]_D$ +65°, and "B," amorphous and *l*-rotatory (*chloroaurate*; *diacetyl* derivative, m. p. about 121°, $[\alpha]_D$ +100°, and its *chloroaurate*). The *methiodide* of methine base "A," after conversion into the methochloride and treatment with hot methyl-alcoholic potassium hydroxide, breaks down into trimethylamine and a *compound*, $C_{36}H_{34}O_7$(?) (sinters at 215°, but does not melt completely; $[\alpha]_D$ + 153·7° or 155° in alcohol or chloroform, respectively), which is oxidised, but not readily, by potassium permanganate to an acidic *compound*. In cold aqueous solution, oxidation of oxyacanthine with mercuric acetate continues for 8 months, yielding ultimately an amorphous intractable *compound*. Apparently the oxidation involves the removal of four hydrogen and the addition of two oxygen atoms.

No definite conclusions as to the structure of the alkaloid are reached, but its possible kinship with *iso*chondendrine is pointed out, and it is suggested that two *iso*chondendrine-like groupings may be united by methylenedioxy-linkings.

W. A. SILVESTER.

***N*-Acyl derivatives of 3-amino-4-hydroxyphenylarsinic acid.** G. W. RAIZISS and B. C. FISHER (J. Amer. Chem. Soc., 1926, **48**, 1323—1327).—3-Amino-4-hydroxyphenylarsinic acid (cf. Raiziss and Gavron, A., 1921, i, 370) forms pale brown prisms when crystallised from water in an atmosphere of nitrogen. Its *N*-acyl derivatives are prepared by the action of the appropriate acid anhydrides on the arsinic acid in aqueous suspension. The following are described: 3-*formamido*-4-*hydroxyphenylarsinic acid*, decomp. when heated, m. p. not below 275°, obtained by boiling the arsinic acid with 85% formic acid [*sodium* salt (+7H_2O)]; 3-acetamido-4-hydroxyphenylarsinic acid ("Stovarsol," cf. U.S.P. 1077462/1913; Raiziss and Gavron, *loc. cit.*; Christiansen, A. 1922, i, 1202), m. p. 240—250° (decomp.) [*sodium* salt (+4H_2O), m. p. about 210° (decomp.)]; 3-*propionamido*-4-*hydroxyphenylarsinic acid* (+1H_2O),

m. p. 228—229° (decomp.) [*sodium* salt (+$2H_2O$)]; 3-*butyramido*-4-*hydroxyphenylarsinic acid*, m. p. 218—219° (decomp.) [*sodium* salt (+$10H_2O$)]; and 3-*chloroacetamido*-4-*hydroxyphenylarsinic acid*, m. p. 238—239° (decomp.) after darkening at 230° [*sodium* salt (+$8H_2O$)]. F. G. WILLSON.

3 : 4-Diaminophenylarsinic acid and some of its derivatives. W. L. LEWIS and H. E. BENT (J. Amer. Chem. Soc., 1926, **48**, 949—957).—When boiled with ethyl malonate in absolute methyl alcohol, 3 : 4-diaminophenylarsinic acid (cf. Jacobs and Heidelberger, A., 1919, i, 50) affords the corresponding *malonyl* derivative, $AsO_3H_2{\cdot}C_6H_3{\cdot}(NH{\cdot}CO{\cdot})_2CH_2$, which, when heated at 139°/10 mm. over phosphorus pentoxide, loses $1H_2O$, with formation of *malonyldiaminophenylarsenic oxide*. Condensation of phthalic anhydride with 3 : 4-diaminophenylarsinic acid yields 3-*amino*-4-*phthalylaminophenylarsinic acid*, m. p. not below 260°. Both the latter and arsanilic acid also lose $1H_2O$ when dried as above (cf. Mann and Pope, J.C.S., 1922, **121**, 1755). That the dehydration takes place from the arsinic group is indicated by the fact that the magnesium salts are unaffected by similar treatment, whilst 3 : 4-*di*-(NN'-*dimethylamino*)*phenylarsinic acid*, obtained by boiling 3 : 4-diaminophenylarsinic acid with methyl alcohol in presence of hydrochloric acid, also loses $1H_2O$ analogously, showing that an amino-group is not involved. 3 : 4-Diaminophenylarsinic acid, which, when dried over calcium chloride at 20°, contains $0{\cdot}5H_2O$, loses $2H_2O$ over phosphorus pentoxide at 140°/10 mm.

The following acylamino-derivatives of phenylarsinic acid, obtained by treating arsanilic and 3 : 4-diaminophenylarsinic acids, respectively, in alkaline solution with the appropriate acyl chlorides, are described: 4-*chloroacetamidophenylarsinic acid*, m. p. not below 260°; 4-*valeramido*-; 4-*phenylacetamido*-; 3-*amino*-4-*acetamido*-, m. p. 265—267°; 3-*amino*-4-*propionamido*-, m. p. 230—235°; 3 : 4-*divaleramido*-; 3 : 4-*di*-*chloroacetamido*-; 3 : 4-*di*-*phenylacetamido*-; 3 : 4-*dibenzamido*-; 3 : 4-*diphthalamido*-; 4-*carbopropoxyamino*-; 4-*carbobutoxyamino*-; 3 : 4-*dicarbethoxyamino*-, m. p. 192—192·5°; 3 : 4-*dicarbopropoxyamino*-, decomp. 249—253°; and 3 : 4-*dicarbobutoxyamino*-*phenylarsinic acid*, decomp. 185—187°.

Treatment of 3 : 4-diaminophenylarsinic acid in alkaline solution with chloroacetamide affords N-(2-*amino*-4-*arsinophenyl*)*glycylamide*, $AsO_3H_2{\cdot}C_6H_3(NH_2){\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, m. p. 234—241° (decomp.) after darkening at 215°, together with a small proportion of 3-*amino*-6-*arsino*-1 : 2-*dihydroquinoxaline*, m. p. 226° (*ammonium* salt, decomp. 200°; *benzoyl* derivative, m. p. 234°), derived by inner condensation of the amino- and carbonyl groups. The quinoxaline is obtained when the glycylamide is treated with alkali. When treated in alkaline solution at 30° with ethylene oxide, it yields 3-*hydroxyethylamino*-6-*arsino*-1 : 2-*dihydroquinoxaline*. Condensation of 3 : 4-diaminophenylarsinic acid with oxalyl chloride affords 2 : 3-*dihydroxy*-6-*arsinoquinoxaline*, whilst bromomalonamide yields analogously 3-*amino*-2-*carbamido*-6-*arsino*-1 : 2-*dihydroquinoxaline*. When the above glycylamide (aminotryparsamide) is boiled under reflux with sodium formaldehydesulphoxylate, the *compound* $C_{17}H_{21}O_4N_6SAs_2Na$ separates at first, then redissolves, and, by adding the filtered reaction mixture, after 15 hrs., to excess of alcohol, the *arseno*-derivative, $[{\cdot}As{\cdot}C_6H_3(NH{\cdot}CH_2{\cdot}CO{\cdot}NH_2)(NH{\cdot}CH_2{\cdot}O{\cdot}S{\cdot}ONa)]_2$, m. p. not below 260°, is precipitated.

N-4-*Arsinophenylaminomalonamide*, m. p. not below 260°, obtained by condensation of 3 : 4-diaminophenylarsinic acid with bromomalonamide, is described.

F. G. WILLSON.

Manufacture of monoacyl derivatives of aminoarylarseno-compounds. G. NEWBERY, and MAY AND BAKER, LTD.—See B., 1926, 420.

Preparation of homogeneous sodium triphenylboryl and the compounds of triphenylboron with the other alkali metals. E. KRAUSE and H. POLACK (Ber., 1926, **59**, [*B*], 777—785; cf. Krause and Nitsche, A., 1922, i, 694; Krause, *ibid.*, 1924, i, 436).—The necessary apparatus for the preparation of pure triphenylboron from magnesium phenyl bromide and boron fluoride, and its recrystallisation from ether in the absence of air and for its interaction with sodium in the presence of ether, is described in detail. Triphenylboron forms yellow *compounds* of the type BPh_3X, with sodium, potassium, lithium, rubidium, and cæsium. The solubility decreases with increasing atomic weight of the alkali metal. The alkali triphenylboryls retain ether often with great tenacity. *Monoetherates* of the sodium and lithium compounds could be isolated, whereas the remaining substances lose ether too readily. The sodium compound is quantitatively converted by iodine in ethereal solution into triphenylboron and sodium iodide. Removal of the sodium can also be effected by prolonged agitation with a large excess of pure mercury, whereas reaction between an ethereal solution of triphenylboron and mercury amalgam containing more than 2·9% of sodium produces sodium triphenylboryl. Triphenylmethyl chloride and sodium triphenylboryl yield triphenylmethyl and, further, sodium triphenylmethyl; the latter substance is also obtained from sodium triphenylboryl and triphenylmethyl. Triphenylboron and triphenylmethyl yield an intensely red, crystalline *compound*. Sodium triphenylboryl reacts instantaneously with alkyl halides or carbon dioxide. Ethereal solutions of sodium triphenylboryl conduct electricity, but to a less degree than those of sodium triphenylmethyl. Tri*cyclo*hexylboron and tri-*n*-propylboron do not react with sodium, whereas tri-*p*-tolylboron resembles the phenyl derivative.

H. WREN.

Organo-chromium compounds. VII. Products of the action of magnesium *p*-bromophenyl bromide on sublimed chromium chloride. F. HEIN and R. SPÄTE (Ber., 1926, **59**, [*B*], 751—756; cf. A., 1924, i, 437, 889).—The action of a well-cooled ethereal solution of magnesium *p*-bromophenyl bromide on chromium chloride yields a semi-solid product which becomes powdery after being washed repeatedly with water, dilute ammonia, and water. Extraction of this residue with cold alcohol yields *chromium tetra*-p-*bromophenyl bromide*, m. p. 90°

when slowly heated or m. p. 115° (decomp.) when placed in a bath preheated to 110°. From the remainder chloroform dissolves *chromium penta-p-bromotriphenylene bromide*, $Cr(C_6H_4Br{\cdot}C_6H_4{\cdot}C_6H_4)_5Br$, decomp. about 120° after darkening. The remaining material, which is insoluble in all media, appears to contain *chromium di-p-bromotetraphenylene hydroxide*, $Cr[Br(C_6H_4)_4]_2{\cdot}OH$ ($+1CS_2$ acquired during the process of purification). H. WREN.

Mercuration of aromatic compounds and its bearing on substitution in the benzene nucleus. S. COFFEY (Chem. Weekblad, 1926, **23**, 194—196).—A *résumé* and discussion of recent results. S. I. LEVY.

Reactions of mercury diphenyl with some acyl halides. H. O. CALVERY (J. Amer. Chem. Soc., 1926, **48**, 1009—1012).—Ethyl chloroformate is without action on mercury diphenyl at the ordinary temperature. In hot benzene solution, mercury phenyl chloride is produced, and the same result is obtained at 95° or above, both in absence of a solvent and in presence of sodium amalgam. The formation of ethyl benzoate was not observed, indicating that the production of the latter from bromobenzene, sodium amalgam, and ethyl chloroformate (cf. Wurtz, Compt. rend., 1869, **68**, 1298) proceeds thus: $PhBr+2NaHg+Cl{\cdot}CO_2Et = Ph{\cdot}CO_2Et + NaCl + NaBr + Hg$, whilst the mercury diphenyl, which appears as a by-product, is produced thus: $2PhBr+2NaHg = Ph_2Hg+2NaBr+Hg$, and is not an intermediate in the formation of ethyl benzoate. Acetyl chloride and mercury diphenyl, alone or in boiling benzene solution, give mercury phenyl chloride and acetophenone. Benzoyl chloride affords similarly, when heated alone or in hot benzene solution, mercury phenyl chloride and benzophenone. At the ordinary temperature, no reaction takes place in absence of a solvent, whilst at higher temperatures the products are mercuric chloride, mercury phenyl chloride, benzophenone, and probably diphenyl. The solubility of mercury phenyl chloride in alkali (cf. Dreher and Otto, Annalen, 1870, **154**, 126) is confirmed. F. G. WILLSON.

Mercuration of aromatic substances. II. *o*-Nitrotoluene. S. COFFEY (J.C.S., 1926, 637—643).—Mercuration readily occurs when *o*-nitrotoluene is heated with mercuric acetate at 140°, and after conversion of the acetomercuri-compounds into chloromercuri-derivatives, 4-*chloromercuri*-2-*nitrotoluene*, m. p. 220·5—221° (corr.), is obtained. The constitution is proved by quantitative conversion of the product into 4-bromo-2-nitrotoluene, m. p. 44·5—45°, and 4-iodo-2-nitrotoluene, m. p. 60·5—61°. 4-*Bromomercuri*-2-*nitrotoluene*, m. p. 241° (corr.), and 4-*iodomercuri*-2-*nitrotoluene*, m. p. 286° (slight decomp.), are obtained from the chloromercuri-compound by the action of potassium bromide and iodide, respectively. Reduction with sodium sulphide converts the chloro-compound into 4-*mercuribis*-2-*nitrotoluene*, m. p. 291°, which quantitatively reverts to the chloro-compound when boiled with mercuric chloride.

In the mercurated nitrotoluenes obtained in the process described above, the presence of 6-*chloromercuri*-2-*nitrotoluene* and of the 3- or 5-*isomeride* is demonstrated by conversion into a mixture of bromonitrotoluenes and reduction of these to bromo-*o*-toluidines; fractional crystallisation of the acetyl derivatives gives pure 6-bromoaceto-*o*-toluidide, m. p. 162—163°, whilst removal of the amino-group followed by oxidation gives a mixture of acids from which *m*-bromobenzoic acid, m. p. 154°, may be isolated.

5-*Chloromercuri*-2-*nitrotoluene*, m. p. 210°, is synthesised by the following method. 2-*Nitrotoluene*-5-*sulphon*-*o*-*nitrotolylhydrazide*, m. p. 157—158° (violent decomp.), prepared from 6-nitro-*m*-toluidine by the action of sulphur dioxide and nitrous acid (cf. Limpricht, A., 1887, 723), is boiled with baryta solution, and the resulting 2-*nitrotoluene*-5-*sulphinic acid* (isolated as *ferric* salt) is converted by prolonged boiling with mercuric chloride into the 5-chloromercuri-compound. By a similar series of reactions, the 4-isomeride is synthesised from 2-nitro-*p*-toluidine; 2-*nitrotoluene*-4-*sulphinic acid* has m. p. 95°. C. HOLLINS.

Mercurated hydroxyazobenzenes. F. C. WHITMORE, E. R. HANSON, and G. J. LEUCK (J. Amer. Chem. Soc., 1926, **48**, 1013—1016).—*Sodium* 4-*hydroxy*-3-*chloromercuri-azobenzene*-4′-*sulphonate*, orange-yellow, is obtained by coupling diazotised sulphanilic acid with *o*-hydroxyphenylmercurichloride in cold alkaline solution, followed by acidification with acetic acid. The free acid could not be prepared, on account of the ease with which the mercury is eliminated. Analogous *sodium* salts were prepared similarly from metanilic and naphthionic acids, and the free acids were isolated in the case of analogous *compounds* prepared from anthranilic and *m*- and *p*-aminobenzoic acids, colours in all cases being yellow to red. Similar condensation of diazotised sulphanilic acid with 2 : 6-diacetoxymercuri-*p*-cresol affords *sodium anhydro*-2-*hydroxy*-5-*methyl*-3-*hydroxymercuri-azobenzene*-4′-*sulphonate*, yellow, from which neither the free acid nor a chloride could be obtained. *Anhydro*-2-*hydroxy*-5-*methyl*-3-*hydroxymercuri*-*azobenzene*-2′-*carboxylic acid*, deep red, and -4′-*carboxylic acid*, obtained analogously, are described. Definite compounds could not be obtained similarly from metanilic, *m*-aminobenzoic, and naphthionic acids. All the above compounds undergo fission at the carbon–mercury linking when treated with hot *N*-hydrochloric acid or hot aqueous sodium iodide, whilst their toxicities are practically the same as those of the parent mercury compounds. F. G. WILLSON.

Phenyltin compounds. R. F. CHAMBERS and P. C. SCHERER (J. Amer. Chem. Soc., 1926, **48**, 1054—1062).—Tin tetraphenyl is obtained in 91% yield by the action of zinc diphenyl (from magnesium phenyl bromide and zinc chloride in ether) on stannic chloride in boiling toluene in an atmosphere of nitrogen. It reacts with iodine in chloroform with formation of tin triphenyl iodide (cf. Polis, A., 1890, 166). When treated with sodium in liquid ammonia, tin triphenyl bromide affords *sodium triphenylstannide*, pale yellow, amorphous, which reacts with oxygen in the same solvent with formation of hydroxytriphenylstannane. The latter is decomposed by

heating into tin tetraphenyl and diphenyltin oxide. Sodium triphenylstannide reacts with organic halides with formation of the corresponding sodium halides, but substitution by the triphenyltin group does not generally occur. Sodium *p*-bromobenzoate appears in this way to form triphenyltin-benzoic acid, but the product is readily hydrolysed. Reaction between sodium triphenylstannide and phenylmercuric iodide in liquid ammonia affords *phenylmercuric amine*, $PhHgNH_2$, m. p. 123·5—124°, which was also prepared by the action of phenylmercuric iodide on potassamide in the same solvent. Condensation of sodium triphenylstannide and sodium monochloroacetate yields similarly *triphenyltin-acetic acid*, $SnPh_3 \cdot CH_2 \cdot CO_2H$, m. p. 122—122·5°. The *sodium* salt is hydrolysed in aqueous solution. Triphenyltin hydride (triphenylstannane), obtained by the action of ammonium bromide on sodium triphenylstannide in liquid ammonia (cf. Foster, Master's Thesis, Clark Univ., 1923), is a colourless liquid, b. p. 173—174°/6 mm., which is decomposed in contact with oxygen with formation of tin triphenyl, whilst the action of sodium in liquid ammonia affords sodium triphenylstannide. Tin diphenyl is obtained as a bright yellow *polymeride*, decomp. 206° (cf. Krause and Becker, A., 1920, i, 340), by the action of sodium on diphenyltin dichloride in liquid ammonia. The action of sodium on diphenyltin dibromide in liquid ammonia affords *disodium diphenylstannide*, which, on treatment with ammonium bromide in the same solvent, is converted into *diphenyltin dihydride*, dark brown. When the latter is freed from ammonia in presence of absolute ether, it decomposes with production of tin diphenyl in unpolymerised condition. Tin tetraphenyl reacts with sodium in liquid ammonia with formation of sodium triphenylstannide, and the latter is converted, by the further action of sodium, into disodium diphenylstannide. F. G. Willson.

Structural isomerism of 2 : 5-diketopiperazines and polypeptides. E. Abderhalden and E. Schwab (Z. physiol. Chem., 1926, **152**, 88—94).—By hydrolysis of the enol form of 2 : 5-diketopiperazines, it is possible to obtain the dipeptide also in the enol form. In the case of glycine anhydride, the enolised form is the more readily hydrolysed. Proteins like silk fibroin and keratin, which are very resistant to hydrolysis, probably contain their anhydride linkings in the stable form, whereas the relatively easily hydrolysed proteins of the foodstuffs contain mainly the more reactive enol and half-enolised rings. It is possible that such compounds may be taken up from the intestine without complete breakdown to amino-acids, and may be the starting point for the synthesis of various cyclic compounds required by the organism. The enol form of glycine anhydride is converted into the stable form by heating to 90—100°. This observation may have importance in connexion with the denaturation of proteins. H. D. Kay.

Proline. E. Abderhalden and H. Sickel (Z. physiol. Chem., 1926, **152**, 95—100).—Proline may be esterified almost quantitatively by passing hydrogen chloride into its alcoholic solution and removing the solvent and catalyst in a vacuum. The hydrochloride of the ester is stable in a vacuum at 120° and is not decomposed by organic solvents. Even in aqueous solution it is not easily hydrolysed. The free ester, on the other hand, is readily decomposed at the ordinary temperature by traces of water. It does not readily form polypeptides or anhydrides, but proline anhydride has been isolated in small yield. H. D. Kay.

Determination of active hydrogen in hæmin, bilirubin, in some of their derivatives, and in pyrroles. H. Fischer and J. J. Postowsky (Z. physiol. Chem., 1926, **152**, 300—312).—The number of atoms of active hydrogen per molecule of the following substances has been determined by the Zerewitinov method (A., 1907, ii, 509; 1908, i, 593; 1911, i, 101), Flaschenträger modification (A., 1925, ii, 999), with a view to confirm their structural formulæ. Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate contains two active hydrogen atoms; bis-(2 : 4-dimethyl-3-ethylpyrryl)methene, one; bis-(3-carbethoxy-4 : 5-dimethylpyrryl)methane, two; tetra-(4-carbethoxy-2 : 3-dimethylpyrryl)ethane, four; tetra-(2 : 3-dimethylpyrryl)-5-ethane, four; bilirubinic acid, four; xanthobilirubinic acid, three; its ester, two; the condensation product of benzaldehyde with bilirubinic acid (see A., 1925, i, 1198), four; its reduction product, three. All the above numbers agree with the requirements of the authors' structural formulæ. Bis-(3-carbethoxy-2 : 4-dimethylpyrryl)-methene gave a value indicating the presence of two active hydrogens instead of one, but this was due to its decomposition into ethyl 2 : 4-dimethylpyrrole-3-carboxylate. In agreement with the authors' formula, bilirubin and mesobilirubin contain seven, and mesobilirubinogen eight active hydrogens (Küster's formula, however, would require only five). Hæmin, according to the formula of Willstätter and Küster, should contain two active hydrogens. Experiment gives, for hæmin, three; for mesohæmin in the cold, two; at 40°, three, and hæmin ester, one active hydrogen. Assuming that the chlorine, which in hæmin is combined with the iron, reacts with the Grignard reagent liberating methyl chloride, the above figures agree fairly well with theory. Ooporphyrin and Kämmerer's porphyrin contain four, ætioporphyrin, uroporphyrin ester, coproporphyrin ester, and tetramethylhæmatoporphyrin each contain two, and mesoporphyrinogen six active hydrogens. P. W. Clutterbuck.

Proteins. III. Constitution of proteins. P. Brigl and R. Held (Z. physiol. Chem., 1926, **152**, 230—248).—The O : N ratio for a number of proteins is as high as 1·28, a value which neither the peptide nor diketopiperazine structures can explain. The high oxygen value cannot be due to the presence of dibasic acids, since the free carboxyl groups are present as amide groupings, nor is it due entirely to the presence of an amount of the difficultly isolable hydroxy-amino-acids greater than previously suspected. It is suggested that protein is composed of a number of parallel polypeptide chains, the terminal amino-groups being united together through a carbonyl group (thus forming a carbamide structure), and the terminal carboxyl groups through a poly-

hydric alcohol. The idea is tested by studying the action of phthalic anhydride, sodium hypobromite, pepsin, and trypsin on diethyl carbonyldiglycylglycine and on the free acid. Phthalic anhydride with the ester readily gave ethyl phthalylglycylglycine. Hypobromite did not react with the ester, owing to its insolubility, but readily reacted at 0° with the acid. Neither the acid nor the ester, however, dissolved in pepsin or trypsin. This must not be regarded as definitely negativing the idea, since Fischer showed that ability of trypsin to attack the polypeptide depended on its structure. The action of pepsin on a number of such carbonyl polypeptide structures must first be studied (cf. A., 1923, ii, 1143; 1924, i, 105). P. W. CLUTTERBUCK.

Transformations of peptide-like substances. VII. Transformation of a cystine-containing diketopiperazine. M. BERGMANN and F. STATHER (Z. physiol. Chem., 1926, **152**, 189—201).—By the union of *l*-cystine (1 mol.) and *dl*-alanine (2 mols.), dialanyl-*l*-cystine is obtained which readily gives a *dianhydride*, $C_{12}H_{18}O_4N_4S_2$, m. p. not below 350°, having two diketopiperazine rings united together by the sulphur bridge of the cystine molecule. This dianhydride, when treated in the cold with sodium hydroxide, quickly loses hydrogen sulphide and sulphur, to give a protein-like substance identical with the polymerised form of 2 : 5-diketo-6-methyl-3-methylenepiperazine previously obtained from the diketopiperazine of alanylserine (cf. Bergmann and others, A., 1925, i, 1474). Identity is established by preparation of the crystalline disodium compound, of the diacetate, m. p. 144—145°, by hydrolysis with hydrochloric acid, giving a chlorotetrapeptide, by mol. wt. determination, and also by catalytic reduction to alanine anhydride. The latter reaction indicates a means of conversion of cystine into alanine *via* the diketopiperazine. Dialanylcystine loses no hydrogen sulphide under conditions in which the corresponding diketopiperazine loses 71% of its sulphur as hydrogen sulphide, thus forming the polymeride, a product completely free from sulphur, but containing the carbon–nitrogen framework of cystine unchanged. P. W. CLUTTERBUCK.

Porphyrins from blood pigment. IV. Constitution of porphyrins. A. PAPENDIECK (Z. physiol. Chem., 1926, **152**, 215—229).—The author's methods of electrolytic reduction and catalytic hydrogenation (A., 1925, i, 711) are applied to the reduction in acid solution of α-hæmatoporphyroidin (hæmaterindicarboxylic acid), hæmatoporphyrin (Nencki, A., 1888, 971), and of hæmoporphyrin, which give, respectively, by addition of hydrogen, mesoporphyrin, hydroxymesoporphyrin, and mesoporphyrin, identification being carried out spectroscopically. The bearing of these results on the constitution of porphyrins is discussed, particularly in respect to the work of Willstätter, Küster, and Fischer (cf. A., 1925, i, 992).

P. W. CLUTTERBUCK.

Binding of acid and alkali by proteins. R. A. GORTNER and W. F. HOFFMAN (Science, 1925, **62**, 464—467).—Experiments with twelve prolamines, casein, and fibrin show that approximately equivalent amounts of hydrochloric, sulphuric, and phosphoric (*M*) acid are bound by a unit amount of protein when the acids are compared on the normality basis. Two types of combination between proteins and acid or alkali are postulated: (*a*) chemical, at p_H 2·5—10·5, (*b*) adsorption, when $p_H<2{\cdot}5$ or $>10{\cdot}5$. It is concluded that the chemical nature of a protein and the power of a protein to bind acid and alkali in stoicheiometrical relationships depend on the chemical groups within the protein molecule and are therefore limited to the range p_H 2·5—10·5.

A. A. ELDRIDGE.

Effect of p_H and of temperature on hydrolysis of caseinogen. D. C. CARPENTER (J. Biol. Chem., 1926, **67**, 647—658).—At 5° no measurable hydrolysis of caseinogen in 1% solution (as determined by increase in free amino-nitrogen) occurs within the range p_H 1—10 over periods of 6 days. At higher temperatures, the rate of hydrolysis, on the acid side of the isoelectric point, bears a simple relation to the p_H; on the alkaline side of the isoelectric point, the relations are more complex, a sudden increase in the rate of hydrolysis occurring as the solution becomes more alkaline than p_H 9. C. R. HARINGTON.

Membrane hydrolysis of neutral sodium caseinogenate. W. STARLINGER (Biochem. Z., 1926, **170**, 1—17).—Neutral solutions of sodium caseinogenate, prepared by electrodialysis and preserved under toluene, exhibited no changes in conductivity or in non-coagulable nitrogen over a period of several months. When submitted to dialysis, there was only a slight increase in the total electrical conductivity, whereas there was an increase, in the dialysate, of the concentration of hydroxyl ions together with the appearance of sodium and of nitrogen, both coagulable and non-coagulable. The increase in c_H of the dialysate was insufficient to account for the sodium present. These results are discussed in relation to the observations of Pólányi (A., 1925, ii, 662) and of Plattner (A., 1923, i, 963) on the significance of the electrical conductivity of caseinogen solutions. R. K. CANNAN.

Alteration of albumins by heat. M. SPIEGEL-ADOLF (Biochem. Z., 1926, **170**, 126—172).—A detailed account is given of the results already published (this vol., 352) on the effects of acid and alkali on heat-coagulated serum-albumin and the properties of the products, particularly in respect of their solubilities and behaviour towards acid, alkali, and neutral salts. The work has been extended to egg-albumin. As with serum-albumin, heat coagulation of solutions of purified egg-albumin is accompanied by a fall in c_H and an increase in electrical conductivity. When the coagulum is dissolved in alkali, and the solution neutralised and submitted to electrodialysis, there results a product having the main characteristics of a globulin. The behaviour of acid– and alkali–egg-albumin towards heat and towards neutral salts is compared with that found in the case of serum-albumin. Suspensions of caseinogen in water, or solutions of its neutral alkali salts, show no change in their solubility in alkali

after heating to boiling. Support is found in these results for the view that the heat coagulation of proteins is connected with the closing of rings between the free groups of the protein. R. K. CANNAN.

Determination of halogen in organic compounds by Stepanoff's method. C. F. VAN DUIN (Rec. trav. chim., 1926, **45**, 363).—Correct results may be obtained in the determination of bromine in substituted αβ-dibromophenylpropionic acids by Stépanoff's method (cf. A., 1905, i, 335) if fifty times the calculated quantity of sodium is employed, and the solution refluxed over a free flame, a temperature above 100° being necessary. J. W. BAKER.

Kjeldahl-Pregl method applied to nitro-compounds. A. ELEK and H. SOBOTKA (J. Amer. Chem. Soc., 1926, **48**, 501—503).—The Kjeldahl method for the determination of nitrogen gives satisfactory results with nitro-compounds if dextrose be added to the reaction mixture in the proportion of 1 g. to 0·1 g. of the substance to be analysed. Equally satisfactory results are obtained with dextrose when using Pregl's method of microanalysis.
F. G. WILLSON.

Determination of alcohols. II. Determination of ethyl alcohol and its homologues and their separation from other substances. W. M. FISCHER and A. SCHMIDT (Ber., 1926, **59**, [*B*], 679—682; cf. A., 1924, ii, 427).—Simplifications are introduced into the method described previously (*loc. cit.*) by omission of the addition of carbamide, immediate introduction of the total quantity of acetic acid after replacing the air in the apparatus by carbon dioxide, and substitution of a four-bulb apparatus containing concentrated sodium hydrogen carbonate solution for U-tubes containing solid sodium nitrite and sodium hydrogen carbonate, respectively. If results need be accurate only to 98—99%, the operation can be completed in ¾—1 hr. Ethyl, *n*- and *iso*propyl, *iso*butyl, and *iso*amyl alcohols may be thus determined. The method is also accurate in the presence of ether, acetone, or acetaldehyde. It cannot, however, be applied to alcohols of high b. p. such as benzyl alcohol, ethylene glycol, or glycerol. It is adapted for micro-analytical measurements. Cocaine may be determined by hydrolysis with sodium hydroxide in a sealed tube to methyl alcohol, benzoic acid, and ecgonine followed by determination of the liberated methyl alcohol. Attempts to apply the method to the determination of primary amines were unsuccessful, since the preliminary transformation of amine into alcohol by nitrous acid does not appear to be quantitative. H. WREN.

Determination of the *iso*propylidenedioxy-group and reaction of polyhydric alcohols with acetone. I. Derivatives of glycerol. A. GRÜN and R. LIMPÄCHER (Ber., 1926, **59**, [*B*], 695—704).—For the determination of the *iso*propylidenedioxy-group, the substance is hydrolysed with hydrochloric acid and the liberated acetone is determined by addition of alkali hydroxide and 0·1*N*-iodine solution followed by acidification with hydrochloric acid, addition of excess of sodium thiosulphate, and final titration with iodine. Quantitative results are obtained with *iso*propylideneglycerol, α-methoxy-βγ-*iso*propylidenedioxypropane, carbethoxy*iso*propylideneglycerol, *iso*propylideneglyceryl stearate, and *iso*propylideneglyceryl laurate.

*iso*Propylidene derivatives can only be prepared with difficulty in 80% yield from monoglycerides and acetone, and the process in this form is therefore not suitable for establishing the homogeneity of monoglycerides. The degree of "acetonisation" may be determined as follows. The substance (about 0·25 g.) is treated with about one hundred times its amount of a 1% solution of hydrogen chloride in acetone in the presence of anhydrous sodium sulphate at 20—23° or 30—33°. After 2 hrs., the mixture is filtered and the residue washed with hot acetone. The filtrate is shaken with lead carbonate and filtered. After addition of 0·2—0·3 c.c. of *N*-potassium hydroxide, the bulk of the acetone is removed from the filtrate at 45—50° in a current of carbon dioxide; the residue is dissolved in ether, the solution washed with water, and filtered through anhydrous sodium sulphate. The ether is removed at 35° in a current of carbon dioxide. The residue is placed in a vacuum, after which the acetone is determined as described above or by a slightly modified method. Under these conditions, "acetonisation" of homogeneous α-monoglycerides occurs to the extent of 97%; the small deficit is constant and hence amenable to correction. It is due to fission of part of the glyceride by the hydrogen chloride into fatty acid and glycerolchlorohydrin. H. WREN.

Identification of lactic acid and its detection in gastric juices. G. CAPELLI (Annali Chim. Appl., 1925, **16**, 53—68).—The colorimetric tests for lactic acid, depending on the formation of acetaldehyde and subsequent reaction with various phenols, are reviewed and found to be not very trustworthy. Phloroglucinol, as suggested by Denigès, is one of the most sensitive, but *p*-cresol is suggested as being possibly more so. Five c.c. of concentrated sulphuric acid, a drop of lactic acid extract, and 0·01 g. (or 3 drops of a 1% alcoholic solution) of phloroglucinol give a deep yellow orange colour at once, changing to a bright red after heating for 2 min. at 100°, whilst *p*-cresol gives a rose, becoming magenta on heating. Both reagents are sensitive to 1 in 100,000 for lactic acid or 1 in 49,000 for acetaldehyde. A blank test should always be performed, as colorations may be obtained in the absence of any acid. Methods for the isolation and identification of the acid in gastric and other juices are given, depending finally on the usual prolonged and repeated ether extraction of the acid from a concentrated syrup. The acid should always be confirmed by the following tests: (1) formation of zinc lactate and recognition microscopically and chemically, (2) iodoform and carbylamine reactions, (3) colour reactions with concentrated sulphuric acid and phenols, and (4) recognition of carbon monoxide by heating to 100° with sulphuric acid. The detection of acetaldehyde in the juices is not sufficient evidence of lactic acid, and Uffelmann's reaction is stated to be useless.
S. B. TALLANTYRE.

Chemical nature of fats. III. Significance of the difference between the upper iodine value and iodine value of a fat; differential iodine value. B. M. MARGOSCHES and H. FUCHS.—See B., 1926, 371.

Identification and determination of cholesterol and other compounds. J. V. STEINLE and L. KAHLENBERG (J. Biol. Chem., 1926, **67**, 425—467).—The action of antimony pentachloride, alone or dissolved in chloroform, on cholesterol, gives a brown, amorphous *substance*, $C_{27}H_{46}O,SbCl_5$, which dissolves in chloroform to give a blue solution; this reaction has been made the basis of a colorimetric method for the determination of cholesterol, which has been applied successfully to blood. The additive product dissolves also to a small extent in carbon tetrachloride to give a pink, and in alcohol to give a green solution. Phytosterol reacts similarly with antimony pentachloride, but the blue colour does not develop so quickly. The blue colour can be obtained with animal, but not with vegetable oils containing large amounts of unsaturated acids, since the latter give a brown colour with antimony pentachloride. Terpenes in general give colour reactions with antimony pentachloride, a blue colour, similar to that given by cholesterol, being obtained with pinene, limonene, borneol, isoprene, caoutchouc, and some resins.

C. R. HARINGTON.

Determination of tyrosine and histidine in protein and of tyramine in mixtures containing protein. Histidine and tyrosine content of various proteins. M. T. HANKE (J. Biol. Chem., 1925, **66**, 475—488, 489—493).—When heated with mercuric acetate and acetic acid, tyrosine forms an insoluble *compound*, $C_9H_9O_3N,2HgCl$, in which it is assumed that each of the hydrogen atoms of the amino-group is replaced by mercurous chloride; under the same conditions, tyramine forms a similar *compound*. Each of these compounds is quantitatively precipitated from a mixture of amino-acids, so that they may be used for the isolation of either substance from the products of hydrolysis of a protein. In general, the protein is hydrolysed with sulphuric acid and the latter removed with barium hydroxide; the histidine fraction is precipitated with silver sulphate and barium hydroxide and the histidine determined colorimetrically (cf. A., 1920, ii, 67); tyrosine is isolated from the filtrate by the method indicated above, and, after recovery from the mercury compound by decomposition of the latter with hydrogen sulphide, is also determined colorimetrically. Should histamine and tyramine be present, these are first separated by extracting the strongly alkaline solution of the products of hydrolysis with amyl alcohol, and are then separately determined in a similar manner.

The method above described has been applied to the analysis of a number of proteins with respect to their content of histidine and tyrosine.

C. R. HARINGTON.

Tryptophan content of proteins; determination of tryptophan. O. FÜRTH (Biochem. Z., 1926, **169**, 117—119; cf. Tillmans and Alt, this vol., 189).—The yellow primary coloration produced by tryptophan and formaldehyde was noticed previously by Fürth and his collaborators; the figures for tryptophan content of proteins cited by Tillmans and Alt were subsequently modified by Fürth and Dische (A., 1924, ii, 576) as a result of further investigation of the reaction.

C. RIMINGTON.

Biochemistry.

Respiration theory and catalase. O. WARBURG (Ber., 1926, **59**, [*B*], 739—740).—Wieland's observation (A., 1925, ii, 1171) that liver catalase is inactivated by methylcarbylamine has no bearing on the "heavy metal" theory of respiration, since, contrary to Wieland's assumption, carbylamines resemble hydrocyanic acid in their ability to give complex compounds with iron. The absence of parallelism between iron content and activity of catalase (Hennichs, this vol., 432) is also not a refutation of the theory, since activity depends, not merely on the percentage of iron, but also on its manner of combination in the molecule.

H. WREN.

Chemical regulation of respiration. R. GESELL (Science, 1926, **63**, 58—62).—Since respiration can be stopped by accelerating the flow of unchanged blood through the respiratory centre, the metabolism of the respiratory centre itself and the volume flow of blood through it must be considered in explanation of the regulation of respiration. The theory regards the respiratory centre as possessing an acid metabolism of its own, diminished oxidation leading to an accumulation of the relatively poorly diffusible lactic acid in a relatively poorly buffered cytoplasm and lymph, no longer protected by the potential alkalinity of the blood, the dual function being disturbed by the diminution in the reduction of hæmoglobin and the liberation of alkali as it passes through the centre. The respiratory centre is sensitive to minute changes in its own hydrogen-ion concentration, thus in its own oxidations, and hence in the oxygen tension of arterial blood. The effects of lactic and carbonic acids are additive.

A. A. ELDRIDGE.

Respiratory changes during an aeroplane flight to high altitudes. E. C. SCHNEIDER and R. W. CLARKE (Amer. J. Physiol., 1926, **76**, 354—359).—In a series of rapid flights to an altitude of 15,000 ft., the average alveolar tension of oxygen fell 50·7 mm. and that of carbon dioxide fell 11·3 mm. In the 15 min. during which the height was maintained, there was a rise of 6·8 mm. in the alveolar tension of oxygen. The carbon dioxide tension remained low for some minutes after the flights were

concluded. The main respiratory effects of aeroplane flights are to be ascribed to anoxæmia.

R. K. CANNAN.

Influence of asphyxiation on blood of marine fishes. F. G. HALL, I. E. GRAY, and S. LEPKOVSKY (J. Biol. Chem., 1926, **67**, 549—554).—Gradual asphyxiation of the menhaden (*Brevoortia tyrannus*) leads to loss of water from the blood with consequent increase in the concentration of the nitrogenous constituents and of phosphates; the chlorides remain almost unchanged and no constant variations in the dextrose concentration can be detected.

C. R. HARINGTON.

Influence of temperature on the equilibrium between oxygen and hæmoglobin of various forms of life. I. MACELA and A. SELISKAR (J. Physiol., 1925, **60**, 428—442).—The oxygen dissociation curves of dilute solutions of human, frog, fowl, tortoise, and *Planorbis* hæmoglobin are rectangular hyperbolæ. The affinity of frog hæmoglobin for oxygen is much lower than that of human hæmoglobin. The heat of reaction with oxygen of 1 g.-mol. of human hæmoglobin is 27·4 cal., and of frog hæmoglobin, 13·6 cal.

A. A. ELDRIDGE.

Formation of bile pigment from hæmoglobin. F. C. MANN, C. SHEARD, J. L. BOLLMAN, and E. J. BALDES (Amer. J. Physiol., 1926, **76**, 306—315).—Blood from the spleen and bone marrow contains more bilirubin (determined spectrophotometrically) than does the arterial blood. Injection of hæmoglobin into the blood entering these tissues increases the output of bilirubin and there is a parallel increase in another pigment, probably hæmatin.

R. K. CANNAN.

Decomposition of blood pigment by yeast. H. FISCHER and F. LINDNER (Z. physiol. Chem., 1926, **153**, 54—66).—By the action of yeast on a pyridine solution of hæmin at 40—50°, a change of colour to greenish-blue is observed, apparently primarily due to oxidation, since it does not occur in an atmosphere of carbon dioxide, hydrogen, or nitrogen. A small quantity of a brown pigment has been isolated from the product of the reaction. Under certain conditions, the colour may pass beyond the bluish-green stage and almost disappear. Many extracts from plant- and animal-tissue exert a similar effect on solutions of hæmin in pyridine. Liver tissue is particularly active. A similar effect on hæmin solutions is caused also by the addition of certain aromatic hydroxy-derivatives, such as pyrogallol, pyrocatechol, gallic acid, adrenaline, dihydroxyphenylalanine, and homogentisic acid, whilst phloroglucinol, guaiacol, and tyrosine show the effect only after a long time. A positive result is also given by thiophenol, thioglycollic acid, cysteine, and phenylhydroxylamine. The reaction appears to be a deep-seated one, and iron is split off from the hæmin.

W. O. KERMACK.

Acetylation of blood proteins. VII. N. TROENSEGAARD and B. KOUDAHL (Z. physiol. Chem., 1926, **153**, 93—110).—Methods are described for the acetylation of a number of proteins, globulin, serum-albumin, fibrin, and globin, and for the fractionation and purification of the acetylated bases so formed.

W. O. KERMACK.

Cholesterol as prosthetic group in serum-globulin. VIII. N. TROENSEGAARD and B. KOUDAHL (Z. physiol. Chem., 1926, **153**, 111—118).—From the product of the acetylation of serum-globulin, followed by extraction, fractional crystallisation, and fractional distillation in a high vacuum, two fractions among others have been obtained having compositions and mol. wts. corresponding with the formulæ $C_{16}H_{28}$ and $C_{18}H_{32}$. When cholesterol esters are acetylated and fractionated in a similar way, a fraction is obtained apparently consisting essentially of the compound $C_{16}H_{27}O(CO\cdot Me)$. It is probable that the serum-globulin contains a firmly-bound cholesterol complex, which when acetylated and fractionated yields a hydrocarbon, the point of junction with the globulin molecule being considered to be the carbon atom of cholesterol to which the hydroxyl group is attached.

W. O. KERMACK.

Binding of alkali by blood-serum of children. J. CSAPÓ and S. HENSZELMANN (Biochem. Z., 1926, **170**, 386—390).—By comparing the p_H of serum diluted with standard sodium hydroxide and of the same amount of sodium hydroxide similarly diluted, the amount of 0·01*N*-sodium hydroxide bound by 100 c.c. of serum is calculated, and this, divided by the percentage of protein, determined refractometrically, gives a quotient which is higher in the case of healthy children than of children suffering from various diseases.

P. W. CLUTTERBUCK.

Calcium content of human serum. DI-FOUTSIN (Biochem. Z., 1926, **170**, 321—325).—The calcium content of the serum of patients who remain in bed for long periods becomes increased.

P. W. CLUTTERBUCK.

Inorganic composition of blood. I. Effects of hæmorrhage on inorganic composition of serum and corpuscles. II. Changes in potassium content of erythrocytes under certain conditions. S. E. KERR (J. Biol. Chem., 1926, **67**, 689—720, 721—735).—I. A single large hæmorrhage causes a slight decrease in the concentration of sodium and chloride in the blood-serum; repeated hæmorrhage intensifies this effect and causes also an increase in the phosphates of the serum and the potassium of the red corpuscles. The results indicate that the dilution of the blood following such hæmorrhage must be accomplished, at least in part, by withdrawal of intracellular fluids from the tissues, these fluids being, relatively to the blood, rich in potassium and poor in sodium. The rise in the potassium content of the red corpuscles indicates that the latter are permeable to potassium ions under some conditions.

Modifications are described of the method of Kramer and Tisdall (A., 1921, ii, 412) for the determination of potassium and of that of Kramer and Gittleman (A., 1925, i, 180) for the determination of sodium.

II. The concentration of potassium in the red blood-corpuscles rose after injection of gelatin and sodium chloride solution (following extensive hæmorrhage),

after overdosage with insulin, and after injection of sodium oxalate. Insulin caused a fall, and sodium oxalate a rise, in the potassium of the serum. The changes in the corpuscles could not be accounted for by changes in their water content, and it must therefore be assumed that potassium may penetrate the corpuscles and may be held in them partly in a non-diffusible form. C. R. HARINGTON.

Dextrose in blood. G. S. LUND and C. G. L. WOLF (Biochem. J., 1926, **20**, 259—262).—Analytical data of the sugar content of diabetic and non-diabetic sheep, bullock, pig, dog, cat, and rabbit bloods as determined by the Hagedorn and Jensen, by the Benedict (A., 1925, i, 994), and by the fermentation methods are given. There is concordance between the results obtained by the Benedict and the Hagedorn and Jensen methods. Lower figures are obtained by the fermentation method than by the reducing methods. This discrepancy is smaller in cases of high total blood-sugar. S. S. ZILVA.

Blood-sugar. M. GILBERT, H. SCHNEIDER, and J. C. BOCK (J. Biol. Chem., 1926, **67**, 629—645).—Curves were constructed from determinations of blood-sugar taken at frequent intervals after ingestion of dextrose by normal individuals. Considerable variations were observed. The large number of determinations revealed, in some cases, a secondary rise in the blood-sugar, which would not have been observed if the samples had been taken at the customary hourly intervals. C. R. HARINGTON.

Action of enzymes on the sugar of the blood. J. GIAJA and X. CHAHOVITCH (Bull. Soc. Chim. biol., 1926, **8**, 306—310).—The addition of the juice of *Helix* to blood leads to a small increase in the reducing power of the blood, which is attributed to an enzymic hydrolysis of part of the combined sugar of the blood. Pancreatic juice did not produce this effect. R. K. CANNAN.

Action of light on blood. D. T. HARRIS (Biochem. J., 1926, **20**, 271—279).—Irradiation of blood with ultra-violet light causes it to give up oxygen at high oxygen tensions and take up oxygen at low tensions. At about 15 mm. tension of oxygen there is gaseous equilibrium, no net change occurring on passing from the dark into the light. The taking up of oxygen by blood in ultra-violet light is a property of the plasma. S. S. ZILVA.

Photo-oxidation of plasma. D. T. HARRIS (Biochem. J., 1926, **20**, 280—287).—The velocity of oxidation of plasma in light may be increased fifty-fold in the presence of minute amounts of certain sensitising substances. Hæmatoporphyrin and chlorophyll cause a very powerful acceleration, whilst many dyes and ionic iron show a marked although somewhat smaller effect. This catalytic effect of hæmatoporphyrin is unaffected by the addition of sodium cyanide to the system. S. S. ZILVA.

Velocity of photo-oxidation of proteins and amino-acids. D. T. HARRIS (Biochem. J., 1926, **20**, 288—292).—Ovalbumin, caseinogen, and edestin take up oxygen when exposed to radiations of the mercury arc, but gelatin, glycine, alanine, valine, leucine, asparagine, aspartic acid, and histidine do not. Tryptophan and tyrosine, on the other hand, are extremely sensitive to light, and the figures obtained with these indicate that the bulk of the oxygen uptake by plasma is due to their presence in it. Cystine shows no photo-sensitivity, but cysteine takes up oxygen so rapidly in the dark that the acceleration produced by light is small and negligible when compared with that of tryptophan and of tyrosine. S. S. ZILVA.

Acetone method of isolation of the hæmolysin in the albumin fraction of hæmolytic immune serum. M. PIETTRE (Compt. rend., 1926, **182**, 1051—1052).—Hæmolytic horse-serum is heated to 56° for half an hour to destroy the alexin, the proteins are then precipitated by treatment with acetone in the cold, washed with ether, and dissolved in water, and a portion of the globulins is precipitated by careful acidification. The hæmolytic activity (towards sheep cells) remains in the solution and is re-precipitated with the proteins by acetone. L. F. HEWITT.

Influence of neutral salts on hæmolysis. W. P. KENNEDY (Biochem. J., 1926, **20**, 243—246).—Hypotonicity in the cell–saponin–sodium chloride hæmolytic system is inhibitory. The effects of various cations in cell–saponin–salt systems are compared with a standard cell–saponin–sodium chloride system and with each other on several bloods. Their effect on hæmolysis is not connected with their mol. wt. Höber and Nast's results (Biochem. Z., 1914, **60**, 131) are not confirmed. S. S. ZILVA.

Bromine content of the organism. II. Physiological bromine content of organs. H. BERNHARDT and H. UCKO (Biochem. Z., 1926, **170**, 459—465).—Employing their previous methods (A., 1925, i, 454), the authors have determined the bromine content of a large number of organs and tissues. Of these, the hypophysis, adrenal bodies, and the wall of the aorta contain the greatest percentage of bromine. P. W. CLUTTERBUCK.

Phosphorus content of the body in relation to age, growth, and food. H. C. SHERMAN and E. J. QUINN (J. Biol. Chem., 1926, **67**, 667—677).—The percentage of phosphorus in the body of the white rat increases from about 0·3% at birth to about 0·7% at full growth. The curves representing the change in phosphorus percentage bear a general similarity to those previously determined for calcium (A., 1925, i, 1001). The percentage of phosphorus in the body of the adult male is greater than that in the female if the latter has borne young, and less if this is not the case. C. R. HARINGTON.

Bromolecithins. II. Bromolecithins of liver and of egg-yolk. P. A. LEVENE and I. P. ROLF (J. Biol. Chem., 1926, **67**, 659—666; cf. A., 1925, i, 1520).—From the product of bromination of lecithin from liver there was obtained an octabromo-derivative which, on hydrolysis, yielded octabromoarachidic, palmitic, and stearic acids, and a hexabromo-derivative which gave hexabromostearic, palmitic, and stearic acids. Bromination of egg-lecithin yielded

di- and tetra-bromo-derivatives, the latter of which, on hydrolysis, gave tetrabromostearic, palmitic, and stearic acids. From these results, it appears that, in the lecithin molecule, each of the unsaturated acids may occur in combination with either palmitic or stearic acid. C. R. HARINGTON.

Colour reaction of the skin relating to the genesis of melanins. P. SACCARDI (Atti R. Accad. Lincei, 1926, [vi], **3**, 155—159).—The skin contains a colourless chromogen which is detectable by the colour reaction it gives with phenylazoxycarbonamide and consists of a pyrrole derivative. T. H. POPE.

Enzymes of the stomach of infants. K. WALTHER (Magyar Orvosi Archiv., 1925, **26**, 522—524).—The stomachs of healthy new-born infants contain chymosin. The quantity increases with age and is independent of individual acidity. The lipase varies with the amount of fat in the food. The amylase content of the stomach behaves similarly to the chymosin. Amylase is found in very young infants and it increases with age. In diseased infants, the rennin content remains about the same, the lipase decreases, and the amylase varies with the lipase. CHEMICAL ABSTRACTS.

Distribution of amino-acids in globulin of thyroid gland. H. C. ECKSTEIN (J. Biol. Chem., 1926, **67**, 601—607).—Analysis, by the method of Van Slyke, of a preparation of the globulin of the thyroid obtained by extracting the gland with 0·85% sodium chloride solution and subsequent half-saturation with ammonium sulphate, yielded the following nitrogen results: amide 6·52, melanin 1·56, arginine 16·55, histidine 11·92, lysine 4·43, cystine 0·96% of the total nitrogen; the preparation contained 5·45% of tyrosine, 2·15% of tryptophan; the total nitrogen was 15·62% and the iodine 1·60%. A second preparation, obtained by acidifying the dilute saline extract of the gland with acetic acid, contained 15·55% of total nitrogen and 1·88% of iodine and, on detailed analysis, gave figures similar to the above. C. R. HARINGTON.

Concentration of diastase in the urine throughout the day. I. COHEN (Biochem. J., 1926, **30**, 253—258).—The rate of appearance of diastase in the urine is greater during the daytime than at night. This is not due to the taking of food. Variations in the total daily and nightly output of the enzyme occur in healthy individuals. S. S. ZILVA.

Factors influencing the excretion of carbamide. II. Diuresis and caffeine. H. BOURQUIN and N. B. LAUGHTON (Amer. J. Physiol., 1925, **74**, 436—450).—The onset of diuresis is accompanied by a high ratio of urinary urea nitrogen to blood-urea nitrogen; this is followed on continued diuresis by a partial fall of the value, and, as diuresis subsides, by a depressed value. Caffeine, during or after diuresis, produces a slight transient increase in urea output. A. A. ELDRIDGE.

Is oxyproteic acid a ureide? W. GIEDROYO (Bull. Soc. Chim. biol., 1926, **8**, 222—250).—The mixed barium salts of the oxyproteic acids from normal urine were completely freed from urea by prolonged extraction with alcohol or by means of urease. The product, on hydrolysis with 10% hydrochloric acid, yielded no urea, nor was any obtained by hydrolysis of a purified preparation of the substance properly called oxyproteic acid. There is no evidence for the view that urea is a constituent of the molecule of this substance or that it forms a loose compound with it. The contrary conclusion of Edlbacher (A., 1924, i, 122) and others was due to failure to eliminate completely urea from the mixed barium salts, together with the fact that urea is precipitated from solutions containing sodium chloride by mercuric acetate as a crystalline salt of the probable composition $CHON_2ClHg_2$. R. K. CANNAN.

Trypsin studies with normal and diseased infants. J. LUKÁCS (Magyar Orvosi Archiv., 1925, **26**, 473—483).—The fæces of new-born infants contain 60—80 units of enzyme during the first few days, compared with 10—30 units for older children. After the meconium period, the amount of enzyme drops to 20 or lower, to rise again during the second to fourth weeks to 20—40, and after 3 months to 40—60. In all cases of infections, the enzymes decrease, and remain on a much lower level than during health. Children with rickets have 160—600 units of trypsin. CHEMICAL ABSTRACTS.

Effect of copper compounds on the growth of carcinoma in the rat. I. HIEGER (Biochem. J., 1926, **20**, 232—236).—A rat bearing a carcinoma and receiving no addition of copper to the food shows from two to four times as much copper % in the tumour as in the rest of the body reckoned on the dry weight. When copper compounds are given to such rats with the food for periods of 2—3 months, the average amount of copper in the body is not increased by more than 75% and in the tumour by about 66%. S. S. ZILVA.

Uric acid in the cerebrospinal fluid. P. BAUMRITTER (Arch. med. enfants, 1925, **28**, 681).—The amount of uric acid in the cerebrospinal fluid is not increased with tuberculous meningitis, but there is a considerable increase of uric acid in epidemic cerebrospinal meningitis. CHEMICAL ABSTRACTS.

Cholesterol in cerebrospinal fluid. G. DEL DIESTRO (Arch. españoles Pediatría, 1925, **9**, 601).—In two cases of attacks of acetonæmia, with symptoms of encephalitis, there was no odour of acetone in the breath, but numerous cholesterol crystals were found in the cerebrospinal fluid. It is suggested that in this recurring hæmacidosis, the hypercholesteræmia represents a defensive reaction against the acetonæmic intoxication. CHEMICAL ABSTRACTS.

Total acid-base equilibrium of plasma in health and disease. VI. Diabetes. J. P. PETERS, H. A. BULGER, A. J. EISENMAN, and C. LEE (J. Clin. Invest., 1925, **2**, 167—211).—Ketosis has a variable effect on the total electrolytes of the serum. Hydrogen carbonate is spared by reduction of chlorides in the serum with consequent liberation of base. In severe cases, loss of chloride also probably occurs by excretion as ammonium chloride. In diabetic toxæmia, loss of salt or base leading to dehydration operates together with primary loss of water leading to loss of salt. CHEMICAL ABSTRACTS.

Protein-fat ratio in diabetic blood. L. O. CHRISTENSEN (Hospitalstidende, 1925, **68**, 969).—In diabetic coma, the protein range was 5·77—10·47%, but that of the fat only 0·06—0·16%; the fat was usually normal when coma was absent or impending. In one case of nephrosis, the serum protein content was 5·09% and the fat content of the blood 0·4%.
CHEMICAL ABSTRACTS.

Changes in the blood resulting from duodenal fistula. W. WALTERS, A. M. KILGORE, and J. L. BOLLMAN (J. Amer. Med. Assoc., 1926, **86**, 186—191).—Increasing alkalosis, decreasing concentration of chlorides in the blood-serum, and progressive rise in blood-urea are always observed. Life may be maintained by intravenous injection of dilute, but not of concentrated, sodium chloride solution; dextrose or sodium sulphate solution has no effect on the blood chlorides. The total amount of hydrochloric acid and chlorides discharged from the gastric fistula sufficed to explain the increase in the alkalinity of the blood and the decrease in its chloride content; none of the effect is attributed to loss of bile and pancreatic secretion. CHEMICAL ABSTRACTS.

Regulation of acid-base equilibrium. Search for a criterion for the study of epilepsy. R. RAFFLIN (Bull. Soc. Chim. biol., 1926, **8**, 294—305).—The use of the Hasselbach constant relating urinary p_H to the ratio of ammonia nitrogen to total nitrogen as a measure of the acid-base regulation of the body is criticised. The mixing of urines of varying p_H leads to considerable variations in the value of the constant. In epilepsy, the values vary no more widely than in normal subjects. R. K. CANNAN.

Clinical calorimetry. XLI. Storage of glycogen in exophthalmic goitre. H. B. RICHARDSON, S. Z. LEVINE, and E. F. DU BOIS (J. Biol. Chem., 1926, **67**, 737—751).—No evidence could be obtained that the mechanism for the storage of glycogen was deficient in patients with exophthalmic goitre; it is probable that the deviation, observed in this disease, from the normal blood-sugar curve, following ingestion of dextrose, is due either to increased rate of absorption of dextrose from the gut or to increased rate of hydrolysis of the glycogen stores in the body.
C. R. HARINGTON.

Chlorine gas treatment for respiratory diseases. H. L. GILCHRIST (Trans. Amer. Electrochem. Soc., 1926, **49**, 313—326).—Subjection to an atmosphere containing chlorine has a beneficial effect on patients suffering from influenza, coryza, bronchitis, asthma, hay-fever, laryngitis, pharyngitis, sinusitis, and whooping-cough, on animals with influenza, and on dogs with distemper. The chlorine should be maintained at a concentration of about 0·015 mg. per litre, and the patient allowed to remain in the atmosphere for 1 hr. The best results are seen when treating the early stages of the disease before the deposition of much mucus or pus. Treatment of the air with chlorine is recommended for the sterilisation of the air of crowded rooms, and for use as a prophylactic. L. F. HEWITT.

Disturbances in calcification in rickets. E. GLANZMANN (Schweiz. med. Woch., 1925, **55**, 683).—The most important factor in rickets is the ratio between the calcium and the inorganic phosphorus in the blood, which is normally 1·95 : 1. If the phosphorus in McCollum's rickets-producing diet is increased without the addition of calcium, or if the latter is reduced, rickets does not develop. An excess of calcium in the diet results in a lowering of the inorganic phosphorus, and in rickets. Predisposition to rickets is explained by its high calcium content, by the high protein content causing increased excretion of phosphorus, and by the low protective effect of the fats. Insulin decreases the phosphorus content of the blood. The phosphorus content is increased by the removal of the parathyroids or by irradiation of rachitic rats. CHEMICAL ABSTRACTS.

Relation of guanidine to parathyroid tetany. J. B. COLLIP and E. P. CLARK (J. Biol. Chem., 1926, **67**, 679—687).—The changes in the concentration of urea and non-protein nitrogen of the blood, during the tetany which follows parathyroidectomy, are different from those which occur in the tetany produced by injection of guanidine or of methyl- or dimethyl-guanidine. It is probable, therefore, that parathyroid tetany is not connected with intoxication by guanidine or its derivatives.
C. R. HARINGTON.

Maintenance requirement of the adult sheep. T. B. WOOD and J. W. CAPSTICK (J. Agric. Sci., 1926, 325—333).—The data obtained in a large number of digestion trials with sheep are utilised to calculate the maintenance requirement of the adult sheep by a statistical method. The figure so obtained is 1·1 lb. of starch equivalent per square metre per hr. (1·26 lb. for a 100-lb. sheep), corresponding with 49 cal./m.^{2}/hr.—considerably higher than the figures of 26 or 31 cal. generally accepted hitherto.
C. T. GIMINGHAM.

Physiology of the liver. XII. Muscle glycogen following total removal of the liver. J. L. BOLLMANN, F. C. MANN, and T. B. MAGATH (Amer. J. Physiol., 1925, **74**, 238—248).—In dehepatised dogs, the amount of glycogen in the muscles decreases as the blood-sugar decreases. Glycogen injected intravenously is converted into dextrose and utilised by the hypoglycæmic animal. The liver, rather than the muscles, is the source of blood dextrose.
A. A. ELDRIDGE.

Rôle of the phosphates in carbohydrate metabolism in skeletal muscle. F. BEATTIE and T. H. MILROY (J. Physiol., 1925, **60**, 379—401).—Under the influence of sodium fluoride, muscle can synthesise 80—90% of the pre-existing free phosphate with glycogen, the glycogen being consumed to a greater extent than is required for esterification; lactic acid, however, ceased to be produced or disappeared. The muscle of the insulinised cat behaved similarly, but a holding-up of the glycogen was observed. The influence of fluoride on adrenalised cat muscle was greatly diminished. The muscle of insulin-treated adrenalised animals, as compared with untreated adrenalised animals, showed a marked improvement

in the synthesis of both the intrinsic and the added phosphate. The effect of the addition of glycogen and phosphate was observed. A. A. ELDRIDGE.

Metabolism of aromatic acids. IX. Fate of halogen derivatives of benzoic acid in the animal body. N. J. NOVELLO, S. R. MIRIAM, and C. P. SHERWIN (J. Biol. Chem., 1926, **67**, 555—566).—After feeding *o*-, *m*-, and *p*-chloro-, bromo-, and iodo-benzoic acids to rabbits, all were excreted unchanged except *o*- and *p*-bromo- and *p*-iodo-benzoic acids, which were recovered from the urine partly in the form of the corresponding hippuric acids. In the case of dogs, all the substances were wholly or partly converted into the hippuric acids except *o*- and *m*-chlorobenzoic acids, which were excreted unchanged. o-*Chlorohippuric acid* has m. p. 176°; m-*chlorohippuric acid*, m. p. 143—144°; p-*chlorohippuric acid*, m. p. 143°; o-*bromohippuric acid*, m. p. 192—193°; m-*bromohippuric acid*, m. p. 146—147° (*nitrile*, m. p. 103·5—104·5°; *ethyl* ester, b. p. 110—118°); o-*iodohippuric acid*, m. p. 170°; m-*iodohippuric acid*, m. p. 167—169°; p-*iodohippuric acid*, m. p. 188—190°. C. R. HARINGTON.

Calcification *in vitro*. P. G. SHIPLEY, B. KRAMER, and J. HOWLAND (Biochem. J., 1926, **20**, 379—387).—Calcification takes place rapidly when rachitic bones from the rat and from children are introduced into aqueous solutions containing the same concentration of inorganic phosphate, calcium, and hydrogen ions as in normal serum. This process is delayed by the addition of egg-albumin and is completely inhibited by heat, by cold, and by protoplasmic poisons. Robison's theory of calcification (A., 1923, i, 730; 1924, i, 904) is critically discussed. S. S. ZILVA.

Possible significance of hexosephosphoric esters in ossification. Reply to Shipley, Kramer, and Howland. R. ROBISON (Biochem. J., 1926, **20**, 388—391). S. S. ZILVA.

Effect of ultra-violet light on the calcium and phosphorus metabolism of the lactating animal. J. McA. HENDERSON and H. E. MAGEE (Biochem. J., 1926, **20**, 363—373).—In four balance experiments on lactating goats, irradiation by the carbon arc lamp reduced the fæcal excretion of calcium. The effect on the excretion of phosphorus was less constant. A definite increase in the urinary excretion of calcium on irradiation was observed only in one case, in which there was already retention of calcium. S. S. ZILVA.

Biological significance of the unsaponifiable matter of oils. I. [Feeding] experiments with squalene (spinacene). H. J. CHANNON (Biochem. J., 1926, **20**, 400—408).—No ill effects were observed when squalene (spinacene) was fed to rats. The compound was partly absorbed, and an increase in the amount of unsaponifiable matter and in the amount of cholesterol in the liver and in the bodies resulted in consequence. The unsaponifiable matter in the liver increased to about 2·6 times the normal, whilst the cholesterol content of this organ increased by about 100%. Squalene was isolated as the hydrochloride from the livers of the animals which received it in their diet. The presence of the hydrocarbon, however, and the increase in cholesterol content in the liver did not wholly account for its increase in the unsaponifiable matter. There was no rapid return of the amount of unsaponifiable matter present in the liver to the normal value after depriving the rats of the squalene in the diet. S. S. ZILVA.

Biological significance of the unsaponifiable matter of oils. II. Unidentified unsaturated hydrocarbon present in mammalian liver. H. J. CHANNON and G. F. MARRIAN (Biochem. J., 1926, **20**, 409—418).—The livers of man, ox, sheep, horse, and pig contain a highly-unsaturated hydrocarbon. The hydrochloride of this compound was obtained by passing gaseous hydrogen chloride into an alcohol–ether solution of the unsaponifiable matter of the liver and by removing the crystalline cholesterol hydrochloride by grinding the mixture with ether. The *hydrochloride* has m. p. 128° and contains 31% of chlorine. The *bromide* contains 68% of bromine and does not melt, but begins to char at 170° and blackens at 180°. The *hydrocarbon* does not distil at a pressure of 2 mm., but decomposes. The compound is probably not identical with squalene. S. S. ZILVA.

Iodine as a biogenic element. B. BLEYER (Biochem. Z., 1926, **170**, 265—276).—A number of tables show the iodine contents of the foodstuffs of districts in which goitre is and is not prevalent both within and without Bavaria, and of the typical soils, rocks, and drinking waters of these districts. P. W. CLUTTERBUCK.

Iodine as a biogenic element. II. Administration of iodine to goats. H. NIKLAS, A. STROBEL, and K. SCHARRER (Biochem. Z., 1926, **170**, 277—299).—Iodine administration in doses up to 180 mg. per animal per day has no influence on the behaviour, health, weight, or sexual activity of goats. Doses of 60—120 mg. of iodine per day did not lead to any increase in the quantity of milk, but 180 mg. caused a considerable increase. After a daily dose of 120 mg. of iodine, the absolute amount of fat became higher, but the percentage lower, due to increased quantity of milk. With 180 mg. of iodine, the absolute amount of fat at first increases and then falls again, whilst the percentage of fat is always lower than normally. P. W. CLUTTERBUCK.

Iodine as a biogenic element. III. Iodine metabolism of animals. H. NIKLAS, J. SCHWAIBOLD, and K. SCHARRER (Biochem. Z., 1926, **170**, 300—310).—Inorganic iodine administered by mouth to goats and pigs is absorbed quantitatively by the intestine, but the iodine content of the body-fluids, even during continued administration (*e.g.*, 100 mg. daily), did not exceed physiological values. P. W. CLUTTERBUCK.

Purine metabolism. I. Variations in the nuclear-plasmic ratio in the adult albino rat. II. Synthesis of purines by the adult mammalian organism. R. TRUSZKOWSKI (Biochem. J., 1926, **20**, 437—446).—In hunger, the nuclear-plasmic ratio in the albino rat falls slightly below normal, indicating a greater relative loss of nuclear than of

cytoplasmic material. Purine feeding does not raise the nuclear–plasmic ratio. Purine compounds can be synthesised by the rat. S. S. ZILVA.

Physiology of sleep. III. Effect of muscular activity, rest, and sleep on the urinary excretion of phosphorus. N. KLEITMAN (Amer. J. Physiol., 1925, **74**, 225—237).—The rate of excretion of phosphorus and of total acid is greater during sleep than during wakefulness, and is unaffected by potassium bromide. Muscular work involves retention of phosphorus. The rate of excretion is greater in the afternoon than in the morning. A. A. ELDRIDGE.

Specific dynamic action of proteins. E. F. TERROINE and R. BONNET (Compt. rend., 1926, **182**, 941—943).—Experiments on the frog indicate that the excess energy produced by ingestion of amino-acids is very nearly the same for all amino-acids (especially acyclic ones) referred to a given quantity of amino-nitrogen, and is equivalent to about 118 cal. per 14 g. of amino-nitrogen. With proteins, the extra energy is about 115·5 cal. per 14 g. of nitrogen, and it is considered that the metabolism of amino-nitrogen accounts for the whole of this energy. L. F. HEWITT.

Permeability of living cells. VI. Penetration of certain oxidation-reduction indicators as influenced by p_H; determination of the r_H of *Valonia*. M. M. BROOKS (Amer. J. Physiol., 1926, **76**, 360—379).—The penetration into the sap of *Valonia* of certain oxidation-reduction indicators has been studied at various hydrogen-ion concentrations of the external fluid and of the cell sap. The latter were altered by previous treatment with carbon dioxide or ammonium salts. In the case of 2 : 6-dibromophenol–indophenol, the dye reaching the sap was in the reduced state, the rate of penetration followed the course of a bimolecular reaction, and the amount at equilibrium was proportional to the concentration of undissociated dye in the external fluid. When the sap was previously made more acid than normal, more dye entered at equilibrium, and when the sap was more alkaline, less dye entered. At higher temperatures and lower concentrations of dye, the rate of penetration followed a course like that of two consecutive unimolecular reactions. On the assumption that only the reduced dye can enter the sap, and that the protoplasm maintains a constant reduction potential against the oxidising capacity of the dye by a relatively slow production of reducing material, the experimental results may be explained by the statement that the rate of penetration is regulated by the product of the concentration of undissociated dye in the medium and the reduction potential of the protoplasm. To explain the behaviour of cells with acid or alkaline sap, it is further postulated that the observed p_H of the medium does not represent the true reaction immediately adjacent to the surfaces of the treated cells. Methylene-blue enters the sap in the oxidised state, the amount being independent of the p_H of fluid or sap. Potassium indigotindisulphonate does not appear to penetrate at all. These results do not support the hypothesis that undissociated molecules only can enter living cells. The r_H of the sap of *Valonia* is about 16—18; that of the protoplasm could not be so closely defined. R. K. CANNAN.

Action of acids on turtle heart-muscle with reference to the penetration of anions. H. W. SMITH (Amer. J. Physiol., 1926, **76**, 411—447).—From determinations of the effect of carbonic acid on the contractility of a special preparation of the excised atria of the fresh-water turtle in the presence of varying concentrations of hydrogen carbonate ions, there have been deduced the concentrations of carbon dioxide and of hydrogen carbonate ion in the tissue. It is concluded that the tissue is freely permeable to carbon dioxide and to hydrogen carbonate ion and that the concentration of the latter in the tissue bears a simple relation to the external concentration. Extension of the experiments to other acids indicated that the tissue was relatively impermeable to primary and secondary phosphate ions, and to lactic and acetic acids and their anions. Permeability to valeric, butyric, and propionic acids and their anions increased with the mol. wt. of the acid. Hydrogen ions penetrate the tissue if there is a sufficient difference in concentration between the tissue and the external fluid, and, at equilibrium, there is a considerable difference in the hydrogen-ion concentration within and without. Confirming work on marine eggs (*ibid.*, 1925, **72**, 347), it is concluded that the apparent penetration of anions into living cells is not a consequence of actual migration from fluid to cell. Since an anion appears to penetrate only when it is the ion of an acid which can enter the cell and when the latter is present, it is suggested that the appearance of the anion within the cell is due to a redistribution of hydrogen and chlorine ion pairs consequent on the penetration of the acid molecule. R. K. CANNAN.

Action of pure phosphatides on the perfused heart of the frog. P. EGGLETON (Biochem. J., 1926, **20**, 395—399).—Pure lecithin and kephalin free from water-soluble impurities do not act as cardiac stimulants. It is suggested that the stimulating activity observed by other workers was due to a water-soluble impurity, possibly an organic base. S. S. ZILVA.

Influence of peroral administration of acids, alkalis, and alkaline mineral waters on the C : N ratio. M. WATANABE (Biochem. Z., 1926, **170**, 432—458).—The urinary carbon and nitrogen contents of alkaline, sugar-free rabbit's urine and the C : N ratio are practically unchanged on keeping for 24 hrs. at 18°. The C : N ratio is increased by peroral administration for several days of 0·004—0·01 g. of hydrochloric acid per kg. body-weight per day, but is decreased by similar administration of 0·01 g. of sodium carbonate, 0·008 g. of sodium hydroxide, or 0·007 g. of calcium hydroxide. Peroral administration of Neuenahr mineral water led to the disappearance of a lævorotatory reducing substance from the urine of a pathological dog, and in one case of slight diabetes in man, the urine previously dextrorotatory became lævorotatory. In a case of slight diabetes, when glycosuria and ketonuria were absent, the C : N ratio was pathologically increased. Since the increase of the C : N ratio indicates the decrease of oxidation of

carbon compared with nitrogen in the body, and a decrease the reverse, the experiments show that administration of small amounts of acid decreases oxidation of carbon, whilst administration of alkali and Neuenahr mineral water favours oxidation of carbon, thus explaining the beneficial action of the mineral water in cases of diabetes mellitus.

P. W. CLUTTERBUCK.

Magnesium hydroxide as antidote to poisoning by mercuric chloride. M. A. RAKUSIN (J. Exp. Biol. Med., 1926, **3**, 55—56).—The action of magnesium hydroxide as an antidote for mercury poisoning depends on the precipitation of the mercury as oxide. Two-thirds of the mercury is so removed from a solution of mercuric chloride in 24 hrs. Charcoal effects a more complete removal. H. P. MARKS.

Production of phenomena peculiar to parathyroid overdosage in dogs by means of certain inorganic salts. J. B. COLLIP (Amer. J. Physiol., 1926, **76**, 472—482).—Injection together of acid phosphate and calcium chloride was followed rapidly by failure of circulation, with highly viscous blood, decreased kidney function, and death. The *post-mortem* findings were almost identical with those of overdosage with parathyroid hormone. The continuous injection of calcium chloride, or of acid or alkaline phosphate alone, was not accompanied by these effects. R. K. CANNAN.

Definition of the enzymic activity of enzymic preparations, solutions, and living cells. H. VON EULER and K. JOSEPHSON (Ber., 1926, **59**, [*B*], 770—773; cf. A., 1923, i, 966).—For preparations and solutions, the activity is denoted by the expressions, $X_1f=k/g$ (enzyme preparation) and $X_2f=k\times g$ substrate/enyzme preparation, in which g is the weight of the enzyme preparation or of the residue of the enzyme solution in grams. The first expression is used when k is independent of the concentration of the substrate, the second when the product, reaction coefficient, amount of substrate, are at least approximately constant. In cases in which several substrates are affected by an enzyme, the particular material used is denoted by a prefix. When living cells are employed, the expressions are modified to $X_1v=k$/number of cells and $X_2v=k\times g$ substrate/number of cells (v="Vermögen"). Xf and Xv are related by the expressions, $Xv=Xf\times g$(enzyme preparation)/number of cells or $Xv=Xf\times$ mean weight of cell. The differences between the enzymic activity, Xf, and purity are given by the expressions Xf=active enzyme/g of dry material, and purity= total amount of enzyme/g of dry material.

H. WREN.

Enzymes of emulsin. II. K. JOSEPHSON (Ber., 1926, **59**, [*B*], 821—827; cf. this vol., 321).—Treatment of almond meal, which has been purified by precipitation by alcohol, with kaolin followed by elution with ammonia gives better results in yield and activity of preparations than does treatment with aluminium hydroxide (*loc. cit.*). The most highly active preparations have $Sal.f=4\cdot8$—$4\cdot9$; they are free from carbohydrates and give only a faint xanthoproteic reaction. The optimum reaction for the adsorption of β-glucosidase by kaolin is p_H 4·4, and is thus identical with that required for optimal enzymic action. Aluminium hydroxide has greatest adsorptive power in nearly neutral solution. The activity–hydrogen-ion concentration graphs for the fission of salicin and helicin by highly-purified preparations resemble one another throughout, and are closely similar to the curves obtained with less active preparations (*loc. cit.*). H. WREN.

Conditions for the autolytic formation of ammonia in the tissues. G. POPOVICIU (Biochem. Z., 1926, **170**, 395—409).—Inorganic phosphate plays the chief part in regulating the autolytic formation of ammonia in the tissues, and other modifying factors, *e.g.*, calcium, sodium, potassium ions, dilution, lactate, and sugar, all act indirectly through their effect on phosphate. The formation of ammonia decreases with the alkalinity of the phosphate solution. Lactate is inhibitory, but more ammonia is formed in alkaline than in acid lactate buffer. The influence of sugar is two-fold, first by giving rise to lactic acid which is inhibitory, and second by formation of carbohydrate–phosphoric acid complexes.

P. W. CLUTTERBUCK.

Intermediary metabolism of carbohydrates. Glyoxalase content of rabbit's muscle. H. W. DUDLEY (Biochem J., 1926, **20**, 314—320).—Foster's failure to detect glyoxalase in an aqueous extract of rabbit's muscle (A., 1925, i, 1495) is probably due to destruction of the enzyme by the acid produced during the mincing and extraction of the muscle. Glyoxalase is actually present in this tissue, since, if the muscle is minced as quickly as possible and then extracted in sodium carbonate solutions, active preparations are obtained. The hypothesis that in muscle there may be two distinct metabolic paths for the production of lactic acid from carbohydrate is therefore deprived of experimental support.

S. S. ZILVA.

Lipase. III. Hydrolysis of esters of dicarboxylic acids by hepatic lipase. D. A. MCGINTY and H. B. LEWIS (J. Biol. Chem., 1926, **67**, 567—577).—Ethyl hydrogen adipate was rapidly hydrolysed by hepatic lipase, whereas ethyl hydrogen malonate was only slowly attacked; the latter fact must be due to a specific resistance to hydrolysis on the part of the ethyl hydrogen malonate, and not, as suggested by Kastle (A., 1902, i, 655), to inability of lipase to combine with an ionised substance. Ethyl fumarate and ethyl succinate were hydrolysed at similar rates, the hydrolysis of the first carbethoxyl groups being rapid and of the second slow. The rate of hydrolysis of ethyl maleate and of ethyl *dl*-malate was much lower. The above results bear a general similarity to those obtained by Skrabal (A., 1920, ii, 239) in the investigation of the alkaline hydrolysis of dibasic esters. C. R. HARINGTON.

Hydrolysis of triacetin by pancreatic lipase in presence of certain compounds of quinine and carbamide. I. A. SMORODINCEV and V. A. DANILOV (Bull. Acad. Sci. Leningrad, 1926, [vi], 3—24).—Unlike that of other substrates, the hydrolysis of 1% aqueous triacetin solution by pancreatic lipase is accelerated

by quinine hydrochloride and sulphate slightly and in proportion to the concentration. The action of the enzyme is enhanced by the presence in the medium of 0·26—0·03% (0·03—0·015%) of the hydrochloride (sulphate), but not by 0·016% (0·007%). The action of the lipase is paralysed by 0·6%, retarded by 0·4—0·16%, and uninfluenced by 0·08% of the double carbamide quinine hydrochloride. Free carbamide exerts no appreciable influence on the hydrolysis, but its hydrochloride (nitrate) in concentrations of 0·07—0·017% (0·09—0·02%) greatly retards the change; when present to the extent of 0·009% (0·01%), however, it has no effect on the process. In the action of quinine compounds on lipase, both anion and cation participate; sulphate ions increase the accelerating effect of the alkaloid. The velocity of the hydrolysis of triacetin by pancreatic lipase in either absence or presence of quinine and carbamide is in accord with the law for unimolecular reactions. Lipase is somewhat less sensitive towards quinine than are tryptase and amylase. T. H. POPE.

Inulin. V. Inulase. H. PRINGSHEIM and R. PEREWOSKY (Z. physiol. Chem., 1926, **153**, 138—146).—Fungi when grown on a solution of sucrose possess a stronger inulase activity than when grown on a solution containing inulin. Inulase acts on natural inulin at the same rate as on inulin prepared by hydrolysis of acetylinulin, in spite of a previous statement to the contrary. The juice from *Aspergillus niger* attains its maximum inulase content relative to the total solids when growth has continued for approximately 22 days. W. O. KERMACK.

Hydrolysis of sucrose solutions by invertase. C. D. INGERSOLL (Bull. Soc. Chim. biol., 1926, **8**, 264—287).—The relation between the rate of hydrolysis and the concentration of sucrose has been critically re-examined. Between concentrations of 8% and 70%, the velocity diminishes in linear relation to the concentration of sugar when the observed velocity, determined polarimetrically, is corrected to constant mass of water. The viscosity of the concentrated solutions does not account for the diminishing velocity. The effect of the addition of the products of hydrolysis is such as may be explained by combination of part of the enzyme with the added reactants. The addition of α-methylglucoside retards the initial reaction in such a way that this becomes constant for concentrations of sucrose varying from 5% to 35%. An effect of the hydrogen-ion concentration on the initial velocity of reaction persists, although in less degree, in concentrated solutions of the sugar. R. K. CANNAN.

Inositol in pepsin. B. L. MOLDAVSKI (J. Russ. Phys. Chem. Soc., 1925, **57**, 13—16).—The supposed inositol extracted from pepsin (of unnamed origin) by Rakuzin and Ivanov (A., 1923, i, 871) has neither the specific rotation nor the m. p. of *d*-inositol, and is stated to respond to Molisch's reaction, which Molisch himself found was not the case with inositol. The author finds that Witte's pepsin, when extracted with 85% alcohol, yields 85·3% of sucrose, which is a substance commonly found in commercial pepsin. T. H. POPE.

Secondary oxidation of substances of physiological interest. D. C. HARRISON and S. THURLOW (Biochem. J., 1926, **20**, 217—231).—When milk peroxydase is added to hypoxanthine in the presence of xanthine oxydase prepared from milk by Dixon and Thurlow's method (A., 1924, i, 1380), the total oxygen uptake of the system is considerably in excess of that required theoretically for the oxidation of the hypoxanthine. With an ether-extracted xanthine oxydase preparation, the uptake is theoretical. It is assumed that some substance in the milk, possibly fat, adhering to the unextracted enzyme preparation is oxidised by the xanthine oxydase in the presence but not in the absence of the peroxydase. The ferrous ion (not the ferric ion), hæmoglobin, and hæmatin can function like peroxydase in this reaction. In the case of hæmoglobin, the pigment is rapidly oxidised to methæmoglobin in the presence of hypoxanthine. An additional oxygen uptake is not observed when the extracted fat is restored to the oxydase in the presence of ferrous iron and of hæmoglobin. Oxidation of lactic acid to acetaldehyde and of β-hydroxybutyric acid to acetoacetic acid can be induced during the aërobic oxidation of cysteine. Lactic and β-hydroxybutyric acids are also oxidised during the aërobic oxidation of hypoxanthine in the presence of xanthine oxydase and ferrous iron. S. S. ZILVA.

Cultivation of yeast in a synthetic medium. E. AUBEL, L. GENEVOIS, and J. SALABARTAN (Compt. rend., 1926, **182**, 989—991).—Yeast grows under aërobic and (very slowly) under anaërobic conditions in synthetic media containing dextrose, lactic acid, or pyruvic acid. The products liberated during growth in the presence of dextrose are the same with or without oxygen, the respective proportions being as follow for aërobic and anaërobic conditions: alcohol 0·92, 1·5; lactic acid 0·029, 0·067; pyruvic acid 0·9, 0·3 g. It is suggested that growth under anaërobic conditions is rendered possible by the presence of nitrates in the medium. Comparisons are made between the metabolism of yeast and of *Bacillus coli*. L. F. HEWITT.

Assimilation of nitrogen by yeast from culture media in the aëration process. H. CLAASSEN (Z. angew. Chem., 1926, **39**, 443—447).—Yeast assimilates the whole of the nitrogen from ammonium sulphate, aspartic acid, and asparagine, the process being very rapid with aspartic acid, and relatively slow with asparagine. Only very small amounts of nitrogen are taken up from betaine and nitrates; with carbamide, about 30% of the available nitrogen is assimilated. Several successive fermentations are usually necessary to ensure maximum assimilation; allowance is also made for nitrogen taken up by the yeast and given up again during the process in a form which cannot be reassimilated. The nitrogen thus lost amounts to 8% of the gain in nitrogen by the yeast as determined by analysis. More than 80% of the nitrogen in germinated malt is assimilated by yeast. B. W. CLARKE.

Action of manganese on alcoholic fermentation. M. ROSENBLATT and A. (J.) MARCH (Biochem. Z., 1926, **170**, 344—354).—A study of the influence of manganese on alcoholic fermentation in

presence of varying concentrations of sugar and of a number of different types of yeast and yeast juice shows that although manganese sometimes stimulates fermentation, it is often inhibitory, the effect depending on the origin of the yeast. The inhibitory action is independent of the medium or the form in which the manganese is added (sulphate or nitrate), but the different results with different types of yeast indicate that the sensitivity of the enzymes produced by the yeast changes with the origin of the yeast and with the composition of the medium. Increasing the concentration of sugar protects the enzymes against the manganese, and thus exerts a weakening effect on both the manganese activation and inhibition of the fermentation reaction. P. W. CLUTTERBUCK.

Influence of fatty acids and their salts on alcoholic fermentation by living yeast. I. Acetic and formic acids and their sodium, potassium, and ammonium salts. H. KATAGIRI (Biochem. J., 1926, **20**, 427—436).—Fermentation experiments with living yeast and dextrose were carried out in 0·5*M*-, 0·2*M*-, 0·1*M*-, 0·05*M*-, and 0·025*M*-solutions of acetic acid plus acetate and of formic acid plus formate buffer solutions in various ratios. The sodium, potassium, and ammonium salts of the acids were employed. In all cases, the rate of fermentation increased rapidly as the total amount of acid decreased, this being independent of the total acetate and formate concentration. Formic acid was found to be 5—8 times more potent in its inhibition of the fermentation than acetic acid. The variation in the rate of fermentation with the changing hydrogen-ion concentration of the medium was independent of the cation used in the buffer solutions.

S. S. ZILVA.

Carbohydrate and fat metabolism of yeast. III. Nature of the intermediate stages. I. S. MACLEAN and D. HOFFERT (Biochem. J., 1926, **20**, 343—357).—The action of yeast has been investigated on ethyl alcohol, acetaldehyde, sodium acetate, glycol, glycollaldehyde, sodium glycollate, sodium glyoxylate, sodium oxalate, sodium lactate, sodium pyruvate, acetone, glycerol, aldol, sodium butyrate, sodium β-hydroxybutyrate, and sodium acetoacetate. With a plentiful supply of oxygen, ethyl alcohol and sodium acetate were utilised by the yeast to form storage fat and carbohydrate as well as being partly oxidised to carbon dioxide. This change was less marked in the case of sodium lactate and sodium pyruvate. The addition of sodium sulphite to the alcohol or acetate medium diminished the storage of both fat and carbohydrate, the ratio of the unsaponifiable matter (sterol) to the fatty acids in the ether extract remaining unaltered. On the other hand, the addition of sulphite to a solution of hexose in which yeast was incubated resulted in an increase of stored carbohydrate, but in no consistent change in the storage of fatty acids. The production of sterol was, however, diminished in this case. It is assumed that the acetaldehyde is first condensed to hexose, which is either converted into storage carbohydrate or directly condensed into higher fatty acids without passing through a fatty aldehyde stage, probably by a direct linking of the hexose molecules. S. S. ZILVA.

Action of yeast on lactic acid. D. HOFFERT (Biochem. J., 1926, **20**, 358—362).—Experiments are described in which the carbon of the carbohydrate, fat, and protein present in the yeast at the beginning and of the lactic acid used in the fermentation is balanced against the carbon of the yeast and of the products of fermentation after incubation. The carbon of the lactic acid which has been destroyed can be accounted for within the limits of experimental error. Fürth and Lieben's view (A., 1922, i, 502, 1219) that a non-hydrolysable carbohydrate or a protein with a higher carbohydrate content is formed in this process of fermentation is not substantiated by these experiments. S. S. ZILVA.

Mechanism of antiketogenic action. I. WEISS and M. ALTAI (Magyar Orvosi Archiv., 1925, **26**, 485—496).—Lundin's statement (A., 1923, i, 1268; 1924, i, 247; J. Metabol. Res., 1923, **4**, 150) that yeast-cells slightly decompose sodium acetoacetate is confirmed. The effect is increased by the addition of fermentable carbohydrates, or of glycerol, acetaldehyde, and pyruvic acid. If the acetaldehyde produced by fermentation is combined with sodium sulphite, the antiketogenic action of the carbohydrate ceases. CHEMICAL ABSTRACTS.

Affinity of invertase. VIII. Effect of previous treatment of yeast on the affinity constant of invertase. II. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **153**, 10—15).—Treatment of yeast invertase with lævulose causes no alteration in the affinity of the invertase for dextrose or for lævulose. Galactose is similarly without effect on the affinity constant of invertase. W. O. KERMACK.

Chemical changes in blood during narcosis. Does ether narcosis produce alkalosis? H. TÓMASSON (Biochem. Z., 1926, **170**, 330—336).—The p_H of the plasma and the calcium, potassium, and sodium contents of the serum were determined in two healthy subjects. The p_H during narcosis was displaced to the alkaline side, this and the variation in electrolytes being opposite to results previously obtained. P. W. CLUTTERBUCK.

C : N ratio in phloridzinised dogs. T. KANAMORI (Biochem. Z., 1926, **170**, 410—431).—In phloridzin poisoning, apart from the excretion of reducing substances, there rarely occurs any increased excretion of dysoxidisable carbon, the C : N ratio, after deduction of the carbon of reducing substances from the total carbon, being but rarely increased. The value of the C : N or of the residual C : N ratios is not influenced by the carbon bound to urinary nitrogen. Similar conclusions are reached in respect to aglycosuric urine (cf. Watanabe, this vol., 639).

P. W. CLUTTERBUCK.

Inhibitory effect of sugars on saponin hæmolysis. E. PONDER and W. P. KENNEDY (Biochem. J., 1926, **20**, 237—242).—The quantitative inhibitory action of dextrose, sucrose, or lactose on saponin hæmolysis conforms to a type shown by certain alkalis and certain amino-acids (see Proc. Roy. Soc., 1926, **B 99**, 461). The inhibitory action of mannose, trehalose, maltose, raffinose, arabinose, xylose, and rhamnose was also studied. All these sugars, with the

exception of arabinose and xylose, are inhibitory in different degrees with sheep cells. With human cells, as with the sheep cells, there are considerable differences in the inhibitory effects of the sugars. The effects of the sugars in the two cases do not run parallel. No sugar was found to produce an acceleration in the hæmolysis unless the specimen was acid.

S. S. ZILVA.

Use of low temperatures in the preparation of pure proteins. T. R. PARSONS (Proc. Fourth Intern. Congress Refrigeration, 1924, **1**, 194).—By simultaneous freezing and centrifuging it was found possible to separate an upper layer of ice and a lower layer of hæmoglobin crystals. It is easier, although theoretically less efficient, to centrifuge during the thawing of the previously frozen solution. Egg-white thus yields a thick layer of ice above a very viscid concentrated solution containing crystals, which mixture, on short exposure to the air, dries to a yellow, glassy mass which can be kept indefinitely without change. The method is suggested as being suitable for the commercial dehydration and concentration of food materials.

CHEMICAL ABSTRACTS.

Variation in the end-products of bacterial fermentation resulting from increased combined oxygen in the substrate. H. D. KAY (Biochem. J., 1926, **20**, 321—329).—*Bacillus communis* and *B. lactis aërogenes* produce from gluconic, glycuronic, and saccharic acids on the whole the same end-products of fermentation as from dextrose or mannitol, namely, lactic, succinic, acetic, and formic acids, carbon dioxide, alcohol, and hydrogen, and, in the case of the last organism, also acetylmethylcarbinol and 2 : 3-butylene glycol. *B. lactis aërogenes* does not produce acetylmethylcarbinol and 2 : 3-butylene glycol from saccharic acid, but does so from gluconic acid. Balance sheets of the substrate carbon destroyed and the carbon found in the products of fermentation are tabulated and compared with those obtained by other workers with these organisms, utilising dextrose and mannitol in the fermentable medium. The more oxygenated the substrate the less alcohol and more acetic acid is produced by the fermentation. Gluconic, glycuronic, and saccharic acids are readily fermented by a large number of organisms of the *coli-typhosus* group. With calcium gluconate as substrate, the intermediate production of a non-reducing carbohydrate which occurs in the early stages of the fermentation of dextrose by *B. coli* (cf. Grey, A., 1920, i, 699) appears not to take place. A marked difference in the relative proportions of end-products resulting from the fermentation of gluconic acid under varying conditions was observed.

S. S. ZILVA.

Heat-stable peroxydase of bacteria. A. B. CALLOW (Biochem. J., 1926, **20**, 247—252).—*Bacillus fœcalis alcaligenes*, *B. pyocyaneus*, *B. fluorescens*, *B. prodigiosus*, *B. proteus*, *B. coli*, *B. paratyphosus* A, *B. paratyphosus* B, *B. subtilis*, *B. megatherium*, and *Staphylococcus aureus* contain a heat-stable peroxydase. *S. acidi lactici* and *B. sporogenes* give only a slight peroxydase reaction. In the case of fresh, young, washed cultures of many bacteria, the blue colour formed in the peroxydase reaction fades away rapidly, but if these organisms are previously boiled, the colour remains permanent. The heat-labile factor responsible for the fading of this colour shows certain points of resemblance to the methylene-blue reducing system, since emulsions of some of these bacteria also lose their methylene-blue reducing power on boiling and, further, substances which accelerate or retard the methylene-blue reduction have a similar effect on the fading of the blue peroxydase colour. Some of the above bacteria also reduce nitrates to nitrites. They lose this property on boiling.

S. S. ZILVA.

Toxic effects of potassium chloride on the lactic acid bacillus at different temperatures. E. BACHRACH (Compt. rend., 1926, **182**, 1042—1043).—Treatment with potassium chloride at 26° sensitises, and at 39—40° partly immunises, the lactic acid bacillus to the toxic effects of the salt.

L. F. HEWITT.

Effects obtained from feeding fresh adrenal cortex, medulla, and whole gland to the standard white rat. E. B. MCKINLEY and N. F. FISHER (Amer. J. Physiol., 1926, **76**, 268—283).—When either desiccated whole glands or fresh glands preserved below 0° were fed in amounts of 0·5 g. to rats, gross gastro-intestinal symptoms resulted. Much larger doses of whole gland fed immediately on removal from cats or rabbits had no serious effect. This toxicity is to be attributed to some product of mild autolysis, and not to the adrenaline of the gland. Feeding fresh or frozen cortical tissue was without untoward effect, but resulted, after 11 weeks, in a somewhat enhanced average growth accompanied by hypertrophy of testes and spleen.

R. K. CANNAN.

Wyss chemical method for assay of insulin. F. BISCHOFF, L. C. MAXWELL, and N. R. BLATHERWICK (J. Biol. Chem., 1926, **67**, 547—548).—The power to inhibit the oxidation of polyhydric phenols by hydrogen peroxide, shown by Wyss (cf. A., 1925, i, 1220) to be possessed by preparations of insulin, is not specific to insulin; solutions of caseinogen of equal nitrogen content possess an equal power of inhibiting this reaction, whilst tyrosine and tryptophan are still more efficient in doing so.

C. R. HARINGTON.

Rôle of insulin in phosphorus metabolism. S. KOLODZIEJSKA and C. FUNK (Biochem. J., 1926, **20**, 392—394).—From experiments on the administration of insulin to rats on phosphorus-free diets under different conditions, it is concluded that insulin plays only an insignificant rôle in the total phosphorus metabolism.

S. S. ZILVA.

Depancreatised dogs before and after the withdrawal of insulin. I. L. CHAIKOFF, J. J. R. MACLEOD, J. MARKOWITZ, and W. W. SIMPSON (Amer. J. Physiol., 1925, **74**, 36—48).—The percentage amounts of sugar and ketonic substances are higher in the blood of fat than in that of thin, depancreatised dogs several days after discontinuing insulin and food; with fat dogs, relatively more acetoacetic acid, and in thin ones more β-hydroxybutyric acid was present, the D : N ratio being considerably reduced.

On giving insulin again, the inorganic phosphates and the hydroxybutyric acid diminished at uniform rates, the acetoacetic acid less rapidly, and the fat not at all. A. A. ELDRIDGE.

Action of liver-tissue and insulin on dextrose. C. LUNDSGAARD and S. A. HOLBØLL (Ugeskrift for Laeger, 1925, **87**, 905).—The liver is considered to serve as a storage place for dextrose as glycogen and to be directly unimportant for the metabolism of dextrose in the organism. Unlike muscle-tissue, liver-tissue is unable to form neoglucose from αβ-glucose under the influence of insulin. CHEMICAL ABSTRACTS.

Transformation of glycogen. C. LUNDSGAARD and S. A. HOLBØLL (Ugerskrift for Laeger, 1925, **87**, 881).—It is assumed that carbohydrates under the action of insulin are partly oxidised and partly deposited as glycogen; when the insulin is no longer in the blood, the deposits of glycogen are split into dextrose. The possibility of neoglucose being intermediate in the production and deposition of glycogen is considered. CHEMICAL ABSTRACTS.

Oxytocic principle of the pituitary gland. W. V. THORPE (Biochem. J., 1926, **20**, 374—378).—The oxytocic principle is not inactivated by pancreatic lipase. The assumption that the hormone possesses a peptide-like and not an ester-like linking thus finds experimental support. The lipase in dried pancreas can be destroyed by long keeping in dilute acetic acid. S. S. ZILVA.

Effect of thyroid feeding on sugar tolerance. H. P. MARKS (J. Physiol., 1925, **60**, 402—410).—Injection of dextrose or of a small dose of insulin into the thyroid-fed rabbit whose liver still contains glycogen is followed by a secondary hyperglycæmia. Adrenaline does not arrest the fatal hypoglycæmia which follows the injection of dextrose into a glycogen-free, thyroid-fed rabbit. A. A. ELDRIDGE.

Thyroxin. I. Isolation of thyroxin from the thyroid gland. C. R. HARINGTON (Biochem. J., 1926, **20**, 293—299).—The desiccated thyroid gland is hydrolysed with dilute barium hydroxide and filtered. The residue is worked up separately by the method here described. The filtrate is precipitated by acidification. This precipitate is then submitted to more intensive hydrolysis with barium hydroxide, and after filtering off the barium salts, the hydrolysate is boiled with alkaline sodium sulphate solution and reprecipitated with acid under certain conditions. The precipitate is then dissolved in alkaline alcohol and precipitated once more with acetic acid. This partly crystalline substance on further purification yields a compound with the empirical formula $C_{15}H_{11}O_4NI_4$, containing 65·3% of iodine and showing physical and physiological properties identical with those of thyroxin obtained by Kendall's method (A., 1919, i, 496; 1920, i, 180). The yield by this method is 0·027%, calculated on the fresh thyroid gland, as compared with 0·0011% obtained by Kendall, who used a more drastic method of hydrolysis. S. S. ZILVA.

Effect of irradiation of the environment with ultra-violet light on the growth and calcification of rats fed on a diet deficient in fat-soluble vitamins. Part played by irradiated sawdust. II. E. M. HUME and H. H. SMITH (Biochem. J., 1926, **20**, 335—339).—Irradiated sawdust exercises a beneficial action on growth and calcification only when consumed by the rats. S. S. ZILVA.

Concentrated vitamin-*B* from brewers' yeast. A. SEIDELL (J. Biol. Chem., 1926, **67**, 593—600).—An aqueous extract of the yeast is freed from coagulable protein and the vitamin-*B* in the filtrate adsorbed on fuller's earth; the vitamin is extracted from the adsorbate with 0·3*N*-sodium hydroxide, the solution neutralised with acetic acid, and concentrated in a vacuum. The greater part of the sodium is then removed as sulphate; some inactive organic matter is precipitated by addition of methyl alcohol to 20—30%; the filtrate is again concentrated in a vacuum to a syrup which, on treatment with successive portions of alcohol, yields an amorphous, non-hygroscopic powder, which contains about one-third of the active material of the original yeast, and protects pigeons on a diet of polished rice against loss of weight, when given in doses of 10 mg. on alternate days. C. R. HARINGTON.

Antineuritic vitamin. B. C. P. JANSEN and W. F. DONATH (Chem. Weekblad, 1926, **23**, 201—203).—For the examination of the vitamin preparations, the tropical bird *Munia maja* is more suitable than the pigeon, the former developing polyneuritis in 9—12 days when deprived of the vitamin, as against 2—4 weeks for the pigeon. The vitamin was extracted from rice bran with dilute sulphuric acid, the extract having an acidity corresponding with p_H 4; the aqueous solution was treated with "acid clay," which adsorbs 80% of the vitamin while not removing dissolved substances; the vitamin was set free from the clay by means of baryta and further purified with "norit." The final product from 100 kg. of the bran was 3—4 g. of a semi-crystalline residue, which did not reduce Fehling's solution and contained 10—11·5% of nitrogen, and of which 0·05 mg. per day protected *M. maja* against polyneuritis. S. I. LEVY.

Growth stimulation of *Aspergillus niger* by a vitamin-*B* preparation. N. J. SCHELLING (Bull. Torrey Bot. Club, 1925, **52**, 291—310).—Vitamin-*B* from yeast stimulated both vegetative growth and reproduction. Excess of the vitamin was used as a source of nitrogen. There is a slight increase in gain in dry weight per g. of sugar consumed when vitamin is present. The effects of the vitamin are two-fold; increase of organic food supply and stimulation analogous to that produced by small amounts of such toxic substances as zinc salts. CHEMICAL ABSTRACTS.

Production by irradiation with ultra-violet light of antirachitic properties in sterols derived from the small Siak illipé nut (*Palaquium Burckii*). E. M. HUME and H. H. SMITH (Biochem. J., 1926, **20**, 340—342).—A mixture of sterols from the fat of the small Siak illipé nut was irradiated with

ultra-violet light, whereby the power of promoting growth and calcification in young rats on a diet deficient in fat-soluble vitamins was imparted to the sterols. The mixture of sterols contained no appreciable quantity of vitamin-*A* either before or after irradiation. S. S. ZILVA.

Antirachitic substances. III. Catalytic formation of an antirachitic cholesterol derivative. C. E BILLS (J. Biol. Chem., 1926, **67**, 753—758).—When a solution of cholesterol in carbon tetrachloride, benzene, toluene, or xylene was boiled with a previously ignited fuller's earth, coloured resinous products were formed and were adsorbed on the fuller's earth. The resin could be extracted from the precipitate with ether or acetone, and was found to possess marked antirachitic properties. The reaction did not take place in solution in ethyl acetate or in ethyl, *n*-propyl, or *iso*butyl alcohols. C. R. HARINGTON.

Hydrogenated vegetable oil as a source of vitamin-*E*. C. KENNEDY and L. S. PALMER (Amer. J. Physiol., 1926, **76**, 316—319).—When hydrogenated vegetable oil replaced the lard in the sterility diet of Evans and Bishop, three generations of rats were successfully reared. It would appear that hydrogenation does not destroy vitamin-*E*. R. K. CANNAN.

Action of certain enzymes of *Fusarium*. C. SIBILIA (Atti R. Accad. Lincei, 1926, [vi], **3**, 165—167).—*Fusarium echinosporum* and *F. fuliginosporum* are able to produce amylase which attacks the surface of the granules of the potato starch on which they are grown and causes incipient transformation of the starch into dextrin. These fungi contain also pectase, the action of which is enhanced somewhat by the presence of a small proportion of oxalic acid. T. H. POPE.

Intensity of respiration and content of peroxydase in leaves of *Acer negundo*. A. I. SMIRNOV (Ber. deut. bot. Ges., 1926, **44**, 99—109).—The green parts of the variegated leaves showed a greater content of soluble carbohydrates and of peroxydase per unit weight of tissue, and a greater output of carbon dioxide, than the colourless parts; the differences in the intensity of respiration are in direct relation to the amount both of soluble carbohydrates and of peroxydase present. These findings are not in accordance with the views of Woods (cf. A., 1900, ii, 234) and others, that the occurrence of colourless leaves or parts of leaves is connected with an increased intensity of respiration and decomposition of chlorophyll by oxidising enzymes. C. T. GIMINGHAM.

Gaseous exchanges in arctic brown algæ exposed at low tide. T. KRASCHENINNIKOFF (Compt. rend., 1926, **182**, 939—941).—The carbon dioxide assimilation of arctic brown algæ exposed to the air at low tide is approximately the same as that of land plants, but the intensity of gaseous exchange is considerably less. The respiratory quotient $CO_2 : O_2$ is less than unity. Temperature appears to have but little effect on the results, but light has a marked influence. L. F. HEWITT.

Oxydases of algæ. O. GERTZ (Biochem. Z., 1926, **169**, 435—448).—Oxydases have been detected by the benzidine, guaiacum, and starch–potassium iodide colour reactions in many species of *Rhodophyceæ*, but not in *Phæophyceæ*, *Chlorophyceæ*, *Characeæ*, or *Cyanophyceæ*. Oxydases are not necessarily absent, but substances may be present which inhibit the colour reactions, since the addition of press-juice of *Phæophyceæ* to the juice of *Rhodophyceæ* inhibits, partly or completely, the oxydase reaction of the latter. The oxydase is quantitatively precipitated from the press-juice by 97% alcohol or saturated ammonium sulphate. The enzyme is inactivated by heating to 70°, at which temperature the cell pigment is also destroyed. It retains its activity for many months in the presence of toluene. It is very soluble in water and readily diffusible. The press-juice of the algæ rapidly decolorises methylene-blue, hence the oxydases are probably respiratory enzymes. E. C. SMITH.

Action of neutral salts on the permeability to hydroxyl ions of plant plasma. II. J. PORT (Biochem. Z., 1926, **170**, 377—385).—The action of neutral salts on the penetration of hydroxyl ions through the plasma of leaf cells of *Viola tricolor* is investigated, the hydroxyl ions being derived from ammonium hydroxide, methylammonium hydroxide, and potassium hydroxide. With ammonium and methylammonium hydroxides, the action is identical at the same p_H; ammonium salts assist penetration, the thiocyanate more than the nitrate, the chloride more than the sulphate; the alkali salts (potassium, sodium, lithium, rubidium, calcium) inhibit penetration, thiocyanates less than nitrates, chlorides and bromides less than sulphates; magnesium and calcium salts inhibit strongly; at the same p_H, the assisting and inhibiting actions of neutral salts of each group is the same, the specific effect of the anion being negligible. With potassium hydroxide, only magnesium salts are inhibitory. Ammonium salts, lithium chloride and bromide assist to the greatest extent, and lithium nitrate, sodium, rubidium, cæsium, and calcium chlorides and cæsium sulphate assist, but to a much less extent. P. W. CLUTTERBUCK.

Permeability of protoplasm to ions. M. M. BROOKS (Amer. J. Physiol., 1926, **76**, 116—120).—*Valonia* was suspended in solutions of arsenic or arsenious acids at different hydrogen-ion concentrations and the rates of penetration of the arsenic into the sap and protoplasm were determined. No relation was found between the concentration of undissociated molecules of the acids and the rate of penetration, and the concentration of arsenic rapidly attained within the cell was in some cases immensely greater than that of the undissociated molecules outside. The results do not support the hypothesis of Osterhout that only undissociated molecules penetrate living protoplasm. The *Valonia* did not appear to have been injured by the arsenic and survived as long as untreated plants. R. K. CANNAN.

Influence of acetaldehyde on the carbohydrate content of plants. T. SABALITSCHKA and H. WEIDLING (Ber., 1926, **59**, [*B*], 650—653).—The

action of acetaldehyde in concentrations up to 0·064% on *Elodea canadensis*, R and M, grown in the dark or light (with exclusion of carbon dioxide, but not of air) caused marked increase of the starch content of the plant, the optimal concentration of the aldehyde being 0·032%. Catalase is not markedly affected by acetaldehyde at a concentration of 0·032%, but is damaged at higher concentration. A temporary increase in gas evolution is brought about by 0·001—0·032% of aldehyde. It appears probable that the plant can directly utilise acetaldehyde in the synthesis of carbohydrates. A similar increase in sugar and starch occurs with formaldehyde, but not with propaldehyde. H. WREN.

Content of various forms of carbohydrates in tobacco. V. S. BALABOOCA (Inst. Exp. Tobacco Cult., Krasnodar, Russia, 1924, No. 20, 23—29).—Starch is absent; the better varieties have a higher carbohydrate content, but the cellulose content is approximately the same. CHEMICAL ABSTRACTS.

Comparative plant chemistry. X. Chemistry of barks. II. J. ZELLNER (Monatsh., 1926, **46**, 309—331; cf. A., 1924, i, 814).—Barks of elm, black alder, walnut, and plane trees have been examined by the methods previously outlined. The light petroleum extract (2·44%) of the bark of elm (*Ulmus campestris*, L.) yields, on hydrolysis, glycerol, phosphoric acid, a *compound*, m. p. 134° (*acetyl* derivative, m. p. 117—118°), and a *compound*, m. p. 74—75°. The former compound gives the phytosterol reaction and resembles Hesse's phytosterol, but is optically inactive, and the carbon content is slightly higher than is demanded by the formula $C_{27}H_{46}O,H_2O$. The compound of m. p. 74—75° does not yield an acetyl derivative, and is possibly a wax ester of a hydroxy-acid which resists hydrolysis. The unsaponifiable portion of the ethereal extract (0·89%) contains a *substance*, $(C_{11}H_{20}O_2)_n$, decomp. above 240°, which gives the Liebermann reaction. The alcohol extract (14·65%) contains phlobaphen, from which pyrocatechol, tannins, and invert-sugar were isolated. The aqueous extract (20·47%) contains mineral matter (1·07%), and polysaccharides (0·31%), the latter yielding, on hydrolysis, pentoses and galactose. The bark contains, in addition: free acid (as KOH) 0·28%; reducing sugars, 3·61%; protein, 0·95%; and ash, 6·93%.

Bark of the black alder (*Alnus glutinosa*, L.) yielded similarly: light petroleum extract, 3·01%; ethereal extract, 5·52%; alcohol extract, 14·93%; water extract, 22·16%; soluble polysaccharides, 1·87%; soluble mineral matter, 0·87%; free acid (as KOH), 1·42%; reducing sugars, 3·51%; tannins, 8·68%; total nitrogen, 1·33%; and total ash, 3·51%. The unsaponifiable portion of the light petroleum extract contains alnulin (cf. A., 1924, i, 814), of which a *bromide*, m. p. 219—220°, is described, together with an *alcohol*, $C_{20}H_{42}O$(?), m. p. 83—84° (*acetyl* derivative, m. p. 67—68°), and a *substance*, $C_{32}H_{52}O$(?), termed *protalnulin*, m. p. 240°, $[\alpha]$ −31·2° in chloroform (*bromine additive* product, m. p. 220—222°). Both alnulin and protalnulin yield benzoic acid on oxidation with nitric acid. The acid portion of the hydrolysed light petroleum extract contains resin acids and chlorophyll derivatives, as well as palmitic, stearic, and phosphoric acids. The unsaponifiable portion of the ethereal extract contains protalnulin and coryliresinol (?) (*loc. cit.*), together with an unsaturated *compound*, m. p. 230—235° (*bromine additive* product, yellowish-brown, m. p. 125—127°), and a *compound*, $C_{43}H_{70}O_2$(?). The alkali-soluble portion of the hydrolysed ethereal extract contains phlobaphens and two *acids*, m. p. 82° (impure) and 220°, respectively. The bark contains considerable quantities of calcium oxalate.

Bark of the walnut (*Juglans regia*, L.) yielded: light petroleum extract, 1·56%; ethereal extract, 3·09%; alcohol extract, 9·15%; aqueous extract, 15·04%; soluble mineral matter, 0·32%; free acid (as KOH), 0·71%; tannins, 7·69%; polysaccharides, 0·52%; total nitrogen, 1·20%, and total ash, 1·73%. The light petroleum extract yielded, in the usual manner, palmitic and stearic acids, a hydrocarbon, m. p. 63—64°, identical with that previously obtained by Püringer (A., 1924, i, 815), a *phytosterol*, $C_{20}H_{36}O$, m. p. 171° (*benzoate*, m. p. 142—143°; *acetate*, m. p. 150—151°), an unsaturated *hydrocarbon*, $C_{24}H_{12}$, m. p. 191—192° (*bromine additive* product, m.p. 156—158°), and a dextrorotatory *substance*, $C_{22}H_{38}O$, m. p. 220—221° (decomp.). The ethereal extract yielded, after hydrolysis, a *substance*, $C_{17}H_{28}O_2$ or $C_{18}H_{30}O_2$, pale yellow, m. p. 232°, and a *substance*, m. p. 278° (decomp.), (*acetate*, m. p. 260—261°). The alcoholic and aqueous extracts yielded phlobaphens and tannins, respectively.

Bark of the plane tree (*Platanus orientalis*, L.) yielded: light petroleum extract, 1·52%; ethereal extract, 3·80%; alcohol extract, 8·25%; polysaccharides, 4·64%; tannins, 5·22%; reducing sugars, 3·91%; water-soluble (total), 16·60%; water-soluble mineral matter, 1·15%; free acid (as KOH), 0·68%; total nitrogen, 1·62%; and total ash, 3·89%. Hydrolysis of the light petroleum extract yielded palmitic and phosphoric acids and glycerol, an unsaturated *compound*, $C_{24}H_{12}O_2$, m. p. 250° (acetate, m. p. 217°; *bromine additive* compound, m. p. 125°), possibly identical with the above-mentioned coryliresinol, the above-mentioned hydrocarbon, m. p. 63°, a *hydrocarbon*, $C_{36}H_{74}$, m. p. 68°, and phytosterol, m. p. 134°. The hydrolysed ethereal extract afforded a *substance*, $C_{24}H_{40}O_3$, decomp. 281° (*bromine additive* product, unstable, m. p. 211°; *acetate*, m. p. 277°, monoclinic, $a:b:c=1{\cdot}29065:2:2{\cdot}63500$, $\beta=94°\ 17'\ 8''$; *potassium* derivative; *monomethyl* derivative, m. p. 214—215°). The name *platanolic acid* is applied to this substance, which appears to be a reduced, polynuclear hydroxy-acid. It cannot be nitrated, and is markedly resistant to oxidising agents. The alcoholic extract afforded phlobaphens and tannins, whilst galactose and mannose were identified in the aqueous extract. F. G. WILLSON.

Comparative plant chemistry. XI. *Sonchus arvensis*, L. F. STERN and J. ZELLNER (Monatsh., 1926, **46**, 459—469).—The whole plant was extracted in turn with light petroleum, ether, alcohol, and water. The petroleum extract amounted to 2·41%, and after saponification it yielded ceryl alcohol, α-lactucerol, and stearic and palmitic acids. The ether extract

amounted to 1·04% and mainly consisted of ceryl alcohol (*acetyl* derivative, m. p. 63—64°, b. p. 292°/24 mm.). The alcoholic extract amounted to 16·87% and consisted of: (*a*) tannin substances from which crude pyrocatechol was isolated; (*b*) reducing sugars in which dextrose predominated over lævulose, showing that only a small proportion of these sugars could be derived from inulin; (*c*) choline. The aqueous extract amounted to 33·24%, and consisted of tartaric acid and polysaccharides.

The light petroleum extract of the latex was hydrolysed with 10% potassium hydroxide solution, and the following products were isolated: (*a*) caoutchouc; (*b*) α-lactucerol, m. p. 193—194° (*acetyl* derivative, m. p. 215°); (*c*) β-lactucerol, m. p. 149—150° (impure *acetyl* derivative, m. p. 228°) (cf. Hesse, A., 1886, 1020); (*d*) a small quantity of a weak acid, m. p. 139—140°, probably a dihydroxystearic acid. The substance known as lactucon (lactucerin) is probably a mixture of the α- and β-lactucerol acetates (cf. Kassner, A., 1887, 605; Hesse, *ibid.*, 1888, 722; Pomeranz and Sperling, *ibid.*, 1904, i, 907). The petroleum-extracted latex was extracted with alcohol. Mannitol separated from the solution and the mother-liquor yielded a substance, $C_6H_{12}O_6$, m. p. 240° (decomp.), $[\alpha]_D$ −57·8° (acetyl derivative, m. p. 52°), probably *l*-inositol. R. W. West.

Physiological rôle of starch deposits in green parenchyma of leaves. V. Lubimenko (Compt. rend., 1926, **182**, 651—653).—In latitudes north of 60° N., starch reserves in the parenchyma are not depleted during the night. South of 50° N. the starch reserves are depleted completely at night on occasion and partial depletion may occur even during the day. In general, maximum starch reserves are found at the end of the first half of the day. Some species (*e.g.*, *Nicotiana tabacum*) have one maximum and one minimum daily, others (*e.g.*, *Phaseolus vulgaris*) have two maxima and two minima on bright sunlit days, and in certain other species (*e.g.*, *Robinia pseudacacia*) a number of maxima of starch content occur during the day, followed by minima. L. F. Hewitt.

Autumnal migration of nitrogenous substances in the oak. R. Combes (Compt. rend., 1926, **182**, 984—987).—By determination of the nitrogen in oak leaves, stems, and roots in 2-year-old plants it has been shown that the nitrogen migrates from the leaves during the autumnal fading and accumulates in the stems and roots, the total quantity in the plant remaining approximately constant.
L. F. Hewitt.

Mechanism of the accumulation of dye in *Nitella* on the basis of the entrance of the dye as undissociated molecules. M. Irwin (J. Gen. Physiol., 1926, **9**, 561—573).—The rate of penetration of brilliant-cresyl-blue into the living cells of *Nitella* indicates that the dye enters as undissociated molecules only; at equilibrium the concentration of the dye in the sap is proportional to that of the free base in the surrounding medium. H. J. Channon.

Effect of p_H, light, and other factors on the penetration of 2 : 6-dibromophenol-indophenol and other dyes into a living cell. M. M. Brooks (Amer. J. Physiol., 1926, **76**, 190).—When the proportion of the undissociated indophenol in a solution in which *Valonia* was immersed was changed by changing the p_H, the amount of dye in the sap at equilibrium was proportional to the concentration of undissociated molecules of dye in the outer solution. Penetration was greatest in diffuse light and decreased with increasing wave-length of the light. The penetration of methylene-blue was not related to the p_H of the external fluid or of the sap. The reduction potential of the sap was between r_H 16 and 18.
R. K. Cannan.

Influence of light on the absorption by plants of phosphoric acid and potassium. M. Nemec and M. Gracanin (Compt. rend., 1926, **182**, 806—808).—The absorption of phosphoric acid by young rye plants remains practically constant whether cultivated under white, green, violet, or red glass. Plants under violet or red light, however, absorb considerably more potash than the others.
B. W. Anderson.

Development of castor-oil plants under the radioactive influence of thorium-*X*. Aversenq, Jaloustre, and Maurin (Compt. rend., 1926, **182**, 804—805).—Castor-oil plants, treated daily with water containing 10 micrograms of thorium-*X*, are found to be markedly superior in size, weight of seeds, etc., to plants watered in the ordinary way.
B. W. Anderson.

Action of radiations from radioactive substances on leaf excrescences. C. Rouppert and H. Jedrzejowski (Compt. rend., 1926, **182**, 864—865).—Leaves of *Piper Ficadatsura* and of *Leea coccinea* were submitted to the action of α-, β-, and γ-rays from radium emanation. The excrescences survived the irradiation even when the portions of the leaf under them were destroyed; this is ascribed to the high potassium-ion content of the excrescences. The multicellular excrescences of *Leea* proved more resistant to the rays than the unicellular ones on *Piper*. L. F. Hewitt.

Value of litmus, bromocresol-purple, and Janus-green milk in a study of the nodule organisms of *Leguminosæ*. J. W. Stevens (J. Agric. Res., 1925, **31**, 997—1000).—Litmus proved to be the most useful indicator. Litmus milk brings out characteristics of the nodule bacteria not shown by plain milk and can be used for separating the organisms into two groups. H. J. Channon.

New form of quinhydrone electrode. W. Mozolovski and J. K. Parnas (Biochem. Z., 1926, **169**, 352—354). E. C. Smith.

Hydrogen electrode for body-fluids containing carbon dioxide. W. Schmitt (Biochem. Z., 1926, **170**, 391—394). P. W. Clutterbuck.

Rapid dialyser for clinical purposes. A. Gutbier and B. Ottenstein (Biochem. Z., 1926, **169**, 427—431).—A modification of the rapid dialyser previously described (A., 1922, ii, 551) for small quantities of physiological material. E. C. Smith.

Method of measuring directly the partial and total pressures of the gases of the blood. E. P. POULTON, W. R. SPURRELL, and E. C. WARNER (J. Physiol., 1926, **61**, 232—244).—Apparatus and technique are described for the determination of the total gas pressure and the partial pressures of oxygen, carbon dioxide, and nitrogen in physiological fluids. The method follows the " bubble " method of Krogh. The scope and accuracy of the method are outlined experimentally. R. K. CANNAN.

Determination of sugar in blood and normal urine. O. FOLIN (J. Biol. Chem., 1926, **67**, 357—370).—The recent method of Benedict (A., 1925, i, 994) for the determination of sugar is confirmed as being of practical utility, but criticised on theoretical grounds. By reduction of the alkalinity of the cupric tartrate solution and modification of the phosphomolybdic acid reagent, results can be obtained by the method of Folin and Wu (A., 1920, ii, 337) which are comparable to those obtained by Benedict's method (*loc. cit.*). The present author agrees with Benedict that the lower results so obtained probably approximate more closely to the true concentration of dextrose. C. R. HARINGTON.

Nephelometric micro-determination of carbamide. Determination of carbamide content of blood. C. AUGUSTE and S. AUGUSTE (Compt. rend. Soc. Biol., 1925, **93**, 639—640, 641—642; from Chem. Zentr., 1925, II, 2179).—Serum or cerebrospinal fluid (0·1 c.c.) is diluted with an equal volume of water. Acetic acid (0·3 c.c.) and xanthhydrol (0·1 c.c. of a 1 : 30 solution in acetic acid), and, after 1 hr., a further 1·2 c.c. of xanthhydrol solution, together with an equal volume of acetic acid, are added, and the determination is made by means of a colorimeter. The determination may also be carried out by diluting 10 c.mm. of blood with 1 c.c. of 50% acetic acid and shaking with 4 drops of a 5% solution of xanthhydrol in methyl alcohol. A nephelometric reading is made after 3 min. If the solution is clear, the azotæmia is normal (about 0·02%). A slight turbidity indicates an azotæmia of about 0·05%. Distinct turbidity indicates pathological azotæmia. G. W. ROBINSON.

Determination of serum-tryptase. L. and X. UTKIN-LJUBOVZOV (Biochem. Z., 1926, **169**, 100—104).—Tryptase is adsorbed by caseinogen. The protein is precipitated, washed, and redissolved, the solution being then adjusted to p_H 7·1, the optimum for the serum tryptase. A determination of the residual nitrogen not removed by colloidal iron after the mixture has been allowed to digest for 24 hrs. at 38° affords a measure of the quantity of tryptase present. An objection to the method is that adsorption by caseinogen is not complete. C. RIMINGTON.

Clinical determination of salicylic acid in serum and cerebrospinal fluid. K. LOBERG (Biochem. Z., 1926, **170**, 173—184).—The serum or cerebrospinal fluid is treated with alcohol and trichloroacetic acid to precipitate the proteins. This procedure was found effective in preventing the retention of salicylic acid by the protein precipitate. After neutralisation of the filtrate and addition of a standard volume of trichloroacetic acid, ferric chloride is added, and the violet colour compared in a colorimeter with that of a standard solution of salicylic acid similarly treated. To compensate for a substance in the filtrate which gives an orange colour with ferric chloride, Bismarck-brown is added to the standard. R. K. CANNAN.

Determination of bilirubin in sera and intestinal fluids. E. ENRIQUES and R. SIVÓ (Biochem. Z., 1926, **169**, 152—160).—The diazo method is modified by the use of caffeine solutions in place of alcohol on the basis of the observations of Adler and Strauss (Klin. Woch., 1923, No. 20). C. RIMINGTON.

Micro-determination of the globulin content of the cerebrospinal fluid. I. NÁDOR (Magyar Orvosi Archiv., 1925, **26**, 519—521).—Ten tubes are prepared containing 0·01—0·1% of serum-globulin dilutions. To an eleventh tube are added 2 drops of cerebrospinal fluid, and after addition of 1 c.c. of 6·75% phenol to each of the tubes, the opacities are compared. CHEMICAL ABSTRACTS.

Determination of nitrogen in urine and in blood. R. FOIT (Biochem. Z., 1926, **169**, 161—168).—The material is oxidised by sulphuric acid and hydrogen peroxide in the absence of any catalyst, and the ammonium sulphate so produced decomposed by sodium hypobromite solution in such a manner that the volume of nitrogen evolved can be measured in a graduated burette. Quantities of nitrogen from 0·2 to 10·0 mg. are suitable and the determination requires 15—20 min. for urine, slightly longer for blood. C. RIMINGTON.

Determination of gold in organic substances. R. COQUOIN (Compt. rend Soc. Biol., 1925, **93**, 584—586; from Chem. Zentr., 1925, II, 2178—2179).—The incinerated material is treated with excess of hydrochloric acid, evaporated to dryness, and ignited. The presence of small traces of gold is shown by a characteristic violet colour, where there is not too great an excess of iron present. After extracting the ignited mass with water, dissolving the residue in chlorine water or bromine water, evaporating to dryness and igniting in a porcelain crucible, the violet coloration is shown with as little as 0·001 mg. of gold. Alternatively, the crystalline antipyrine chloroaurate may be prepared from the hydrochloric acid solution. By this method, 0·01 mg. of gold may be determined. Gold may be detected in the urine 10 min. after injection of sodium gold thiosulphate. The rate of excretion can be observed for more than 48 hrs. G. W. ROBINSON.

Fairhall (chromate) method for determining minimal amounts of lead in fæcal specimens. ANON.—See this vol., 592.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JULY, 1926.

BIBLIOTEKA POLITECHNIKI

General, Physical, and Inorganic Chemistry.

Application of the method of Kurlbaum and Günther-Schulze to the photometry of spectral lines. C. HEINRICH (Z. Physik, 1926, **36**, 782—785; cf. Verh. Physikal. Ges., 1903, **5**, 428).—The measurement of the energy of a spectral line by comparison with a continuous spectrum depends on the width of the slit. The conception of the "black body temperature of a spectral line for a certain width of slit" is introduced, and an equation is deduced which is in agreement with the experimental results obtained by varying the width from 0·20 to 0·08 mm. E. B. LUDLAM.

Greater dispersion in the extreme ultra-violet. R. J. LANG and S. SMITH (J. Opt. Soc. Amer., 1926, **12**, 523—528; cf. A., 1925, ii, 609).—A vacuum grating spectrograph is described capable of accommodating a grating of 2 metres radius of curvature, and of being maintained at the very low pressure necessary for the production of the high potential spark. Means are provided for introducing and removing the photographic plate and for altering the focus and inclination of the grating while the vacuum is maintained. The C II doublets at 858 and 687 Å. have been resolved, the frequency separations being 62 and 64·5, respectively. The observed separations for the carbon doublets at 1335 and 1036 Å. and for the Si III doublet at 457 Å. were 65·7, 62·6, and 153, respectively.

A. B. MANNING.

Intensities and reflecting powers in the Lyman region of the hydrogen spectrum. A. H. PFUND (J. Opt. Soc. Amer., 1926, **12**, 467—472).—The total energy of radiation emitted by a hydrogen discharge tube has been compared with that fraction of it which is transmitted by a glass or fluorite screen. The discharge tube was attached directly to a bell jar, in which the light from the tube was reflected from a concave glass mirror on to the junction of a thermocouple connected to a sensitive galvanometer. Reflexion of the beam was necessary to prevent the stream of ions and electrons issuing from the discharge tube directly affecting the thermocouple junction. A glass or fluorite screen, controlled by an external magnet, could be moved into or out of the beam. To measure the reflecting power of the glass mirror, a second similar mirror was so mounted that the energy of radiation after two reflexions could be compared with that after one. The pressure in the whole apparatus was reduced until the secondary hydrogen spectrum disappeared, and the energy intensities were compared. Identical results were obtained with the glass or the fluorite screen, whence it was concluded that the Lyman series (1216—912 Å.) was the carrier of the absorbed energy. This energy was 8·8 times that carried by the other hydrogen series. The reflecting power of a number of surfaces in the Lyman region has been determined. Metals reflect only 5—8% of the incident radiation in this region. The highest reflecting power observed, 13·5%, was that of crystalline quartz.

A. B. MANNING.

Spark line 4686 of He^+. P. KUNZE (Ann. Physik, 1926, [iv], **79**, 610—636).—The 4686 ($3d$—$4b$) line is suitable for the investigation of fine structure with glass apparatus, and the results have been compared with the requirements of the Sommerfeld relativistic theory (compare Paschen, *ibid.*, 1916, **50**, 901). Echelon gratings and Lummer plates have been used in conjunction with the sources: (*a*) hollow cathode, condenser discharge; (*b*) electron tube, field space; (*c*) hollow cathode, direct current; (*d*) electron tube, no field. Different combinations of apparatus lead to the following separations using Paschen's nomenclature (*loc. cit.*) in Å.$\times 10^{-3}$: I_{ab}—II_{ab} in field, 99·5, 117, 108, 103; I_{ab}—III_{ab} in field, 499·1, 495·5, 496; I_a—II_b no field, 102·5, 102·1, 106; I_a—III_c no field, 422·1, 421. The last figure quoted is in each case due to Paschen. The III_{ab} line is foreign, and a weak foreign line also coincides with I_{ab}. The only way to excite the structure free from foreign lines appears to be by electron impacts. Both the structures with and without a field occur by this means, although they are less sharp than when the hollow cathode tube is run on direct current. R. A. MORTON.

Extension of *X*-ray spectra towards the ultra-violet. The *K* spectrum of carbon. A. DAUVILLIER (Compt. rend., 1926, **182**, 1083—1085).—Using a graphite cathode in an *X*-ray tube, the author has succeeded in recording directly a line at 45·3 Å. This is the $K\alpha_2$ line of carbon. The rays were dispersed by a thin film of melissic acid supported on lead. A "grating" of this substance gives spacings of 87 Å. Fogging of the plates by diffuse light was troublesome, and was avoided by introducing a screen of magnesium, sputtered on to a thin film of celluloid. S. BARRATT.

Spectrum of ionised oxygen (O II). R. H. FOWLER and D. R. HARTREE (Proc. Roy. Soc., 1926, **A**, **111**, 83—94).—The terms observed in this spectrum (this vol., 445) are accounted for almost completely by the theory of Heisenberg and of Hund (A., 1925, ii, 729, 1104). The deepest term is probably a quadruplet S term, although no lines involving this have so far been identified. R. CUTHILL.

Intensity relations of the ($2s$—$2p$) combinations of the neon spectrum under different conditions of excitation. H. B. DORGELO and W. DE GROOT (Z. Physik, 1926, **36**, 897—901).—The combinations of the $2s$—$2p$ terms of neon were measured in the spectra from the positive column, the negative glow, impact of electrons of 23·5 volts, and resonance radiation. The ratio of the intensities $(2s_x—2p_k) : (2s_y—2p_k) : (2s_z—2p_k)$ were equal for each value of k under all conditions; but the ratio $(2s_m—2p_x) : (2s_m—2p_y) : (2s_m—2p_z)$ was in each case different. E. B. LUDLAM.

Secondary standards of wave-length in the spectra of neon and iron. G. S. MONK (Astrophys. J., 1925, **62**, 375—386).—A comparison of 20 neon lines with a primary cadmium standard, and of 110 lines of the iron arc with the neon spectrum. Systematic variations from tables already published (U.S. Bur. Standards, Bull. 478) are disclosed. The use for secondary standards of an iron arc in a vacuum is not recommended. A. A. ELDRIDGE.

Sodium arc in a vacuum. F. H. NEWMAN (Phil. Mag., 1926, [vii], **1**, 940—944).—With a modified sodium arc lamp it has been found that under high vacuum conditions the heat from the arc itself was sufficient to produce the vapour necessary for the discharge. The arc will not persist with a current of less than 1·5 amp. and will not strike with an applied voltage less than 90 volts, although when once started it will persist with a $P.D.$ of 40 volts. Initially, the spectra obtained are due to residual nitrogen, hydrogen, and oxygen, with special prominence of the lines belonging to the positive bands between 6878 and 5754 Å. With removal of all the air, the Balmer series of hydrogen appears, the Fulcher band in the red being specially predominant. Finally, as the quantity of sodium vapour increases, the lines of the principal and subordinate series of sodium predominate. If the current is then decreased so as to give a lowering of the arc temperature and a reduction of the vapour pressure of the metal, the character of the radiation changes from yellow to the green observed by Rayleigh (Nature, 1914, **93**, 32). A. E. MITCHELL.

Natural width of spectral lines and widening due to pressure. R. MINKOWSKI (Z. Physik, 1926, **36**, 839—858).—The sodium D-line begins to widen when the sodium vapour reaches a pressure of 10^{-2} mm. The natural half width of the line was found to be $0{\cdot}62\times10^{8}$ sec.$^{-1}$. The magnitude of the effect of pressure indicates powerful mutual action of like atoms on each other. E. B. LUDLAM.

Irregularity of the $K\alpha$ doublets in the elements of lower atomic numbers. D. M. BOSE (Physical Rev., 1926, [ii], **27**, 521—529).—An explanation of the deviation of the experimental from the calculated values of $\Delta\nu/R(Z-3{\cdot}5)^4$, where Z is the atomic number, is based on the assumption that the difference in energy radiated by the emitting atom in the two states corresponding with the two orbits of the radiating electron is due, not only to the relativity change of mass of the latter, but also to the change in the magnetic energy of the atom in these two states. The anomalous behaviour of the $K\alpha$ doublets of the elements scandium to copper is accounted for if it is assumed that in the atoms of these elements strong inner magnetic fields exist, whereby the author's hypothesis of the successive formation of the M_{33} and M_{32} sub-levels is supported. A. A. ELDRIDGE.

Displaced series in the spectrum of chromium. C. C. KIESS and O. LAPORTE (Science, 1926, **63**, 234—236).—The ultra-violet spectrum of the chromium spark contains a triplet, 2055·51, 2061·50, 2065·43 Å., in the position anticipated from a consideration of series relationships. The normal state of Cr^+ is now considered to be ^6S (five 3_3 electrons). The normal states of the neutral, ionised, and doubly ionised atoms of scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, eka-manganese, ruthenium, rhodium, palladium, silver, and cadmium are tabulated. A. A. ELDRIDGE.

Absorption spectra of tellurium, bismuth, chromium, and copper vapours in the visible and ultra-violet. R. V. ZUMSTEIN (Physical Rev., 1926, [ii], **27**, 562—567).—Tellurium at 1600° shows four absorption lines corresponding with the arc lines 2385·793, 2383·268, 2259·02, and 2142·94 Å., the last two being broad. New arc lines were observed reversed at 2001·87 and 1994·07 Å. Of 8 bismuth absorption lines, 4 are new. Three chromium triplets were observed in absorption; of 19 copper absorption lines, 9 are new, the latter being from excited states. A. A. ELDRIDGE.

[Manganese] doublet $K\beta_1$. G. ORTNER (Nature, 1926, **117**, 823).—A criticism of Seljakov and Krasnikov's inference (this vol., 446) that the lines $K\beta_1$ and $K\beta'$ in the X-ray spectrum of manganese form a relativity doublet characterised by the energy difference $M_{II}—M_{III}$. Wentzel's hypothesis is preferred. With iron compounds, the intensity ratio is estimated to be also 2 : 1, but with titanium and vanadium a considerably larger value was obtained. A. A. ELDRIDGE.

Fundamental level of the iron atom. O. LAPORTE (Nature, 1926, **117**, 721—722).—Polemical against Sur (this vol., 329). The author seeks to show that no other term lower than ^5D can exist, and that only ^5D can be the fundamental lower level of the iron spectrum. A. A. ELDRIDGE.

Second spark spectrum of iron. L. BLOCH and E. BLOCH (Compt. rend., 1926, **182**, 1018—1020; cf. J. Phys. Radium, 1924, [vi], **3**, 51).—The arc and spark spectra of iron have been mapped in the region 2300—1850 A., and here show no similarity. The lines of the spark spectrum are separated into

two series, designated E_1 and E_2, which appear on the negatives as long and short lines, respectively, and probably correspond with spark spectra of the first and second order (Fe II and Fe III). The E_2 series is absent from the arc spectrum. The following wave-lengths are observed: E_1, 2164·30, 2161·99, 2161·09, 2150·58, 2147·64, 2146·00, 2136·45, 2110·69, 2080·20, 2065·87, 2063·60, 2051·05 Å.; E_2, 2100·85, 2099·21, 2097·62, 2097·37, 2091·25, 2090·04, 2084·27, 2078·88, 2070·43, 2068·17, 2061·60 (double), 2059·59, 2058·49 Å. F. G. SOPER.

New method of using diffraction gratings applied to Millikan's study of the ultra-violet. J. THIBAUD (Compt. rend., 1926, **182**, 1141—1143; cf. this vol., 333).—The spectra of a number of metals in the extreme ultra-violet have been studied using a vacuum spectrograph and a diffraction grating employed in the manner previously described. The lines obtained by Millikan and Bowen (A., 1924, ii, 214) extending to 211 Å. have been confirmed. The extreme rays obtained for iron and for platinum are about 350 Å. F. G. SOPER.

Arc spectra of copper. C. G. BEDREAG (Compt. rend., 1926, **182**, 1209—1211).—The arc spectrum of copper is made up from Rydberg doublets, from rays belonging to a second complex spectrum consisting of doublets and quadruplets, and from combinations of these. The division of the rays between these categories, and also their respective terms (T), have been re-determined using the relation $T = n_{kj}$ cm.$^{-1}$, where n, k, and j are the principal, azimuthal, and interior quantum numbers, respectively. New rays, obtained by the use of intense electric fields (200 volts) which produce the Stark effect, are recorded. J. GRANT.

Quartet terms in arc spectrum of copper. C. S. BEALS (Proc. Roy. Soc., 1926, **A**, **111**, 168—181).—By Zeeman measurements a number of complete quadruplet multiplets have been identified in the above spectrum, these including many of Shenstone's terms (A., 1925, ii, 1014). By combination of the new terms with terms of the old doublet system, their absolute values have been calculated. Since the spectra of the alkali metals contain no quadruplet terms, doubt is cast on the accuracy of Bohr's atomic structure of copper. R. CUTHILL.

New lines ($1S$—$2p_{1,3}$) of zinc, cadmium, and mercury. M. FUKUDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 171—176).—The mercury line ($1S$—$2p_3$) at 2656 Å. has been obtained previously only by Frank and Einsporn (Z. Physik, 1920, **2**, 18), who used the method of ionisation by impacts of electrons on atoms. The authors have obtained the line by passing a condensed discharge through a tube with a conical-shaped capillary. They have obtained it also by means of a heavy condensed discharge in a Geissler tube of very narrow capillary. The cadmium lines $1S$—$2p_1$ and $1S$—$2p_3$ at 3141 and 3320 Å., respectively, and the zinc line $1S$—$2p_1$ at 3040 Å. were obtained from the analysis of the end-on emission from a discharge tube, using a heavy condensed discharge. The cadmium line, $1S$—$2p_1$, and the zinc line, $1S$—$2p_3$, were observed in the heavy current vacuum arc. The current densities required for their emission were about 120 and 200 amp./cm.^{2}, respectively. A. E. MITCHELL.

Spectra of rubidium and krypton. O. OTSUKA (Z. Physik, 1926, **36**, 786—794).—The ultra-violet part of the spark spectrum of rubidium was measured, and tables are given of the wave-lengths. The spectrum of krypton from the red up to 3665 Å. was measured and tables are given. The cyanogen bands also appear, but with a displacement of intensities towards bands of smaller rotation quanta. E. B. LUDLAM.

Spectral structures for elements of the second long period. W. F. MEGGERS and C. C. KIESS (J. Opt. Soc. Amer., 1926, **12**, 417—447; cf. A., 1925, ii, 612; this vol., 446).—Further progress has been made in the analysis of the spectra of elements of the second long period, in particular of yttrium, zirconium, niobium, and molybdenum. The doublet system for Y I and the triplet system for Y II have been revised and extended, and the inter-system combinations have been tabulated. Similarly, new wave-length measurements and Zeeman effect data have been used to extend the analyses of Zr I, Zr II, Nb I, Nb II, Mo I, and Mo II. Some of the multiplets in the Ru I and Rh I spectra are also tabulated. With increasing atomic number, deviations from the interval rule for multiplets are observed in all types of levels. Deviations from the Landé g values for the splitting of spectral levels in low magnetic fields are also found. The rule that the *raies ultimes* are related to the normal state of the atom receives additional support from these analyses. A. B. MANNING.

Change of wave-length of the cadmium red line 6438·7 Å. M. FUKUDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 167—170).—The wave-length of the cadmium red line 6438·7 Å., produced in an ordinary Geissler tube, with an inductive and a non-inductive circuit, has been examined with the aid of a Nagaoka "interferential prism" interferometer. When a self-inductance of 8×10^{-4} henry was removed from the circuit, a shift of wave-length of 0·044 Å. towards the red end of the spectrum was observed. The current flowing in the tube was 600 milliamp. as against the 25 milliamp. specified when obtaining this line for use as a primary wave-length standard. The shift observed in the experiment is not considered likely to influence the evaluation of standards of length. A. E. MITCHELL.

***K*-Emission spectra for the elements tin (50) to hafnium (72).** J. M. CORK and B. R. STEPHENSON (Physical Rev., 1926, [ii], **27**, 530—537).—Measurements were made of the K-series emission wave-lengths of tin, antimony, tellurium, iodine, cæsium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, thulium, ytterbium, lutecium, and hafnium. Tabulated data concerning λ, ν/R, and $\sqrt{\nu/R}$ are given for $K\alpha$, $K\alpha'$, $K\beta$, $K\beta'$, and $K\gamma$ emission lines, together with curves showing the

relation of $\sqrt{\nu}/R$ and of the wave-length differences, $(\alpha'-\alpha)$ and $(\beta-\gamma)$, respectively, to the atomic number. A. A. ELDRIDGE.

L-Absorption limits of tungsten; photometric measurements. C. B. CROFUTT (Physical Rev., 1926, [ii], **27**, 538—541).—Photometric values are for L_1 1·2117, and L_2 1·0708, more trustworthy values being 1·2122 and 1·0716 Å., respectively, obtained by direct measurement. A. A. ELDRIDGE.

L-Emission series of mercury. C. E. EDDY and A. H. TURNER (Proc. Roy. Soc., 1926, **A**, **111**, 117—124).—The results of Müller (A., 1921, ii, 569) have been confirmed by a more accurate method and some new lines have been measured. R. CUTHILL.

Time of excitation of hydrogen atoms. J. S. MCPETRIE (Phil. Mag., 1926, [vii], **1**, 1082—1094).—The time of excitation of the H_β line of the Balmer series has been determined by two methods. One involves the excitation by means of high-velocity positive rays, whilst the other employs rays of slow and medium velocity. The first method gives a time of excitation of about 10^{-8} sec., whilst the second gives times of 2×10^{-8} and $7{\cdot}5\times10^{-9}$ sec. for excitation and emission, respectively. The variations in the observed times of excitation are discussed. Dempster (Physical Rev., 1920, [ii], **15**, 138) has shown that the combined time of excitation and emission is about 5×10^{-8} sec. It is shown, therefore, that the time of excitation is comparable with that required for emission. The existence of a finite time of excitation is regarded as necessary to bring the measurements of Stark (Ann. Physik, 1914, [iv], **43**, 968; 1915, **48**, 194) into line with Wien's results on the rate of decay of emission in the beam. The emitted line has a definite frequency which must correspond with a definite time in which an electron occupies an excited orbit. A. E. MITCHELL.

Duration of light emission from atoms of alkali metals, oxygen, and nitrogen. H. KERSCHBAUM (Ann. Physik, 1926, [iv], **79**, 465—488).—Wien's methods (A., 1924, ii, 362) have been adapted to the excitation of bright canal rays of the alkali metals. Earlier experiments on oxygen and nitrogen have been extended towards the red. The Döppler effect has been used to determine the velocity of oxygen, nitrogen, lithium, and sodium positive rays, and thence the mean value of the duration of light and the damping constants have been evaluated. The decay of intensity of spectral lines has been measured photometrically using a quartz spectrograph and a wedge-shaped trough containing a solution the absorption curve of which is known accurately.

The following results were obtained, in which 2α is the damping constant and T, its reciprocal, the mean value of the duration of light in sec.:

			Nitrogen.		Oxygen.		
Element.	Hydrogen.	Lithium.	Spark.	Arc.	Spark.	Arc.	Sodium.
$2\alpha\times10^{-7}$	5·54	1·54	7·40	1·06	6·54	0·67	2·7
$T\times10^{8}$	1·81	6·51	1·35	9·45	1·53	14·9	3·7

For mercury, Wien found by this method $1{\cdot}82\times10^{-8}$ for 4353, and $9{\cdot}8\times10^{-8}$ for 0·2536 Å., whilst an entirely different method led to values of T for mercury of $1{\cdot}0\times10^{-8}$ and for sodium of $1{\cdot}35\times10^{-8}$ sec. R. A. MORTON.

Absorption spectra produced by the explosion of various elements. T. HORI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 59—78).—The explosion spectra of various elements have been examined by the method of Anderson. The requisite continuous background has been found to be satisfactorily developed by the explosion of mercury either at atmospheric or under diminished pressures. A large number of absorption lines, both series and non-series, due to excited atoms of copper, mercury, and iron were obtained on this background. With copper and iron, complete reversal was obtained. The order in which various lines are reversed under different exploding voltages has been examined. In the visible region, the continuous spectrum of incandescent carbon atoms has been made to provide the background; and the explosion spectra, in this region, of various elements of groups I and II have been examined. A large number of reversals has been obtained. The results are tabulated and many spectrophotographs are reproduced. A. E. MITCHELL.

Spectra of metals under heavy current excitation. M. FUKUDA, T. KUYAMA, and Y. UCHIDA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 177—188).—The spectra of zinc and cadmium emitted from a specially constructed vacuum arc have been examined and are found to resemble the emissions from the constricted arc used previously by Takamine and Fukuda (A., 1925, ii, 166, 725). The lines of the diffuse series suffer broadening, whilst those of the sharp series remain fairly sharp. The amount of broadening in the pd series increases with the term number, and it is suggested that this is due to a Stark effect brought about by the close gathering of the ions. A large number of lines not obtained in an ordinary arc, and including many which, according to the selection principle, should be absent, have been observed, and their wave-lengths and series notations are tabulated. Some lines of the series $1S-p_{1,2,3}$ the emission of which should be precluded by inner quantum conditions have been observed. The newly-observed terms have been arranged in sequences and their energy levels calculated approximately. In the cadmium spectrum, the group of emission lines identified by Ruark and Chenault (A., 1925, ii, 725, 1103) as belonging to the pp' doublets has been observed. Of six possible members, those involving the $2p'_1$ term were missing. A. E. MITCHELL.

Fine structure and Zeeman effect of complex mercury lines. A. E. RUARK (Phil. Mag., 1926, [vii], **1**, 977—995; cf. A., 1925, ii, 1103).—A general review and analysis of the existing data on the Zeeman effect of complex lines in the spectrum of mercury with some results for cadmium and thallium. It is shown that the existing data do not enable deductions of general rules for the prediction of Zeeman patterns to be made from a knowledge of

the quantum numbers of a given level. It is established, however, that in all the definitely investigated patterns, the main line has the Zeeman pattern appropriate to simple lines of the same series notation. In general, many of the mercury satellites show the same type of frequency separation as the main lines.
A. E. MITCHELL.

Stark effect. C. E. DEPPERMANN (Astrophys. J., 1926, **63**, 33—47).—A study of the zinc triplet $1s$—$1p$ under fields of 3—4×10^4 volts/cm., and dispersions of 10—4 Å./mm., revealed a negligible, if any, Stark effect. Preliminary results for the $1s$—$1p$ triplet of cadmium and the thallium line 1π—1σ are similar. A. A. ELDRIDGE.

Spark discharge in heterogeneous media. The mechanism of lightning discharge. T. TERADA, U. NAKAYA, and K. YUMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 129—160).—Various types of spark discharges have been investigated on the surface of balloon fabrics impregnated with aluminium dope and in suspensions of metallic powders in dielectrics. The type of discharge obtained is intimately connected with the granular structure of the fabrics and analogous substances, the surfaces of which are considered as a complicated system of multiple spark gaps. Then, as was actually observed, the effect of repeated sparking is gradually to tear off the granules so that the gaps are widened, which for a given applied *E.M.F.* increases the potential between the gaps, whilst decreasing the field between them, thus giving the observed increase of spark intensity with continued discharge. This multiple gap effect is considered to be responsible for the intensity of the effects in lightning discharges.
A. E. MITCHELL.

Photo-electric effect in very high vacuum and its dependence on the pressure. O. RIETSCHEL (Ann. Physik, 1926, [iv], **80**, 71—108).—The question whether the photo-electric effect is due to adsorbed gas has been investigated. An improvement in the vacuum reduces the adsorption of gas on the photo-metal and increases the photo-electric effect, and *vice versa*. If the metal has been well outgassed, a high vacuum in the tube renders the true metal effect possible by hindering adsorption; a poor vacuum increases the conductivity of the tube and masks the high photo-electric effect.

The use of badly outgassed metal leads to a small effect only in a relatively poor vacuum, and good photo-electric effects are observed only with metal which has been well outgassed when the general vacuum is good. R. A. MORTON.

Thermionic phenomena caused by vapours of rubidium and potassium. T. J. KILLIAN (Physical Rev., 1926, [ii], **27**, 578—587).—The degree of thermal ionisation was consistent with Saha's equation. At low temperatures, a tungsten filament in rubidium or potassium vapour becomes covered with a layer of adsorbed atoms; with rise of temperature the electron emission increases logarithmically with the reciprocal of the temperature, reaches a maximum, and then decreases on account of evaporation. The positive ion emission increases logarithmically with the reciprocal of the temperature until a discontinuity occurs, when further rise of temperature causes every atom to be ionised. The vapour pressures of rubidium and potassium are given by the expressions $\log p(\text{bars})=10{\cdot}55-4132/T$ and $\log p(\text{bars})=11{\cdot}83-4964/T$, respectively, where T is the absolute temperature. A. A. ELDRIDGE.

Magnetic moment of the electron. R. DE L. KRONIG (Proc. Nat. Acad. Sci., 1926, **12**, 328—330; cf. this vol., 448).—The spinning electron hypothesis (Uhlenbeck and Goudsmit, Naturwiss., 1925, **13**, 953; this vol., 215) is criticised on the grounds that, in order to account for observed Zeeman effects, it assigns to an electron spinning with an enormous velocity a magnetic moment of two Bohr magnetons, and that it apparently involves a magnetic moment of the nucleus, which would make Zeeman effects quite different from what they are. J. S. CARTER.

Motion of electrons in hydrogen and helium. H. B. WAHLIN (Physical Rev., 1926, [ii], **27**, 588—595).—Using the Rutherford alternating potential method, determinations were made of the mobilities of electrons in hydrogen and helium at 760 mm. for fields from 0·5 to 46 volts/cm. Limiting mobilities for zero field are computed for hydrogen, 6700, and for helium, 10,840 cm./sec. per volt/cm. If the electron is assumed to lose on impact a fraction of its energy which for hydrogen is 2·16 and for helium 8·6 times what it should be on the basis of elastic impacts, the results are in accord with Compton's theory of electronic mobilities. Values for the mean free path for 1 mm. pressure computed, respectively, from the limiting mobility and from the kinetic theory are: for hydrogen, 0·04080, 0·0842 cm.; for helium 0·0660, 0·1313 cm. A. A. ELDRIDGE.

Work of escape of electrons from oxide cathodes. H. ROTHE (Z. Physik, 1926, **36**, 737—758).—It is impossible to eliminate gas from an oxide cathode, as the stream of electrons crossing the layer of oxide decomposes it, producing new gas. The emission comes from the metal particles embedded in the oxide. The work of escape calculated from the cooling effect agrees with Richardson's equation for saturation current, but is less than the calculated value for smaller currents. The fatigue effect is probably due to gradual decomposition of the oxide. E. B. LUDLAM.

Excitation and intensity of nitrogen bands resulting from electronic impacts. H. O. KNESER (Ann. Physik, 1926, [iv], **79**, 597—609).—The excitation of nitrogen band groups by collisions with measurably accelerated electrons has been observed spectroscopically, employing the method of Hertz (A., 1924, ii, 932). The excitation potentials in volts are: strongest band of 1st positive group $10{\cdot}9\pm0{\cdot}4$; null band of 2nd positive group $14{\cdot}8\pm0{\cdot}4$; null band of negative group $19{\cdot}5\pm0{\cdot}4$. The origin of the first positive group is discussed, and the intensities of the visible bands are determined.

For the second positive and especially for the

negative group, the increase of intensity occurs with decreasing initial quantum number n.

R. A. MORTON.

Theory of the excitation of atoms by collisions. L. NORDHEIM (Z. Physik, 1926, **36**, 496—539).—A correspondence relationship is worked out between the mechanical disturbance of the electrons in the atom as the result of a collision and the probability of an electron jump. The extinction of resonance fluorescence and the production of sensitised fluorescence are discussed, and found to be in qualitative agreement with the theory. E. B. LUDLAM.

Velocities of ions under radiation pressure in a stellar atmosphere and their effect in the ultra-violet continuous spectrum. M. C. JOHNSON (Month. Not. Roy. Astr. Soc., 1926, **86**, 300—319; cf. *ibid.*, **85**, 813).—In a stellar atmosphere the tendencies of electrons and positive ions to separate under differential gravitational forces and under differential radiation pressure reach equilibrium with the electrostatic fields set up by separation of charges. The breakdown of this equilibrium becomes probable only when the effective temperature of a star exceeds 25,000°. Helium, calcium, silicon, carbon, nitrogen, and oxygen tend to move at high speeds through the outer chromosphere. Hydrogen remains comparatively stationary at the boundary of such a star. The electron captures made by the hydrogen are considered in relation to the continuous spectrum.

R. A. MORTON.

Chemical effects in ionised gases. S. C. LIND and D. C. BARDWELL (Science, 1925, **62**, 422—424; cf. A., 1924, ii, 11, 840; 1925, i, 493; this vol., 4).—In presence of radon, methane, propane, and butane, like ethane, condense with elimination of hydrogen; ethane, propane, and butane also yield methane. The ratio of hydrogen to carbon in the liquid condensation products is about 1·8 : 1. Cyanogen yields a black solid resembling paracyanogen, and some nitrogen; hydrogen cyanide yields "parahydrocyanic acid" and nitrogen. Ethylene yields a liquid with much hydrogen, and acetylene a solid with little hydrogen. The principle of exclusivity of oxidation, exhibited by carbon monoxide with oxygen, applies also to methane, ethane, cyanogen, and acetylene, the last two giving unidentified products. The hydrogenation of acetylene and cyanogen is not "exclusive," *i.e.*, polymerisation and hydrogenation both occurred. The presence of nitrogen increases the rate of polymerisation of acetylene, cyanogen, and hydrogen cyanide, the phenomenon being termed "ionic catalysis." A. A. ELDRIDGE.

Explosive reactions in gaseous media. Ionisation in gas explosions. W. E. GARNER and S. W. SAUNDERS (Trans. Faraday Soc., June 1926, advance proof).—The use of more sensitive measuring instruments has rendered possible the detection of ionisation in gaseous chemical reactions, under conditions for which the thermal ionisation is negligible, of the order of 10^{-15}. In gaseous explosions, however, calculations of the thermal ionisation by means of Saha's equation yield curves usually agreeing with the practical measurements, indicating that the ionisation in such cases is mainly thermal. When a process of ignition occurs by heating or adiabatic compression, ionisation plays no part. Dixon has shown, by measurements of the effect of a magnetic field, that propagation of the detonation wave is not due to ionisation of the gas in front of the wave. Although Malinowski found evidence to the contrary, he took no precautions as to removal of electronic disturbances due to the electrodes. Wendt and Grimm's theory that the "knock" and "anti-knock" effects are ionic in character is based on the fact that the latter are compounds of the heavy electronegative elements, and produce changes in ionisation catalytically. The effects of these substances on conductivity measurements of the gases do not support this. J. GRANT.

Conductivity of clouds dispersed from an arc. H. P. WALMSLEY (Phil. Mag., 1926, [vii], **1**, 1266—1281).—Types of ionisation curves obtained from cadmium oxide clouds produced, in dry air free from dust and carbon dioxide, by an arc discharge are described. The average mobility of the ions and the mobility of the slowest moving ions present at any time diminish with the age of the cloud. The dimensions of the ions and of the particles are of the same order of magnitude, indicating that the ions are charged cloud particles. The decrease of mobility with age indicates a coagulation of the particles. Under some conditions, the ionisation curves after decreasing show a rise in current strength due to recombination of ions, indicating a production of new charges, mainly on particles of low mobility, as the clouds age. The results are in complete agreement with all the previous deductions of Whytlaw-Gray (cf. B., 1923, 211A) on clouds.

A. E. MITCHELL.

Limits of accuracy of physico-chemical methods for the determination of atomic weight. E. MOLES (Ber., 1926, 59, [*B*], 740—750).—A detailed reply to the criticisms of the German Commission on Atomic Weights (*ibid.*, [*A*], 2—11). H. WREN.

Actinium series and lead ratios in rocks. T. R. WILKINS (Nature, 1926, **117**, 719—720).—In explanation of the observed discrepancy in the position of the first ring in Joly's pleochroic haloes, a theory is proposed indicating a half-period of about $2{\cdot}5\times10^{8}$ years for actinouranium I, the α-ray being assigned a range of 3·2 cm. The theory would eliminate actinouranium I from an explanation of the departure of the atomic weight of uranium from an integral value. Actinouranium II is also necessary, the corresponding range being 3·4 cm. The effect of the assumptions on the estimated ages of rocks determined from lead or helium ratios is considered.

A. A. ELDRIDGE.

Estimates of geological time, with special reference to thorium minerals and uranium haloes. A. HOLMES (Phil. Mag., 1926, [vii], **1**, 1055—1074).—It is shown that, owing to the incompleteness of the knowledge of the geochemical cycle of sodium salts, estimates of geological time based on the sodium content of rocks and waters must be untrustworthy. Minerals rich in thorium give lead

ratios that vary from those of uranium minerals of the same geological age down to very low values, and it is suggested that this value is no more trustworthy than the helium ratio. The variation of the lead ratios and the ratio of thorium to uranium is quite irregular, which fact leads to the conclusion that uranium cannot have disintegrated more rapidly in the past than at present. The observed discrepancies in thorium minerals may be due to the fact that lead present as oxide or silicate would be more readily removed by percolating waters and kinetic exchange than the lead in uranium minerals which is most likely present as the highly insoluble uranate. The evidence of uranium pleochroic haloes does not confirm the contention of Joly (Proc. Roy. Soc., 1923, **A**, **102**, 682) that uranium has disintegrated more rapidly in the past than at present. One possible explanation of Joly's results involves the assumption that a hypothetical actinouranium postulated by Russell (A., 1923, ii, 719) as the isotope of uranium giving rise to actinium was formerly slightly more abundant than it is at present. Generally it is claimed that uranium has always disintegrated at substantially the same rate as at present, and that the age of a fresh primary mineral free from ordinary lead is given to the right order by the expression $Pb/(U+0{\cdot}37Th) \cdot 6{\cdot}6\times10^8$ years. A reduction varying up to 3% is necessary in all cases to allow for the fact that the amounts of thorium and uranium now in a mineral must be less than those present when it was first crystallised. A further reduction of 1—3% will be necessary if the head of the actinium series be identified as a uranium isotope.

A. E. MITCHELL.

Adsorption experiments with radium-*D* and radium-*E*. J. P. MCHUTCHISON (Proc. Roy. Soc., 1926, **A**, **111**, 134—143).—The adsorption of radium-*D* and radium-*E* in equilibrium in solutions by precipitates formed in the solution and by added solids has been studied. Precipitation of lead, bismuth, mercuric, and ferrous sulphides completely removes both radium-*D* and radium-*E*. Added lead and mercuric sulphides adsorb radium-*E* in greater quantity than its equilibrium amount of radium-*D*, whilst bismuth and copper sulphides preferentially adsorb radium *D*. In the case of the precipitation of lead, silver, and mercurous chlorides, radium-*D* is in general more readily adsorbed in acid solution and radium-*E* in neutral solution. An isotopic precipitate displays no abnormal absorptive power unless it is formed under such conditions that one of the two analogous radioactive compounds is soluble, when it manifests a preference for its own isotope. In presence of a soluble lead salt, blood charcoal adsorbs radium-*E*, but not radium-*D*, and in this way radium-*E* has been obtained in the pure state and its half-life period found to be 4·9 days.

R. CUTHILL.

Hypothetical emanation of potassium. B. KRACKE (Physikal. Z., 1926, **27**, 290).—Sensitive radioactive methods for the examination of natural gas from a potash mine negative the existence of a possible potassium emanation.

R. A. MORTON.

Possibility of excitation of *X*-rays by the collision of α-particles and positive rays. C. GERTHSEN (Z. Physik, 1926, **36**, 540—547).—The existing experimental data are discussed. It is concluded that the law of conservation of momentum is applicable. Experimental work is in progress.

E. B. LUDLAM.

Capture of electrons by α-particles in hydrogen. J. C. JACOBSEN (Nature, 1926, **117**, 858).—Experiments indicate that the probability of capture of electrons by α-particles is considerably greater in air than in hydrogen under conditions in which the probability of loss is the same. The mean free paths for capture and loss, respectively, in air (*N.T.P.*) are 2·1 and $1{\cdot}0\times10^{-2}$ mm. for a velocity of α-particles of $1{\cdot}75\times10^9$ cm./sec., when the mean free path for loss in hydrogen is $7{\cdot}8\times10^{-2}$ mm. The mean free path for capture in hydrogen is not less than 200 mm.

A. A. ELDRIDGE.

Ionisation curves of rays from radium-*C'*. (MLLE.) I. CURIE and F. BEHOUNEK (J. Phys. Radium, 1926, [vi], **7**, 125—128).—Ionisation curves of α-rays from radium-*C'* have been determined in air with the apparatus previously described (A., 1925, ii, 834), in which the distance from the source to the ionising chamber is varied, and the rays are rendered parallel as near to the source as possible; the pressure was varied from 76 to 200 mm. A slight correction was applied for the penetrating γ-radiation. The ionisation curve, when corrected to 15° and 760 mm., rises to a maximum at a distance of 6·5 cm. and then falls rapidly, this portion of the curve being rectilinear for almost its entire length. The extrapolation of the rectilinear portion to zero ionisation cuts the distance axis at 6·96 cm., in good agreement with previous results, but the shape of the curve is markedly different from that of Henderson (A., 1921, ii, 617), owing to the use of different types of apparatus. Additional values have been determined for polonium.

W. HUME-ROTHERY.

Application of the Compton theory to β- and γ-rays from radioactive substances. (MME.) P. CURIE (J. Phys. Radium, 1926, [vi], **7**, 97—108).—The majority of β-rays are due to photo-electrons expelled from the inner electron levels of an atom by the homogeneous γ-rays emitted by the nucleus of the same atom. The continuous β-ray spectrum, however, may be due to exchange of momentum and energy between the γ-ray quanta and the loosely-bound outer electrons on the basis of the Compton theory, which indicates a band of diffused γ-rays limited on both frequency sides, and a band of β-rays (recoil electrons) limited on the side of high velocity only. The width of the diffused γ-ray bands increases with the frequency of the initial γ-rays. Equations are deduced for this effect, and also for the energy and momentum distribution of the β-ray recoil electrons. The effect of the type of apparatus on the β-ray magnetic spectrum is discussed. Existing data permit no definite conclusion as to the validity of the Compton theory in these cases.

W. HUME-ROTHERY.

β-Rays associated with scattered *X*-rays. J. M. NUTTALL and E. J. WILLIAMS (Phil. Mag., 1926, [vii], **1**, 1217—1235).—The short β-ray tracks, associated by Compton (Bull. Nat. Res. Coun., 1922, **20**, 19) with the recoil electrons from scattered *X*-rays, produced in various gases when traversed by *X*-rays, have been investigated by the Wilson cloud method. The results were obtained for the tracks produced in oxygen by *X*-rays of wave-length 0·709, in nitrogen and argon by rays of wave-length 0·614 and 0·545, in hydrogen by rays of wave-length 0·614, and in air by rays of wave-length 0·57 and 0·35 Å. The distribution of the short tracks, the origins of which are separated by more than 1 mm. from those of the long ones, produced in oxygen and nitrogen, has been found to be a random one. The fraction of the scattered quanta which gives sufficient energy to the scattering electrons to enable them to leave their parent atoms has been calculated on certain assumptions and an expression obtained for it in terms of the binding energies of the electrons and the wave-length of the incident radiation. When this fraction is employed, according to the theory of Compton and Hubbard (Physical Rev., 1924, [ii], **23**, 448), to calculate the ratio of the number of the short to the long tracks, the results obtained are in close agreement with the observations. The ratio varies from 0·029 for argon and a wave-length of 0·545 to 3·5 for hydrogen and rays of wave-length 0·614 Å. The results are thus in agreement with Compton's quantum theory of *X*-ray scattering.

A. E. MITCHELL.

Scattering effect of γ-rays in water and the origin of the penetrating radiation at the sea level. G. HOFFMANN (Physikal. Z., 1926, **27**, 291—297).—The residual ionisation ascribed to penetrating radiation appears to be one eighth of that which has generally been assumed when lead is used as the screening agency; recent observations (this vol., 221), on the contrary, point to marked effects when water is used. Experiments on the penetration of considerable masses of water by γ-radiation from radium-*C* indicate that at distances exceeding 1 metre the ionisation is increased by about 70%, due to scattering. Scattering becomes a very noticeable factor in determining the absorption of water. This new effect does not appear to be large enough to account for the discrepancy between radium content and radiation intensity for water. The idea advanced by Hess and Millikan that the ionisation arises from secondary γ-radiation resulting from Compton scattering of ultra γ-radiation appears to give an explanation of the difference of absorption in lead and water. The need for further evidence for the assumption is stressed. The author's work with lead screens ascribes to the ultra γ-radiation a maximum direct effect at the sea level of 0·1 ion per c.c. per sec. Some evidence has been obtained that "electron" radiation plays a part in the residual ionisation. Interpretations are discussed polemically.

R. A. MORTON.

Distribution of radioactive matter in free air. W. SCHMIDT (Physikal. Z., 1926, **27**, 371—378; cf. A., 1918, ii, 213).—The distribution in free air of radioactive products has been recalculated on a revised theoretical basis; the calculation leads to a more rapid decrease in activity with increasing distance from the ground than was computed earlier. For the following, the activity at a height of 1 metre is reduced to a half and a tenth, respectively, at the heights (in metres) indicated; radon and radium-*A* + *B* + *C*, 13 and 150; thoron and thorium-*A*, 1·15 and 1·6; thorium-*B* + *C*, 5·8 and 32; actinon and actinium-*A*, 1·07 and 1·2; actinium-*B* + *C*, 2·2 and 6·0. Radium-*D* + *E* + *F* should apparently be much more uniformly distributed. Wigand's observations (Physikal. Z., 1924, **25**, 684) are in good agreement with the calculations for radon. Current estimates of the emanation content of the atmosphere as a whole are probably inaccurate. R. A. MORTON.

Natural ionisation in gases. J. W. BROXON (Physical Rev., 1926, [ii], **27**, 542—554).—Fruth's experiments (*ibid.*, 1923, [ii], **22**, 109) were repeated, and the results confirmed, except in respect of the supposed anomalous behaviour of nitrogen, in which true saturation values were not observed. The effects of the size of the chamber, the nature of the lining, the presence of water vapour, and time were examined.

A. A. ELDRIDGE.

Scattering of positive rays by hydrogen. G. P. THOMSON (Phil. Mag., 1926, [vii], **1**, 961—977).—A method of measuring the scattering of positive rays in a gas, by measuring the blackening caused by the impact of the scattered rays on a photographic plate, is described. The density–exposure curve for positive rays is shown to be similar to that for light. In hydrogen the scattering angles investigated are of the order of 0·5°. The shape of the scattering curve is the same for all gas pressures, whilst the proportion of neutralised rays increases with the pressure. It is concluded that the scattering is due to single collisions. It is found that the collision relation corresponds with centres of force acting as the inverse cube rather than as the inverse square of the distances.

A. E. MITCHELL.

Synthesis of elements in the *X*-ray tube. F. H. LORING (Chem. News, 1926, **132**, 311—312).—An *X*-ray spectrum of potassium phosphate containing calcium and aluminium showed the presence of bromine. This may have been derived from the commercial potassium salt used in making the phosphate, but the author also suggests that it may have been produced from the potassium and calcium in the phosphate by four electrons entering the nucleus in the condensation of the two metals so as to reduce the atomic number to the correct value: (K)19 + (Ca)20 − 4 = (Br)35. A. R. POWELL.

Transformation of gold into mercury. A. GASCHLER (Z. Elektrochem., 1926, **32**, 186—187).—Mercury has been detected spectroscopically in a vacuum tube in which gold was bombarded with hydrogen nuclei in the form of positive rays.

R. CUTHILL.

Stability of the atomic nucleus. L. STRUM (Z. physikal. Chem., 1926, **119**, 368—376).—Speculative. L. F. GILBERT.

Quantisation of an ideal monatomic gas. E. FERMI (Z. Physik, 1926, **36**, 902—912).—If Nernst's heat theorem is applicable to perfect gases, their behaviour will not be in accord with the classical laws for perfect gases at low temperatures. The reason for this degradation is the quantisation of the molecular motions. The equations of state and internal energy of a perfect gas are deduced from the hypothesis that in the gas there is not more than one molecule with the given quantum numbers S_1, S_2, S_3. The values for the entropy at high temperatures agree with those of Stern and Tetrode. E. B. LUDLAM.

Rotation-oscillation bands according to quantum mechanics. (FRL.) L. MENSING (Z. Physik, 1926, **36**, 814—823).—The new matrix mechanics is applied to the rotating oscillating diatomic molecule. The pure rotational energy is such that the zero line does not appear in the band spectrum; the transference probabilities are calculated; the formula obtained for the intensities of the single bands is the same as that of Fowler.
E. B. LUDLAM.

Quanta and chemistry. E. HERZEN (Bull. Soc. chim. Belg., 1926, **35**, 109—116).—A *résumé*.

Electronic orbits on relativity theory. O. R. BALDWIN and G. B. JEFFERY (Proc. Roy. Soc., 1926, **A**, **111**, 104—110).—A mathematical determination of the possible circular orbits of a charged electron about a charged nucleus, using the relativity theory, and assuming that the effect of the reaction on the nucleus is negligible. Nothing resembling Bohr's orbits emerges. R. CUTHILL.

Application of relativity to atomic and molecular systems. T. DE DONDER (Compt. rend., 1926, **182**, 1380—1382).—Mathematical.

Chemical inertia of the monatomic gases from the point of view of the electronic theory of the atom. H. DAMIANOVITCH (Anal. Asoc. Quim. Argentina, 1925, **13**, 243—254).—Theoretical. The electronic theory is not inconsistent with the possibility that under certain conditions these elements may form compounds. The theory of zero valency is based on negative experiments which require repetition. G. W. ROBINSON.

Orientation of the oxygen molecule in a magnetic field. L. C. JACKSON (Phil. Mag., 1926, [vii], **1**, 1193—1198).—The soap-film method of Dewar has been employed to observe any variation of the thickness or intensity of a jet of oxygen when acted on by a non-homogeneous magnetic field. In no case was an effect observed. This result is considered to show that the oxygen molecule can, after collision, take up any one of the possible quantum orientations, passing eventually through them all, and that the separation of the various spacially quantised states is not possible by the method adopted by Stern,Gerlach, and others for the separation of the various states of silver, copper, and other metals. A. E. MITCHELL.

Explanation of some phenomena in spectra of molecules. F. HUND (Z. Physik, 1926, **36**, 657—674).—The application of the modern theory of atomic spectra to the band spectra produced by molecules is discussed. An explanation is given of the similarity of the fine structure in molecular spectra to that of the spectra of atoms containing the same number of outer electrons. E. B. LUDLAM.

Flame spectra and chemical reaction. (MISS) C. E. BLEEKER (Trans. Faraday Soc., 1926, **21**, 479—483, and Z. physikal. Chem., 1926, **120**, 63—68).—Measurements of the relative intensities of members of the first and second subordinate series in the flame spectra of alkali metals have been continued in the cases of sodium and potassium (cf. A., 1925, ii, 77). From the author's formula for the variation of the ratio of these intensities an attempt is made to determine to what extent the results may be explained by temperature radiation and by chemical reaction (oxidation). Using an hypothesis adapted from Bohr's correspondence principle, the transition probabilities and thence the ratio of the intensities of the members of the subordinate series are calculated. As these are independent of temperature, they cannot be due to thermal excitation alone, and it is concluded that the total intensity of each line is composed of two parts. In the case of the principal and subordinate series, the temperature radiation and chemical reaction effects predominate, respectively. Anomalies in the cases of sodium and potassium may be due to the greater experimental error owing to the regions in the spectrum in which their lines are situated.
J. GRANT.

Magnesium hydride band spectrum. W. W. WATSON and P. RUDNICK (Astrophys. J., 1926, **63**, 20—32).—The first two sets of P, Q, and R branches in both the 5211 and 5622 Å. groups, together with one set of branches in the 4845 Å. group, have been found, and assignments of rotational and vibrational quantum numbers made. All the branches are composed of doublets, the frequency separations of which are small and nearly constant for all but the lowest values of m. In the P branch, at least, the abnormality is associated with departure from equal intensities. The combination involving the Q branch does not hold in any one band. The expected isotope effect is observed. The source of the bands is considered to be a chemical compound of magnesium and hydrogen. The moment of inertia of a dipole carrier is computed to be $4{\cdot}6\times10^{-40}$ g. cm.^{2}, giving an internuclear distance of 1·7 Å. A. A. ELDRIDGE.

Systematic relations between electronic structure and band-spectrum structure in diatomic molecules. III. Molecule formation and molecular structure. R. S. MULLIKEN (Proc. Nat. Acad. Sci., 1926, **12**, 338—343; cf. this vol., 451, 452).—A discussion of the band-spectra of HgH, H_2, Na_2, HCl, AlH, CN, BO, and CH in the light of the author's postulates. J. S. CARTER.

Electron levels of some band spectra. R. MECKE (Z. Physik, 1926, **36**, 795—802).—Comparison of the term separation of the band spectra of the hydrides of zinc, cadmium, and mercury with the line spectra of neighbouring elements shows that they resemble the spectra of the elements which immediately precede them. The terms of the ground state are 50,000—55,000, the separations for HO, BO,

C^+O, and NO are all about 126 cm.$^{-1}$, and comparable in magnitude with that of the nitrogen atom. This similarity of separation indicates that the radiating electron has an orbit round the oxygen nucleus. Deductions are also made regarding the term formulæ for the energy of rotation. E. B. LUDLAM.

Relative intensities of band lines in the infra-red spectrum of a diatomic gas. E. C. KEMBLE and D. G. BOURGIN (Nature, 1926, **117**, 789).—In a study of the hydrogen chloride band at 3·5 μ, absorption curves were obtained for six absorption paths from 0·1 to 3 cm. The values of the integral absorption coefficients, α, are in harmony with the summation rule. The statistical weight formula $p=2m+1$; $m=\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$, in which m is the nuclear rotational quantum number, is believed to be incorrect; the formula $p=2m$ is preferred.
A. A. ELDRIDGE.

Infra-red emission from gaseous explosions. W. E. GARNER, C. H. JOHNSON, and S. W. SAUNDERS (Nature, 1926, **117**, 790—791).—The explosion infra-red spectrum of carbon monoxide and oxygen is qualitatively the same as the flame spectrum, but the ratios of the intensities of the bands at 2·8 μ and 4·4 μ are, respectively, 1 : 1 and 1 : 11 for gases dried over phosphorus pentoxide, and 2 : 1 and 1 : 10 for gases saturated with water vapour. The intensity of infra-red emission is greater for the dry than for the wet gases, the ratios of the galvanometer deflexions being 3 : 2 for the band at 2·8 μ, and 3 : 1 for that at 4·4 μ. Since the absorption of infra-red radiation by the water vapour in front of the explosion wave is negligible, it is suggested that the internal energy of those activated molecules which emit the 2·8 and 4·4 μ bands may be converted by collision with the water molecules into kinetic energy, although an absorption mechanism is also possible. Similar results, in more marked degree, are obtained in the presence of ethyl iodide or nitrate. A. A. ELDRIDGE.

Absorption spectrum of carbon dioxide and the structure of the carbon dioxide molecule. C. SCHAEFER and B. PHILIPPS (Z. Physik, 1926, **36**, 641—656; cf. Dennison, this vol., 222).—Ten absorption bands between 1·465 μ and 2·092 μ are described and discussed; three are regarded as fundamental, others as combinations of these, and this indicates a triangular molecule for carbon dioxide in the gaseous phase, not one in which the carbon atom is equidistant from the oxygen atoms and in the same straight line as in the solid state. The greater moment of inertia is about 50×10^{-40}, the smaller is 1×10^{-40} gm. cm.^{2}; the distance between the carbon atom and one of the oxygen atoms is $1{\cdot}02\times10^{-8}$ cm.
E. B. LUDLAM.

Spectra resulting from the excitation of certain nitrogen compounds. H. O. KNESER (Ann. Physik, 1926, [iv], **79**, 585—596).—The glow discharge of streaming gases has been investigated. The gases nitrogen, nitrous oxide, nitric oxide, nitrogen peroxide, and ammonia exhibit the desired effect of spectra differing in the different regions of the positive column. The intensities of the nitrogen band groups have been compared, and conclusions concerning the carriers advanced. The yellow phase of the column is due to nitrogen peroxide, the green colour possibly to nitric oxide, although the green colour in the peroxide is identical with that in nitric oxide. Similarly, the violet colour is identical in nitrogen peroxide and nitrous oxide. In the red region, the decomposition into nitrogen and oxygen occurs, since the intensity relationships agree with those found in the nitrogen spectrum. The first positive and the negative band groups occur with almost equal intensities, but, as Wien has shown, identical carriers are improbable. The former is connected with N_2^- and the latter with N_2^+. In the spectrum of ammonia the third positive and the negative band groups are missing. Similar streaming effects were observed with chlorine and water vapour, but not for hydrogen, oxygen, and hydrogen chloride.
R. A. MORTON.

Mechanism of ammonia synthesis in low-voltage arcs. A. R. OLSON (J. Amer. Chem. Soc., 1926, **48**, 1298—1299).—Arcs in hydrogen–nitrogen mixtures were found by Kwei (this vol., 7) to show ammonia bands at 23 volts, but not at 17 volts (cf. A., 1923, ii, 631). This is explained by the presence of activated atomic nitrogen at the higher voltage only (Hogness and Lunn, A., 1925, ii, 839; Sponer, this vol., 8), so that activated ammonia molecules, essential for the production of bands, are absent from the lower voltage arc. S. K. TWEEDY.

Absorption of light in coloured alkali halides. W. FLECHSIG (Z. Physik, 1926, **36**, 605—614).—For sodium chloride the absorption curve was obtained for temperatures −180° and +90°; for sodium bromide, potassium chloride, rubidium chloride, and potassium bromide, the curves were taken for the ordinary temperature and for −180°. In all cases, lowering the temperature gave a curve which had a higher maximum, was narrower and displaced towards shorter wave-lengths than at higher temperatures. Good natural crystals showed the effect better than artificial crystals, defects in the crystal producing the same general effect as rise of temperature. Excitation with light of photo-electrically active wave-length also produced the same effect as increased temperature. E. B. LUDLAM.

Two kinds of coloured rock salt. T. E. PHIPPS and W. R. BRODE (J. Physical Chem., 1926, **30**, 507—520).—The deep-blue, naturally-occurring halite (Stassfurt) and halite coloured by heating in contact with alkali metal vapour have been compared with reference to their alkalinity in water, using a specially-constructed hydrogen electrode, and also spectrophotometrically. The Stassfurt halite gave no alkaline reaction, which, however, was invariably shown by the halite coloured by sodium. The spectrophotometric data at the ordinary temperature and over wider ranges show a distinct difference to exist between the two colours. The natural halite yields absorption bands at 5240 and 6400—6600 Å., the ratio between the intensities of the two bands being approximately constant in all cases. The crystals coloured by sodium show various colours with different heat treatment, but, on a second heating to low redness in air, the chief colours developed are

purplish-blue and deep pink. The former has an indefinite vibration centre near 5890, the latter, an intense, sharp band at 5520 Å. These colours lighten with rising temperature through amber to pale straw just below the m. p. of the crystal and are irreversible. The shifts of the bands with temperature for both kinds of halite are described and discussed.

Under the influence of light from a quartz mercury-vapour lamp, the purplish-blue of the crystal coloured by sodium changes to a pale straw identical with that obtained by heating the crystal and with that produced in a colourless crystal by radium emanation. No such effect occurred with the Stassfurt halite, the colour of which is considered to be electronic in nature, and not due to the presence of colloidal sodium. L. S. THEOBALD.

Absorption spectrum of potassium and calcium permanganates. E. ADINOLFI (Atti R. Accad. Lincei, 1926, [vi], **3**, 196—201).—The identity of the absorption spectra of potassium and calcium permanganates and the fact that electrolytic dissociation does not influence the absorption (A., 1920, ii, 721) indicate that the vibrator is the group MnO_4, to which must be attributed the characteristic frequencies either of quanta of rotation or of those depending on variations of energy due to longitudinal vibrations. It is shown that this absorption spectrum is one of oscillation and rotation. Contrary to what is the case with gases, the band representing the normal state of the molecule is not only present, but also is the most intense and represents the most probable state of the vibrator.

The moment of inertia of the group MnO_4 is of the order of 10^{-42} g. cm.^{2}, with a radius of gyration of 10^{-10} cm.; these values of the mechanical constants of the resonator are appreciably smaller than those for gases and may be an effect of the surface pressure, which should favour approach of the vibrating atoms. Replacement of the solvent water by alcohol increases the moment of inertia, probably owing to the diminution of the surface pressure from 10,700 to 2400 atm. Depression of the temperature of the solution causes a fall in the moment of inertia, owing to increase of the surface pressure. T. H. POPE.

Absorption spectra of compounds of the rare earths. J. BECQUEREL, H. K. ONNES, and W. J. DE HAAS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 264—275).—A more detailed account of work already published (this vol., 14).

Infra-red absorption bands of methane. J. P. COOLEY (Astrophys. J., 1925, **62**, 73—83).—The three absorption regions of methane at 7·7, 3·31, and 2·35 μ have been partly resolved into lines. The lines of the bands at 7·7 and 3·31 μ have been arranged in positive and negative series, between which is a narrow region of intense absorption, the lines of which have not been resolved. The frequency difference between adjacent lines near 7·7 μ is 5·41 cm.$^{-1}$, and near 3·31 μ, 9·77 cm.$^{-1}$. A. A. ELDRIDGE.

Molecular structure and infra-red spectrum of methane. D. M. DENNISON (Astrophys. J., 1925, **62**, 84—103).—A theoretical consideration of Cooley's results (preceding abstract), it being assumed that in the normal state the four hydrogen nuclei lie at the corners of a regular tetrahedron with the carbon nucleus at the centre, and that, following an infinitesimal displacement of the nuclei, the potential energy depends on the squares of the displacements along the lines between the nuclei. The model yields four fundamental frequencies which can be made to correspond with Cooley's results. The molecule of methane is considered to possess a resultant electronic angular momentum fixed in direction in the molecule of amount $0{\cdot}5h/2\pi$. A. A. ELDRIDGE.

Ultra-violet absorption spectrum [and dissociation] of formic acid. H. C. RAMSPERGER and C. W. PORTER (J. Amer. Chem. Soc., 1926, **48**, 1267—1273).—The equilibrium constants between 25° and 80° for the dissociation $(H{\cdot}CO_2H)_2 \rightleftharpoons 2H{\cdot}CO_2H$ were measured (Pettersson and Ekstrand, A., 1880, 841, 868), from which the heat of evaporation is 121·2 cal./g. at the b. p. The free energy of solution and of formation of the acid and the heat of dissociation of the bimolecular form are −2960, −84,960, and 13,900 cal./mol., respectively, at 25°. The bimolecular form of the acid is mainly responsible for the absorption between 2260 and 2500 Å., although the unimolecular form also exhibits appreciable absorption. The complete photochemical decomposition of formic acid vapour yields 18% each of carbon dioxide and hydrogen and 32% each of carbon dioxide and water. S. K. TWEEDY.

Spectroscopical study of amino-acid anhydrides. I. Constitutions of some simple amino-acid anhydrides. Y. SHIBATA and T. ASAHINA (Bull. Chem. Soc. Japan, 1926, **1**, 71—74).—Solutions of the anhydrides of glycine, alanine, and sarcosine when examined spectroscopically showed no selective absorption. These substances therefore probably exist only in the keto-form in aqueous solution. B. W. ANDERSON.

Production of fluorescence in the *X*-ray region. P. AUGER (Compt. rend., 1926, **182**, 1215—1216; cf. this vol., 551).—Measurements of the yields of characteristic *X*-rays excited by the photo-electric effect are extended to the *K* and *L* levels of xenon and values of 0·7 and 0·25 are obtained, respectively. For argon, krypton, and xenon, whether considering the same level in the different elements or different levels in the same element, the amount of fluorescence produced increases with the frequency of the corresponding rays. J. GRANT.

Uranium as an activator [of luminescence]. E. L. NICHOLS and M. K. SLATTERY (J. Opt. Soc. Amer., 1926, **12**, 449—466).—Solid solutions of uranium salts in sodium phosphate, potassium phosphate, borax, sodium fluoride, and calcium fluoride containing only traces of uranium, exhibit luminescence under photo- or cathodo-excitation. The intensity of the luminescence excited by the radiation from a mercury arc filtered through deep purple glass passes through a maximum for a definite concentration of uranium, *e.g.*, about 1 mol. in 200 mols. for sodium phosphate, and about 1 mol. in 2000 mols for sodium fluoride. The luminescence spectra consist of several bands which widen when the solid

solution is subjected to heat treatment. If the heating is prolonged, the luminescence disappears in the first three salts above mentioned, due to the expulsion of water of constitution. The bands are made up of numerous overlapping components, which may be arranged in sets, the frequency intervals between members of a given set being constant or some exact multiple of a constant, which was 18 for all the spectra analysed. The position of the brightest component of each spectrum moves towards the violet with increase of the mol. wt. of the solvent. None of the solid solutions shows any phosphorescence. They are inert under *X*-rays, but after exposure to *X*-rays become thermo-luminescent.

A. B. MANNING.

Triboluminescence and crystal luminescence. H. LONGCHAMBON (Bull. Soc. franç. Min., 1925, 48, 130—211; from Chem. Zentr., 1926, I, 840).—Triboluminescence is brought about by electrical radiation, which causes gas present at fractures to become luminescent. The phenomenon is often complicated by phosphorescence and fluorescence. A number of cases of crystal luminescence, where destruction of the crystal is accompanied by a rise of temperature, are due to triboluminescence. In other cases, the effect is probably due to the existence of an electrical double layer at the crystal surface. Triboluminescence does not occur when crystals are broken along their cleavage planes, if these are not perpendicular to an axis of pyroelectricity. J. S. CARTER.

Luminescence of solidified gases and its relation to cosmical processes. L. VEGARD (Ann. Physik, 1926, [iv], 79, 377—441; cf. A., 1924, ii, 436, 509, 584, 642, 713, 805; 1925, ii, 474, 630).—Twenty-three lines occurring in the spectrum of aurora borealis are shown to correspond in respect of wave-lengths and intensities with the lines excited when solid nitrogen is bombarded by slow cathode rays. The outstanding wave-lengths in Å. in the visible region are designated N_1 (5577), N_2 (5230), N_3 (6569, 6230—6420), and N_4 (5944). When pure nitrogen is used, N_1 and N_2 are broadened and the characteristic green line of the northern light spectrum (5577) is not reproduced. At heights exceeding 100 km. the atmosphere probably consists of a belt of finely-divided particles of solid nitrogen in a highly rarefied condition at a temperature below 35·5° Abs. This "pseudogas" becomes electrically charged by solar photo-electric radiation, resulting in the emission of the 5577 line and other lines. Experiments with condensed inert gases containing traces of nitrogen show that as the nitrogen concentration diminishes the N_1 band tends to contract to a line at 5577. The effect is partly specific to the ideal diluent and partly due to diminution in the size of the aggregates of solid nitrogen embedded in the solidified inert element. When argon is employed, the approach to the aurora line is more complete than with neon. The green line seems to be the limit of the N_1 band when an approximation to the pseudogaseous state is attained in the laboratory. The relations of the N_1 and N_2 bands under these conditions support the theory of the auroral spectrum. Excitation with canal rays give both N_1 and N_2 and a spectrum differing from the auroral spectrum in all other respects.

A diffuse band series (A) appears in the blue, and suffers some shift to a series (α) in the argon–nitrogen mixtures. Their absence from the auroral spectrum indicates that the exciting entity is not positively charged. The stronger lines of these series correspond with lines measured by Rayleigh in the spectrum of the light of the night sky, indicating a positively charged source for the phenomenon.

Solid nitrogen exists in α and β modifications with a transition point at 35·5° Abs. Excitation occurs only at temperatures below 35·5° (*i.e.*, the β-form is inactive). When solid nitrogen is bombarded for some time with canal- or rapid cathode-rays, an afterglow is produced which may persist unchanged for hours. At the transition point the stored-up energy gives rise to an intense light in which N_1, N_2, N_3, N_4, and the A series appear. Solid argon is inactive, but if traces of nitrogen are present, canal ray bombardment excites the emission of N_1, N_2, and two series α and β. Increase in the amount of nitrogen in the argon causes the appearance of numerous band series which are ascribed to α solid nitrogen, and are all oscillation series. The new series all seem capable of interpretation by the usual methods. R. A. MORTON.

Photo-luminescence of benzene and some derivatives in different states of aggregation and of solution. A. RIEMANN (Ann. Physik, 1926, [iv], 80, 43—70).—Relatively few substances have been investigated for luminescence in the solid–liquid–vapour states. The case of benzene is peculiarly suitable for investigation on account of its relatively simple structure and the wealth of related information available. At pressures up to 1 mm., benzene vapour exhibits a fluorescence spectrum consisting of relatively few bands and depending on the wave-length of the exciting light. By increasing the vapour pressure, numerous new bands appear, which beyond a certain limiting pressure do not appear to vary with either the source of excitation or the pressure. This band system is ascribed to collisions of the second kind. The pure liquid and solutions in alcohol exhibit broad bands without structure, which correspond in general outline with shifted bands observed in the fluorescence of the vapour. The amount of shift increases with increasing concentration and a concomitant loss of definition occurs. When pure liquid benzene is allowed to crystallise without fall of temperature, the fluorescent intensity becomes much greater and simultaneously the sharp edges of the unsymmetrical bands attain the sharp definition found in dilute alcoholic solutions. The emission from solid benzene shows a definite afterglow. Similarly, certain simple benzene derivatives which are scarcely fluorescent in the liquid state show the phenomenon well on crystallisation without fall of temperature. At the temperature of liquid air, the broad bands found in benzene solidified at 0° are resolved into numerous fine bands closely resembling, but not identical with, the vapour spectrum. When a solution in alcohol is solidified at −190°, the broad bands gain in definition and sym-

metry without exhibiting structure. The fluorescence spectrum of benzene vapour at higher pressures is expressed by the linear formulæ $1/\lambda=39{,}490-1000n-163p$, $1/\lambda=39{,}400-1000n-163p$. Marsh's work (A., 1925, ii, 470, 625), in which the fluorescence spectrum is brought into formal similarity with Henri's application of the Heurlinger–Kratzer–Lenz theory of band spectra to the vapour absorption spectrum is criticised (cf. A., 1925, ii, 181).

R. A. MORTON.

Ionisation potential of hydrogen fluoride. A. N. KAPPANNA (J. Indian Chem. Soc., 1926, **3**, 59—62; cf. Glockler, A., 1925, ii, 1105).—From published data of the lattice energies of potassium fluoride and chloride and other thermochemical data, the ionisation potential of hydrogen fluoride is calculated to be 14·02 volts. J. W. BAKER.

Dielectric constants of benzene solutions. J. R. PARTINGTON and J. F. J. RULE (Phil. Mag., 1926, [vii], **1**, 1035—1039).—The dielectric constants of benzene solutions of *m*-dinitrobenzene at 20° and of phenol and benzoic acid at 18° have been determined. With *m*-dinitrobenzene and phenol, the dielectric constants increased steadily with increasing concentration and appeared to approach those of the pure solutes in the fused state. With benzoic acid solutions, the dielectric constant increased with concentration to a maximum of 3·94 at a concentration of 0·082 mol./litre and then decreased steadily.

A. E. MITCHELL.

Variation of the dielectric constant of liquid oxygen with temperature. W. WERNER and W. H. KEESOM (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 306—313).—The dielectric constant of liquid oxygen, from b. p. to m. p., has been determined by the high-frequency oscillation method (cf. this vol., 559). Its mean value at the b. p. 90·14° Abs. is 1·4837. This agrees very closely with the value calculated from the dispersion of light in liquid oxygen, indicating that there are no electrical doublets in oxygen, a conclusion which is confirmed by a calculation of the constants in Debye's formula $PT=a+bT$. The Clausius–Mosotti function is constant to 0·5% from the b. p. to 58° Abs., but increases on further cooling. M. S. BURR.

Quantum theory of the dielectric constant of hydrogen chloride and similar gases. L. PAULING (Physical Rev., 1926, [ii], **27**, 568—577).—A more detailed account of work already abstracted (this vol., 225). A. A. ELDRIDGE.

Molecular and atomic volumes. X. Complex cobalt salts. E. BIRK and W. BILTZ (Z. anorg. Chem., 1926, **153**, 115—125; cf. this vol., 110).—When the anion is univalent and not too large, complex cobaltic compounds have the same mol. volumes as the corresponding cobaltous compounds. Thus *aquopentamminecobaltous fluoride* and *aquopentamminecobaltic fluoride* have the same mol. volume; hexamminecobaltous thiocyanate, nitrate, and perchlorate also have the same volumes as the corresponding cobaltic salts. When the anion is bivalent or very large, the mol. volume is the sum of the volumes of the constituents at 0° Abs. This is the case for hexamminecobaltous β-naphthalenesulphonate, sulphate, and *oxalate*, and the corresponding cobaltic salts. The volume of ammonia in these salts is 18—20, of fluorine (F) 7·5, and of hydrofluoric acid 7·7. Complex *salts* of the constitutions $[Co(NH_3)_5.H_2O]F_3,6HF$ and $[Co(NH_3)_6]F_3,6HF$ are also described.

A. GEAKE.

[Additivity of the molecular volumes of volatile inorganic compounds.] G. M. SCHWAB (Ber., 1926, **59**, [*B*], 737—738).—A claim for priority against Rabinovitsch (this vol., 226). H. WREN.

Change of volume in the formation of bases and acids. J. SASLAVSKY (Ber., 1926, **59**, [*B*], 712—714; cf. A., 1925, ii, 933).—Application of the formula $C=MV/\varepsilon AV$ shows that the "contraction" is greater in the formation of basic than of acidic oxides. In hydroxides, stronger basic properties are characterised by greater "contraction," whereas the reverse is the case with acids. H. WREN.

Effect of salts on rotatory power. E. DARMOIS (Compt. rend., 1926, **182**, 1211—1214).—Values of $[\alpha]_v$ for mixtures of malic or tartaric acid with boric acid, and malic acid with molybdic acid, at various concentrations, in neutral salt solutions differ considerably from the corresponding values in water. *M*- and 0·2*M*-potassium chloride and 0·05*M*-calcium chloride produce rises in the values of $[\alpha]_v$ over those for water, the actual curve obtained depending on the nature of the neutral salt used. Salts of the above complex acids show analogous results. This is explained by the displacement of the equilibrium existing between the complex acids and the uncombined active acid by the neutral salt, and by hydrolysis in the case of salts. The variations of $[\alpha]$ and the p_H with the amount of potassium hydroxide required for progressive neutralisation of solutions of potassium chloride containing mixtures of antimony trichloride, tartaric and hydrochloric acids, give curves analogous to those obtained with dimolybdomalic acid. Antimonious oxide is deposited beyond the maximum value of $[\alpha]$. Mutarotations show similar variations. J. GRANT.

Rotatory power of tartaric acid in dilute solution using ultra-violet light. G. BRUHAT and M. PAUTHENIER (Compt. rend., 1926, **182**, 1024—1026).—The specific rotation at 20° of tartaric acid in 1% and in 0·25% solutions, respectively, for light of the following wave-lengths is: 5780 Å., 13·8°, 19·8°; 5460 Å., 14·9°, 21·4°; 4360 Å., 17·6°, 31·4°; 4050 Å., 17·3°, —; 3660 Å., 6·4°, 16·3°; 3130 Å., −54·7°, −49·5°. The results for the 1% solutions are subject to an error of 1°, and those for the 0·25% solutions to an error of 3°. Anomalous dispersion exists even in dilute solution in accordance with the views of Lowry and Austin (A., 1924, i, 940), but their value for the wave-length at which maximum rotation occurs (4360 Å.) appears to be too high. The rotation is not a linear function of the concentration, and the observed specific rotation in 0·25% solution for yellow and green light is about 4° higher than the extrapolated value (Lowry and Austin, *loc. cit.*). It is concluded that in dilute solution, ionisation superimposes on the anomalous rotatory dispersion of the

acid the normal rotatory dispersion of the neutral tartrates. F. G. SOPER.

Rotatory power of camphor. R. LUCAS (Compt. rend., 1926, **182**, 1022—1024; cf. this vol., 337; Lowry and Cutter, A., 1925, ii, 356).—The specific rotation of camphor in phosphoric acid solution (1 g. camphor in 50 c.c. of 87% phosphoric acid) is −2·1°, −1·7°, −1·5°, −1·2°, −0·25°, +8·8°, and +15·5°, for light of wave-lengths 6708, 6103, 5893, 5780, 5460, 4602, and 4358 Å., respectively. It is found that the expression $\{[\alpha]C_6H_{12}-[\alpha]H_3PO_4\}/\{[\alpha]C_6H_{12}-[\alpha]H_2SO_4\}$ is constant and equal to 0·512±0·0014 over the range of wave-lengths examined, $[\alpha]C_6H_{12}$, $[\alpha]H_2SO_4$, and $[\alpha]H_3PO_4$ being the specific rotations in *cyclo*hexane, sulphuric acid, and phosphoric acid, respectively. The dispersion curves can thus be deduced one from another in accordance with Biot's law of mixtures and this affords strong evidence for the view that camphor is a mixture of two active molecular types of different dispersivity. It is probable that a single Drude term is insufficient to represent the behaviour of an active molecular type, for it is unlikely that rays of very short wave-length are sensible to molecular asymmetry. The Drude equation, $[\alpha]=\Sigma k''(\lambda^2-\lambda_0{}^2)$, on this assumption reduces to $\Sigma k''/\lambda_0{}^2=0$, and at least two terms are therefore necessary for each active variety. F. G. SOPER.

Optical rotatory dispersion. T. S. PATTERSON (Nature, 1926, **117**, 786—787).—Polemical. A. A. ELDRIDGE.

[Optical rotatory dispersion.] T. M. LOWRY (Nature, 1926, **117**, 787).—A reply to Patterson (preceding abstract). A. A. ELDRIDGE.

Chemical valency in the light of contemporary theories. W. SWIENTOSLAWSKI (Rocz. Chem., 1926, **6**, 1—14).—Theoretical. Valency theories are considered from chemical and physical points of view, and an attempt is made to reconcile certain contradictory views. R. TRUSZKOWSKI.

Valency of nitrogen and hydrogen. A. A. BLANCHARD (J. Amer. Chem. Soc., 1926, **48**, 1195—1198).—The precise definition of valency is possible only with the aid of postulates regarding electron arrangements. The non-polar valency of nitrogen in the ammonium radical, *i.e.*, the number of electron pairs held in common, has the maximum value of 4, whereas the polar valency, *i.e.*, the net charge of the nitrogen atom including the electron pairs held in common, is −3. The polar valency, which is different from a chemical bond, might also be defined as the net charge on the kernel, and is +5 for nitrogen. The non-polar valency of phosphorus in its pentachloride may be +5, and that of sulphur in its hexafluoride, +6. The hydrogen linking is considered to be a hydrogen atom holding in its valency layer one electron of the valency layer of each of the two atoms thus bound together. S. K. TWEEDY.

Dynamic model of the chemical bond and its application to the structure of benzene. L. PAULING (J. Amer. Chem. Soc., 1926, **48**, 1132—1143).—Substances are classified as ionic or molecular, according as the valency linking results from the transfer of an electron from one atom to another or from the sharing of electron pairs by two atomic nuclei. Gradual transition from one class to the other is impossible. On the basis of Knorr's dynamic bond (A., 1924, ii, 34; Grimm, *ibid.*, 1925, ii, 1123), experimental evidence in support of which is reviewed, a structure for benzene is deduced in which the six carbon atoms and the six hydrogen atoms are arranged at the corners of two concentric plane hexagons. Each carbon atom is connected by pairs of λ-orbits (*i.e.*, enlarged *L*-orbits), perpendicular to the hexagon plane, to the two adjacent carbon atoms, and to one proton, the angles between the pairs of orbits being 120°. These λ-shells resemble those in Latimer and Rodebush's carbonate ion (A., 1920, ii, 537) and in graphite. There are also two electron orbits (possibly μ-orbits) connecting opposite carbon atoms, forming six crossed orbits which confer stability on the compound. The symmetry of this model is D_{6h}; it requires all mono- and all *o*-disubstituted benzenes to be identical and illustrates why a substituent group directly influences the *para*-position. Similar plane structures are given for naphthalene and anthracene; the computed dimensions of these molecules agree with those determined by *X*-ray measurements. S. K. TWEEDY.

Main and subsidiary groups of the periodic system. M. CENTNERSZWER (Ber., 1926, **59**, [*B*], 786—788).—An arrangement is described in which the elements of each group are distributed into main and subsidiary sub-groups. The elements of the main sub-group exhibit the characteristics of the group with regard to maximal valency, physical properties, and chemical nature. The elements of the subsidiary sub-group differ more or less sharply from those of the main sub-group chiefly in their ability to exhibit multivalency and subsidiary valency. H. WREN.

Ion charges in crystals of tetrahedral structure. K. F. NIESSEN (Physikal. Z., 1926, **27**, 299—306).—Mathematical. In support of Grimm and Sommerfeld's theory (this vol., 560) of electronic valency, it is shown that in compounds such as carborundum, aluminium nitride, beryllium oxide, and zinc blende the ionic charges are greater the further the group of the elements in question is removed from group IV of the periodic classification. W. A. CASPARI.

Space model for crystal structures. R. W. G. WYCKOFF and C. J. KSANDA (Amer. J. Sci., 1926, [v], **11**, 377—380).—Instead of balls connected by rods, a series of horizontal glass plates is recommended, each of which is adjustable at any desired height by means of nuts working along four uprights. The atom or molecule models consist of paper discs gummed down on the plates. Illustrations are given showing the use of the apparatus for β-quartz and β-cristobalite. W. A. CASPARI.

Atomic numbers and the properties of ions in the crystal lattice. II. Characteristic frequency and the constraint. A. F. SCOTT (J. Physical Chem., 1926, **30**, 577—594; cf. A., 1925, ii, 369).—The characteristic frequencies of the elements and the alkali halides have been calculated substituting the values found by *X*-ray analysis for the

nearest approach of the ions in a lattice, in Lindemann's formula (Physikal. Z., 1910, **11**, 609). The characteristic frequency, ν, is connected with other properties of the elements, particularly with those forces which are regarded as chemical. Atomic number, Z, and ν are connected with e, the valency electron, by the function $\nu=\alpha f(Ze)$, where α is a constant factor or parameter for a particular group in the periodic table. In support of this, straight lines result when the values of ν for the elements of a group are plotted against those for the alkali metals, with the corresponding parameters as tangents. Linear graphs are also obtained with the alkali chlorides against the alkali halides.

The constraint on an ion, *i.e.*, the restoring force per unit displacement, is the resultant of two forces, repellent and attractive, and on this postulate the distance between ions is shown to vary with the square root of the constraint, which can be expressed for elements and salts by a linear equation involving atomic numbers. L. S. THEOBALD.

Results of crystal analysis. L. VEGARD (Phil. Mag., 1926, [vii], **1**, 1151—1193).—Crystals of zircon, rutile, cassiterite, and anatase which were analysed previously by the X-ray spectrometer method (A., 1916, ii, 405, 593) have been examined by the powder method. The examination has been extended to scheelite and powellite. The structures originally assigned to rutile and cassiterite have been confirmed, and it is concluded that these minerals with a space-group D_{4h}^{14} are not exactly isomorphous with zircon with the space-group D_{4h}^{19}. The ionic radii have been calculated to be as follows: anatase 1·32, 0·63 Å. for oxygen and titanium; rutile 1·31 and 0·67 for oxygen and titanium; cassiterite 1·30 and 0·75 for oxygen and tin; zircon, 1·18, 0·99, and 0·49 Å. for oxygen, zirconium, and silicon, respectively. Without the oxygen atoms, zircon and scheelite have the same space-groups. Consideration of the oxygen atoms, however, reduces the symmetry of scheelite to the space-group C_{4h}^{6}. The crystal molecule consists of eight scheelite molecules, each tungsten atom being surrounded by four oxygen atoms, the centres of which are at the corners of a tetrahedron which is somewhat compressed in the direction of the c-axis, whilst each calcium atom is in contact with eight oxygen atoms, and each oxygen atom touches two calcium, one tungsten, and two other oxygen atoms. The lattice dimensions are for scheelite $a = 7{\cdot}44$, $c = 11{\cdot}35$, and for powellite $a = 7{\cdot}4$, $c = 11{\cdot}44$ Å. When the proper space-filling conditions are realised, the ionic diameters are: scheelite, 1·125, 1·11, and 1·04 Å. for oxygen, calcium, and tungsten, respectively; powellite, 1·12, 1·12, and 1·03 Å. for oxygen, calcium, and molybdenum, respectively. A. E. MITCHELL.

Intensity of reflexion of X-rays by crystals. W. L. BRAGG, C. G. DARWIN, and R. W. JAMES (Phil. Mag., 1926, [vii], **1**, 897—922).—A general review of the formulæ describing the intensity of reflexion of X-rays from a crystal, with special reference to those of Darwin (*ibid.*, 1914, [vi], **27**, 315, 675) for the cases of reflexion from an imperfect and from a perfect crystal. Numerical comparison shows that rock-salt, fluorspar, and barytes approximate closely to the imperfect type, whilst calcite is intermediate. It is considered that most crystals approach the imperfect type, but that their degrees of perfection are sufficiently high to warrant the modifying of the mosaic formula by means of the corrections for primary and secondary extinctions described by Darwin (A., 1922, ii, 416). A. E. MITCHELL.

Reflexion of X-rays from crystals. R. SCHLAPP (Phil. Mag., 1926, [vii], **1**, 1009—1025).—A mathematical analysis of the principal phenomena of the X-ray optics of perfect crystals composed of a periodically stratified medium in which the specific inductive capacity is a periodic function of distance from a given plane. The analysis leads to values of the factors representing the influence on the intensity of reflexion, of polarisation, structure, and temperature, which are in agreement with the later results of Darwin and of Ewald (Physikal. Z., 1924, **26**, 29). A. E. MITCHELL.

Scattering powers of calcium and fluorine for X-rays. R. W. JAMES and J. T. RANDALL (Phil. Mag., 1926, [vii], **1**, 1202—1214).—The absolute intensities of reflexion have been measured for a series of X-ray spectra from fluorite. The spectra group themselves into three sections, corresponding with structure-amplitudes of the types Ca+2F, Ca, and Ca − 2F. The spectra of the type Ca − 2F become more important relatively to those of the types Ca and Ca + 2F as the magnitude of the glancing angle increases, thus showing that the scattering power of fluorine is less important relatively to that of calcium at large scattering angles. Calculations, by different methods, of the scattering power of fluorine lead to divergent results, which are corrected by assuming that the divergence is due to increased absorption due to extinction and that the extinction is proportional to the observed intensity of the reflected radiation. The values of the scattering powers for fluorine and calcium obtained from the observations are compared with those calculated by Hartree (A., 1925, ii, 735) when there is a considerable disagreement in the values for calcium at large glancing angles; the observed values are higher than those calculated. It is suggested that the differences are due to the increasing fraction of the incident radiation, which, at high angles of scattering, will undergo Compton scattering and therefore not play any part in the interference. A. E. MITCHELL.

***X*-Ray analyses. II. Photometric determination of X-ray spectral lines by the silver grain method.** P. GÜNTHER and G. WILCKE (Z. physikal. Chem., 1926, **119**, 219—246; cf. A., 1925, ii, 237).—Results accurate to 0·1% can be obtained by the silver-grain method of Eggert and Noddack (cf. A., 1923, ii, 526; Meidinger, *ibid.*, 1925, ii, 143) provided that the relative darkening is not greater than 1 : 3. When comparison is made between strong and weak lines, a suitable aluminium screen should be interposed so as to reduce the effect of the former. The method is used to determine the composition of gadolinite and to follow the fractionation of rare earths. H. TERREY.

Evaluation of the size of ions. H. G. GRIMM and H. WOLFF (Z. physikal. Chem., 1926, **119**, 254—274).—From crystal structure and physical properties having the dimensions of length only the sizes of uni-, bi-, ter-, and quadri-valent ions have been calculated with results correct to about 10%. Differences in passing from one column to the next in the periodic classification are of the same order except for oxygen and barium. H. TERREY.

Lattice constants of the platinum metals and of silver and gold. The lanthanide contraction. T. BARTH and G. LUNDE (Z. physikal. Chem., 1926, **121**, 78—102).—The following values of a_0, expressed in Å., have been obtained by the method previously employed (this vol., 114): silver, 4·078; gold, 4·070; iridium, 3·823; ruthenium, 2·695; osmium, 2·724. For the last two, c_0=4·273 and 4·314, respectively. With increasing pressure, the difference between the lattice dimensions of silver and gold diminishes and ultimately disappears at 14,000 atm. The increase in lattice dimensions in passing from one element to the next higher element in the same group of the periodic classification decreases with increasing atomic number, from which it is inferred that some other effect besides the lanthanide contraction comes into play. R. CUTHILL.

Crystallography of 2 : 1 sodium sulphate–carbonate. A. F. ROGERS (Amer. J. Sci., 1926, [v], **11**, 473—476).—The compound $2Na_2SO_4,Na_2CO_3$ separates when the brine of Searles Lake, California, is heated above 25°. The system Na_2CO_3–NaCl–Na_2SO_4–H_2O has been studied at various temperatures. The crystals now described were deposited on a lump of sodium chloride that was suspended in a saturated solution of sodium sulphate and sodium carbonate at 50°. They are orthorhombic with $a : b : c = 0·579 : 1 : 1·213$; n_α 1·463, n_β 1·469, n_γ 1·480. L. J. SPENCER.

Electrostatic potential energy, and rhombohedral angle, of carbonate and nitrate crystals of calcite type. S. CHAPMAN, J. TOPPING, and J. MORRALL (Proc. Roy. Soc., 1926, **A**, **111**, 25—56).—A detailed description of the method of calculation and the results of Bragg and Chapman (A., 1925, ii, 92), together with an extension to the case of sodium nitrate. For this salt the rhombohedral angle is calculated to be 102° 26′, the observed value being 102° 42·5′. The results can be used to calculate the distance between the electrostatic centres of the oxygen ions in the carbonate and nitrate groups from the observed rhombohedral angles. R. CUTHILL.

Crystal structure of the fluorides of certain bivalent metals: anhydrous FeF_2, CoF_2, NiF_2, and ZnF_2. A. FERRARI (Atti R. Accad. Lincei, 1926, [vi], **3**, 324—331).—These fluorides all exhibit the same tetragonal crystalline lattice of the rutile type, the dimensions of the elementary cell, which contains two molecules, being:

	a in Å.	c in Å.	Vol. in Å.^{3}	d(calc.).	d(exp.).
FeF_2	4·670	3·297	71·91	4·333	4·09
CoF_2	4·695	3·193	70·38	4·574	4·43
NiF_2	4·710	3·118	69·17	4·641	4·63
ZnF_2	4·715	3·131	69·60	4·932	4·84

T. H. POPE.

X-Ray investigation of the crystal lattices of manganous fluoride and manganese dioxide. A. FERRARI (Atti R. Accad. Lincei, 1926, [vi], **3**, 224—230).—Manganous fluoride and various forms of natural and artificial manganese dioxide have been examined by the X-ray method, use being made of an anti-cathode of chromium. Manganous fluoride crystallises in the tetragonal system and has a rutile structure, the axial ratio $c : a$ being 0·675: the elementary cell contains two molecules; a=4·865, c=3·284 Å.; d (calc.) is 3·97, d (exp.) 3·98. Manganese dioxide exhibits the same lattice as the fluoride, but with somewhat different dimensions: a=4·380, c=2·856 Å.; d (calc.) 5·27 exceeds the highest experimental value, 5·08, and the axial ratio, $c : a$=0·625, is appreciably below that found crystallographically, 0·664. X-Ray examination shows that the dioxide exists in only one crystalline form, which is the tetragonal form of polyanite. The supposed rhombic form, pyrolusite, is certainly pseudomorphous. T. H. POPE.

Crystal structure of α- and β-cadmium sulphide and wurtzite. F. ULRICH and W. ZACHARIASEN (Z. Krist., 1925, **62**, 260—273; from Chem. Zentr., 1926, I, 862—863).—α-Cadmium sulphide, prepared by heating the precipitated substance at 700—800° in an atmosphere of sulphur vapour, is apparently identical with greenockite and isomorphous with wurtzite and forms hexagonal crystals having the space-group, C_{6v}^4; a=4·142, c=6·724 Å. Co-ordinates: Cd ($\frac{2}{3}$, $\frac{1}{3}$, 0), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$), S ($\frac{2}{3}$, $\frac{1}{3}$, p), ($\frac{1}{3}$, $\frac{2}{3}$, $p+\frac{1}{2}$), parameter $p=\frac{3}{8}$. β-Cadmium sulphide, prepared by precipitation of a solution of cadmium sulphate with hydrogen sulphide and subsequent drying at 70°, forms regular crystals isomorphous with zinc blende; a=5·820 Å. Wurtzite: a=3·836, c=6·277 Å. J. S. CARTER.

Crystal structure of perowskite and related substances. T. BARTH (Norsk. Geol. Tids., 1925, **8**, 1—16; from Chem. Zentr., 1926, I, 11).—Application of the Debye-Scherrer method to perowskite, $CaTiO_3$, shows that the structure is pseudo-regular. Assuming one molecule in the parallelepiped, the edge of the cube is 3·795 Å. Dysanalyte exists as mixed crystals of $CaTiO_3$ and $NaNbO_3$, and is pseudo-cubic, the edge being 3·826 Å. Prepared $NaNbO_3$, which in the form of fine crystals is double-refracting, is also pseudo-cubic, the edge being 3·890 Å. The atom positions in perowskite are: Ca (0, 0, 0), Ti ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), O (0, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{2}$, 0, $\frac{1}{2}$), ($\frac{1}{2}$, $\frac{1}{2}$, 0). J. S. CARTER.

Crystal structure of cinnabar isomorphs. W. HARTWIG (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1926, 79—80).—Measurements of d_{100} in Å. and of the density of the following minerals, all of the zinc-blende type, were made by means of X-ray powder photographs: metacinnabarite, MgS, 5·822, 7·722; guadalcazarite, (Hg,Zn)(S,Se), 5·781, 7·396; onofrite, Hg(S,Se), 5·906, 7·920; tiemannite, HgSe, 6·069, 8·199; coloradoite, HgTe, 6·444, 8·025. W. A. CASPARI.

X-Ray diffraction patterns of mullite and sillimanite. R. W. G. WYCKOFF, J. W. GREIG, and N. L. BOWEN (Amer. J. Sci., 1926, [v], **11**, 459—472).—Laue, powder, and spectrographic photographs

of natural fibrolite and of artificial and natural mullite gave almost identical results, the unit cell being taken as $a=5{\cdot}70$, $b=7{\cdot}66$, $c=2{\cdot}85$ Å. for both. This unit contains 2 mols. of fibrolite (Al_2O_3,SiO_2) or 0·75 mol. of mullite ($3Al_2O_3,2SiO_2$). These puzzling and anomalous results are discussed. The suggestion that mullite breaks down on cooling into a mixture of fibrolite and amorphous alumina is not considered probable. L. J. SPENCER.

Temperature of paramorphic transformation of cristobalite. R. WEIL (Compt. rend., 1926, **182**, 1165—1167; cf. A., 1925, ii, 757).—A reply to Longchambon (A., 1925, ii, 1131). The experimental procedure by which a constant transition temperature can be observed is described. Each portion of the crystal is transformed suddenly at constant temperature, although different portions may have different transition temperatures. F. G. SOPER.

Colour and structure of quartz. R. KLEMM and G. O. WILD (Centr. Min., **A**, 1925, 270—273; from Chem. Zentr., 1926, I, 41).—Consideration of the colour and crystallography of different types of quartz suggests that rock-crystal, citrine, and smoky quartz should be classified together, amethyst being abnormal. Spectral examination, using the carbon arc, failed to detect the presence of impurity elements in the various types. J. S. CARTER.

Spectroscopic examination of minerals. I. Sapphire. G. O. WILD and R. KLEMM (Centr. Min., **A**, 1925, 273—274; from Chem. Zentr., 1926, I, 41; cf. preceding abstract).—A bluish-green natural specimen and a prepared sapphire were examined spectroscopically using the carbon arc. The mineral had a higher proportion of titanium to iron than the prepared specimen, both specimens containing magnesium. A colourless true sapphire from Ceylon was free from iron. Two lines of silver and seven of germanium were clearly seen. J. S. CARTER.

Imperfect crystallisation in certain long chain compounds. A. MÜLLER (Nature, 1926, **117**, 721).—Stearolic and behenolic acids are monoclinic, space-group C_{2h}^4. A crystal flake of behenolic acid, $CH_3{\cdot}[CH_2]_7{\cdot}C{\equiv}C{\cdot}[CH_2]_{11}{\cdot}CO_2H$, proved to be built up of small crystal elements oriented with their b axes in common. The degree of freedom required to explain the powder photograph effect consists in rotation round the b axis. Similar effects are obtained with crystals, *e.g.*, of rock salt or maleic acid, bent so that one crystal axis remains undistorted, whereby an internal breaking up of the crystal takes place. Behenolic and stearolic acids, and probably many other long chain compounds, are deposited abnormally, first by orientation of small crystal elements in parallel layers, and secondly by orientation of these elements parallel to a definite direction in the layer. A. A. ELDRIDGE.

Crystal structure of pentaerythritol. I. NITTA (Bull. Chem. Soc. Japan, 1926, **1**, 62—63; cf. Mark and Weissenberg, A., 1923, i, 1055).—Laue photographs show that there are no planes of symmetry parallel to the c axis. S_4^2 and C_4^5 are the only possible space-groups. Whichever be proved to be the space-group, it will follow that the central carbon atom is tetrahedrally placed with regard to the $CH_2{\cdot}OH$ groups. W. A. CASPARI.

X-Ray investigations of highly polymerised organic substances to determine the limiting values of their mol. wts. R. O. HERZOG (Physikal. Z., 1926, **27**, 378—379).—Ott's work (this vol., 460) is criticised. The method described has been tested on eight substances of known structure with poor results; it indicates, however, the general order of magnitude of the mol. wt. R. A. MORTON.

Laue photographs of crystalline benzene. B. BROOMÉ (Z. Krist., 1925, **62**, 325; from Chem. Zentr., 1926, I, 827).—Laue photographs of crystalline benzene show that the crystals belong to the rhombic system, having $a:b:c=1:0{\cdot}770:0{\cdot}728$. The elementary parallelepiped containing 4 mols. suggested by the author (Physikal. Z., 1923, **24**, 124) as a result of Debye–Scherrer measurements is thus confirmed: $a=9{\cdot}76$; $b=7{\cdot}39$; $c=6{\cdot}85$ Å. J. S. CARTER.

Evidence in favour of a dual-theory of metallic conduction. E. H. HALL (Proc. Nat. Acad. Sci., 1926, **12**, 326—328).—The observed Peltier development of heat where an electric current changes direction within a metal crystal (Bridgman, A., 1925, ii, 1136) is readily explained by the dual-theory formula previously suggested by the author (Proc. Nat. Acad. Sci., 1921, **7**, 63). J. S. CARTER.

Magnetic properties of single crystals of iron. K. HONDA, S. KAYA, and Y. MASUYAMA (Nature, 1926, **117**, 753—754).—The magnetisation curve for single crystals of iron is almost vertical up to an intensity of magnetisation of 1000 c.g.s.u.; it then shows two sharp bends, saturation being attained at 1710 c.g.s.u. The hysteresis loss of a single crystal of pure iron is only about 10% of that of sheet iron containing silicon; single crystals show a very large magnetic expansion, variations in the value of which are discussed. A. A. ELDRIDGE.

Magnetic properties of single crystals of iron. W. L. WEBSTER (Nature, 1926, **117**, 859).

Arrangement of atoms in tetragonal crystals of the mercurous halides. Calculation of the optical double refraction of mercurous chloride. E. HYLLERAS (Z. Physik, 1926, **36**, 859—896).—A more detailed account of work already published (this vol., 114).

[Hardness of] diamond. W. F. EPPLER and H. ROSE (Centr. Min., **A**, 1925, 251—253; from Chem. Zentr., 1926, I, 40).—The hardness of diamond is not the same in all directions, being least parallel to the cube faces, greater parallel to the rhombododecahedral faces, and greatest parallel to the tetrahedral faces. J. S. CARTER.

Hardness of carbon steels at high temperatures. I. G. SLATER and T. H. TURNER.—See B., 1926, 491.

Ratio of tensile strength of steel to the Brinell hardness number. R. H. GREAVES and J. A. JONES.—See B., 1926, 491.

Behaviour of single crystals of aluminium under static and repeated stress. H. J. GOUGH, D. HANSON, and S. J. WRIGHT (Phil. Trans., 1926, **A**, **226**, 1—30).—Investigation of the effect of repeated stress on various metal aggregates indicated that fracture occurred when hardening by slip had exceeded a limiting value (cf. B., 1923, 1182A). Further evidence is obtained from the behaviour of single crystals of aluminium subjected to reversed direct stresses, reversed torsional stresses, single blow tensile impact, and slow cycles of repeated tensile loading. Single crystal test pieces up to 0·5 inch diameter were used, and changes in structure were followed microscopically and by means of *X*-rays. It was established that slip bands formed under repeated stress represent traces of slip planes on the surface of the specimen. In the early stages slip takes place on all four octahedral planes of the crystal, but is subsequently confined to a conjugate pair of (111) planes. Change in the relative position of the specimen and crystal axis during test indicated that the direction of slip was the (110) direction, and this was confirmed by the distortion of the test piece, which became elliptical in section. The effect of slip is to produce greater resistance to slip, not only on the slipping planes, but also on planes which intersect them. The single crystal has no primitive elasticity, and plastic strain occurred under the lowest stress used. Hardening is attributed to a rumpling of the crystal planes, and not to a uniform bending. C. J. SMITHELLS.

Influence of the mean principal stress on the flow of iron, copper, and nickel. W. LODE (Z. Physik, 1926, **36**, 913—939).—Experiments are described on tubes of iron, copper, and nickel subjected to tension and to internal pressure. The elastic limit, rate of flow, dependence of the stress causing flow on the nature of the flow, and the influence of the mean principal stress on the greatest difference of tension in the plastic state are fully discussed. E. B. LUDLAM.

Properties of gold–silver–copper alloys. L. STERNER-RAINER (Z. Metallk., 1926, **18**, 143—148; cf. B., 1925, 552).—The m. p., hardness, tensile strength, and elongation of alloys of the gold–silver–copper series have been determined and the results are reproduced in graphical form. The minimum m. p. of the series (790°) occurs in alloys containing a large proportion of the silver–copper eutectic, *i.e.*, in alloys containing 25—35% Cu with 0—40% Au and the rest silver. The maximum hardness of alloys annealed at 740° and quenched from above 400° to avoid formation of gold–copper compounds is 150 with the alloy containing 50% Au, 25% Cu, and 25% Ag, whilst the strongest alloy (tensile strength 61 kg./mm.^{2}) is that containing 50% Au, 33·3% Ag, and 16·7% Cu. The tensile strength of 14-carat alloys increases as copper is substituted for silver, first rapidly, then more slowly to a maximum with 27·7% Cu, then falls slightly; the hardness increases from 40 with 41·5% Ag to a maximum of 140 with 24·9% Cu and 16·6% Ag, then falls to 82 with 41·5% Cu, and the elongation falls slightly from 40% with 41·5% Ag to 34% with 25% Ag, then increases somewhat irregularly to more than 50% with 41·5% Cu. In all cases, cold-rolling increases the hardness and tensile strength, but has no effect on the shape of the tensile strength curve. The hardness curves of cold-worked 14-carat alloys show maxima at 16·5% Cu and 31·1% Cu and a well-marked minimum at 27·7% Cu; severely cold-worked alloys have the same elongation whatever the composition. A. R. POWELL.

Strength and plasticity of bismuth crystals. M. GEORGIEFF and E. SCHMID (Z. Physik, 1926, **36**, 759—774).—The breaking strain of bismuth crystals by a force perpendicular to the plane of splitting is 324 g./mm.^{2}. It is independent of temperature between − 80° and + 20°. The plastic deformation begins at a definite critical tension which diminishes with rising temperature up to 200° and then remains about constant until the m. p. is reached. Whether a crystal is ductile or brittle depends on its orientation in the bismuth wire. E. B. LUDLAM.

Mechanical force exerted by growing crystals. C. W. CORRENS (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1926, 81—88).—The conditions are discussed which underlie the known phenomenon of the lifting of a glass plate by an alum crystal growing in its saturated solution. If the surface tensions between crystal and solution, between crystal and glass, and between solution and glass be $\sigma_{1,2}$, $\sigma_{1,3}$, and $\sigma_{2,3}$, respectively, then the surface energy $w(\sigma_{1,3}-\sigma_{1,2}-\sigma_{2,3})$, where w is the area, does work in lifting the plate. In the process, an infiltration of solution between crystal and glass takes place. It is found that if plates of muscovite are laid between crystal and glass, whereby $\sigma_{1,3}$ is reduced and becomes nearly equal to $\sigma_{1,2}+\sigma_{2,3}$, no appreciable lifting effect is observed. W. A. CASPARI.

Plastic deformation of single metallic crystals. W. E. W. MILLINGTON and F. C. THOMPSON (Nature, 1926, **117**, 720—721).

Micro-method for the determination of mol. wts. from vapour density. J. A. SÁNCHEZ (Anal. Asoc. Quím. Argentina, 1925, **13**, 478—490).—The author describes a micro-modification of the ordinary Hoffmann method for determining vapour pressure which gives good results. G. W. ROBINSON.

Electrical conductivity of metals. S. PROCOPIU (Bull. Acad. Sci. Roumaine, 1926, **10**, 8—12).—A formula $\rho=KCT$, expressing the relation between the specific resistance ρ, specific heat C, and absolute temperature T, similar to an empirical one previously given by Grüneisen (A., 1918, ii, 287), is deduced theoretically. This has been verified for lead over a wide range of temperature, although the constant K increases slightly with the temperature. To explain this slight divergence, another constant, α, is introduced, and it is shown mathematically that the formula may be modified by substituting $K'(1+\alpha T)^2$ for K, when it becomes $\rho=K'CT(1+\alpha T)^2$. C. J. STILL.

Behaviour of selenium exposed to the action of mesothorium radiations. W. DEL REGNO (Atti R. Accad. Lincei, 1926, [vi], **3**, 201—205).—Measurements are recorded of the action of mesothorium radiation on a Griffin cell consisting of a

very thin layer of selenium of high resistance. The mesothorium was covered with thin mica and in 1915 had an activity equal to that of 27 mg. of radium. With the mesothorium in its nearest position to the selenium, the sensitiveness of the cell, *i.e.*, the relative variation in the electrical resistance of the cell, was marked, the variation being 52% of the original value of the resistance for an exposure of 4 min. As the distance between cell and mesothorium is increased, the sensitiveness diminishes rapidly at first and slowly later. In producing this effect, the action of the γ-rays is small compared with that of the β-rays. The law according to which the sensitiveness of the cell varies with the duration of excitation is also modified with change in the distance between the cell and the mesothorium.

If the excitation is not too intense, a relatively short time suffices for the cell to recover conditions of sensitiveness almost identical with those preceding the excitation. With alternate equal periods of excitation and rest, the cell exhibits, after the first few cycles, an almost constant variation in the resistance, so that a single excitation is insufficient to indicate the time taken by the selenium to recover its original sensitiveness after excitation. T. H. Pope.

Conductivity of fused salts. W. Klemm and W. Biltz (Z. anorg. Chem., 1926, **152**, 225—234; cf. A., 1925, ii, 127).—The conductivities of the following salts in the fused state have been measured at various temperatures: mercuric, mercurous, stannous, yttrium, lanthanum, and calcium chlorides, and mercuric iodide. With the exception of the first, all are good conductors, and the conductivity increases with rise of temperature. R. Cuthill.

Conductivity and molecular state of fused salts. W. Biltz and W. Klemm (Z. anorg. Chem., 1926, **152**, 267—294).—A review of published data for the conductivities of fused metal halides in which the following generalisations emerge. Most halides in the fused state have a specific conductivity of either about 0·1—1·0 or less than 10^{-5}. The conductivity, referred to the volume of a g.-equivalent, of the lower chloride of a metal is greater than that of a higher chloride of the same metal. Poor conductors have relatively low m. p., and good conductors relatively high m. p. R. Cuthill.

Electrical conductivity in single crystals and in crystal aggregates. G. von Hevesy (Z. Physik, 1926, **36**, 481—483).—The increase in conductivity in crystal aggregates and in cracked crystals as compared with single crystals is not to be attributed to "bad places" in the crystal lattice, but more probably to surface conduction resulting from the absence of ions on one side. The loosening of the lattice resulting from rise of temperature is not due to the previous existence of "bad places" in the lattice. E. B. Ludlam.

Influence of elastic deformation on the magnetic disturbance of the superconductivity of tin. Hysteresis phenomena. G. J. Sizoo, W. J. de Haas, and H. K. Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 221—232; cf. this vol., 230).—The transition between the normal conductive and the superconductive states of a metal under the influence of a magnetic field may be represented by a continuous curve, the "magnetic transition curve." By the elastic deformation of tin, its magnetic transition curve may be displaced, the displacement with increasing pressure being in the direction of lower fields. The curves obtained with an increasing and a decreasing field, respectively, are not coincident, but give a hysteresis figure of a peculiar form. There are indications that the descending curve is not continuous. The exact effect of variation of current strength was difficult to determine owing to the heterogeneity of the field.
M. S. Burr.

Magnetic disturbance of the superconductivity of mercury. I and II. W. J. de Haas, G. J. Sizoo, and H. K. Onnes (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 233—249, 249—263; cf. preceding abstract).—The magnetic transition curves of highly purified mercury in a homogeneous field show hysteresis, indicating that the phenomenon is not due to the presence of iron. In general, the descending curves, and in one case the ascending curve, have been shown to be discontinuous. It is suggested that these discontinuities depend on the crystalline state of the wire, since a single-crystal tin wire gave a much simpler curve. The breadth of the hysteresis figure increases a little with decreasing temperature.
M. S. Burr.

Decomposition of hydrogen peroxide by suspensions of certain hydroxides. (Mlle.) S. Veil (Compt. rend., 1926, **182**, 1028—1031; cf. A., 1925, ii, 412).—The hydroxides of iron and of chromium in contact with solutions of hydrogen peroxide behave similarly to that of nickel and become continuously less magnetic. The corresponding values of the molecular coefficient of magnetisation of the oxides pass through a maximum. F. G. Soper.

Magneto-chemical reactions of hydroxides in the presence of hydrogen peroxide. (Mlle.) S. Veil (Compt. rend., 1926, **182**, 1146—1148; see preceding abstract).—Although the state of oxidation of cobaltous and cupric hydroxides changes during the decomposition of hydrogen peroxide, the variation in the magnetic properties of these hydroxides and their corresponding oxides obtained by calcination is analogous to that of other hydroxides previously studied. F. G. Soper.

Discontinuities in the magnetisation of nickel. Realisation of a state with a simple cycle. R. Forrer (J. Phys. Radium, 1926, [vi], **7**, 109—124).—See A., 1925, ii, 486, 639.

Glowing of lead wire. D. Damianos (Physikal. Z., 1926, **27**, 289—290).—The glowing of lead (m. p. 327°) is surprising, since substances rarely glow below 500°. It is shown that the glowing wire is actually liquid, but that in spite of its temperature exceeding 500°, it does not flow because a thin film of oxide possessing a high tensile strength is formed on heating the wire in air. This acts as a tube retaining the liquid metal. If the heating of a fresh wire is carried out in an atmosphere of nitrogen or hydrogen, the lead melts and runs without glowing. In air or

oxygen the resistance changes suddenly at the m. p., the wire sags, and on further heating glows without running. R. A. MORTON.

Ratios of specific heats of nitrogen at atmospheric pressure and between 10° and −183°. J. H. BRINKWORTH (Proc. Roy. Soc., 1926, **A**., **111**, 124—133).—Using the method of Clément and Desormes and substituting Callendar's gas equation for the ideal equation, the ratio, γ, of the specific heat at constant pressure to that at constant volume is found to be 1·4054 at 10°, 1·4103 at −78°, and 1·4454 at −183°. From these values and from the same equation, the molecular heats at constant volume, C_v, at these temperatures are found to be 4·922, 4·910, and 4·914, respectively, whilst the specific heats at constant pressure, c_p, are 0·2468, 0·2471, and 0·2535. If Berthelot's equation be used throughout, the same values for γ, C_v, and c_p are obtained at 10° and −178°, but the values at −183° are 1·4596, 4·988, and 0·2597, respectively. Combination of Dixon and Greenwood's relation (A., 1924, ii, 144) connecting C_v and the temperature with Callendar's equation gives values for c_p which closely approximate to those above. R. CUTHILL.

Thermal constants of solid and liquid carbon dioxide. O. MAASS and W. H. BARNES (Proc. Roy. Soc., 1926, **A**, **111**, 224—244).—The specific heat at constant pressure of the solid has been measured between −183° and −78·5°, and the specific heat of the liquid between 25° and −78·5°. Over the range −56° to −110°, the values of the former can be represented by the expression $0{\cdot}400-0{\cdot}00283T+0{\cdot}0000125T^2$, where T is the absolute temperature. By direct measurements the latent heats of fusion and sublimation are found to be 45·3 and 136·9 cal./g., respectively. The latent heat of evaporation is computed to be 88·1 cal./g. The coefficient of expansion of the solid has been determined between −90° and −164°, and proves to be abnormally large, which may account for the values of the molecular heat, obtained by direct measurement, being much in excess of those deduced for carbon dioxide in combination at much higher temperatures. Trouton's constant for liquid carbon dioxide is calculated to be 20·7, thus indicating the absence of association. The density of liquid propane has been measured at −183·3°, −139·0°, and −133·3°. R. CUTHILL.

Heat capacity of non-polar solid compounds. E. O. SALANT (Proc. Nat. Acad. Sci., 1926, **12**, 334—337).—An expression for the molecular heat capacity of a non-polar solid compound is developed. The various terms express the contributions of molecular vibrations, linking frequencies, and the vibrations of atoms across their linkings. This equation will be applied to various organic solids, the approximations previously recorded (A., 1925, ii, 1042) being discarded. J. S. CARTER.

Heat capacities and heats of crystallisation of some isomeric aromatic compounds. D. H. ANDREWS, G. LYNN, and J. JOHNSTON (J. Amer. Chem. Soc., 1926, **48**, 1274—1287).—The m. p., the latent heats of fusion, and the specific heats of the liquid and of the solid at the m. p. and of the solid at 25°, are recorded for some aromatic compounds. The specific heats of the solids at 25°, especially *o*-, *m*-, and *p*-isomerides, fall within a narrow range, but the heats of fusion and the specific heats at the m. p. are greater for the *p*- than for the corresponding *o*-isomerides. The *m*-isomerides show no regularity. S. K. TWEEDY.

Specific heats of isomerides of the type *ortho*, *meta*, and *para* C_6H_4XY from 110° to 340° Abs. D. H. ANDREWS (J. Amer. Chem. Soc., 1926, **48**, 1287—1298).—The specific heats of some disubstituted benzene derivatives were measured between 110° and 340° Abs. by a rapid calorimetric method accurate to 1—2%. The structural differences between *o*-, *m*-, and *p*-isomerides have almost no effect on the specific heat, which is a linear function of temperature; hence the entropies, heats of formation, and free energies of formation of such isomerides are probably very nearly equal. S. K. TWEEDY.

Theory of specific heat of solutions. F. ZWICKY (Physikal. Z., 1926, **27**, 271—286).—A more detailed account of work already abstracted (this vol., 462; A., 1925, ii, 1138). Intermediate mathematical steps are displayed. The pressure effect due to the water dipole leads to a correction in the Milner–Debye theory of osmotic effects. The theory can under certain conditions harmonise with Tammann's internal pressure conception of an equation of state for electrolytic solutions. R. A. MORTON.

[Latent] heats of fusion of chloroform, acetone, and carbon disulphide. S. MITSUKURI and S. AOKI (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 61—71; cf. this vol., 356).—A more detailed account of work already published (this vol., 568).

Heats of combustion of cyclic hydrocarbons. D. P. KONOVALOV (J. Chim. phys., 1926, **23**, 359—362; cf. J.C.S., 1923, **123**, 2184).—The following heats of combustion are determined (Cal.[15]): *cyclo*hexene, 898·8; methylene*cyclo*hexane (b. p. 101—102°), 1054·9; (0, 1, 3) *dicyclo*hexane (b. p. 79·6—80·2°), 912·5. These and existing data are in good agreement with the formula of the author (*loc. cit.*), $Q=48{\cdot}8n+x+5{\cdot}3h$, where n and h are the number of oxygen and hydrogen atoms used in the complete combustion of 1 mol. of the hydrocarbon and x is a constant for a particular series. For benzene and its simple derivatives $x=15$, but the presence of a side-chain with a double linking near the benzene ring increases the value to $x=30$ in styrene, and α- and *p*-methylstyrene. For the polymethylenes *cyclo*hexane, *cyclo*pentane, and methyl*cyclo*butane, $x=0$. For *cyclo*hexene and methylene*cyclo*hexane $x=15$, whilst for *dicyclo*hexane $x=30$. The same formula can be used for the heats of combustion of mixtures of hydrocarbons. W. HUME-ROTHERY.

Melting points of normal saturated dibasic acids. D. A. FAIRWEATHER (Phil. Mag., 1926, [vii], **1**, 944—950).—The m. p. of the even members of the series of normal saturated dicarboxylic acids from succinic to *n*-dotriacontanedicarboxylic acid decrease steadily, with the increasing length of the methylene chain, up to hexadecanedicarboxylic acid, after which they are almost constant. Those of the

odd members are lower than those of the even and increase steadily with the increasing length of the methylene chain until the m. p. curves for the two groups approach one another asymptotically. The m. p. of the diethyl esters of the series increase steadily with the increasing length of the methylene chain, those of both the odd and even members falling on the same smooth curve. An explanation of these and associated phenomena is based on the view of Challenor and Thorpe (J.C.S., 1923, **123**, 2480) that whilst the polarities in the even group are crossed, those of the odd tend to reinforce one another.

A. E. MITCHELL.

Schleiermacher's method for measuring thermal conductivity of gases. H. BUSCH (Ann. Physik, 1926, [iv], **80**, 33—42; cf. Schneider, this vol., 462).—A new theoretical treatment is advanced and the correction terms employed by Weber (Ann. Physik, 1919, [iv], **54**, 327, 437) are found to be little different from the new values.

R. A. MORTON.

Dilatometric investigation of the A3 and A4 transformations in pure iron. S. SATO (Phil. Mag., 1926, [vii], **1**, 996—1007).—The thermal expansion of pure electrolytic iron up to about 1500° has been measured by means of a special differential dilatometer in which cobalt, which exhibits no transformations in the temperature region investigated, was used as a standard of reference. During heating, the A4 transformation is accompanied by an expansion and the A3 transformation by a contraction. The transformations were reversible. The ratio of the magnitudes of the change of length due to the A3 and A4 changes is about 10 : 3. The thermal dilatation curve of δ-iron is a prolongation of that of α-iron. It is concluded, therefore, that α-iron and δ-iron are identical. A. E. MITCHELL.

Temperature of the acetylene flame. C. HEINRICH (Physikal. Z., 1926, **27**, 287—288).—The temperature of burning acetylene has been determined by spectral pyrometry for wave-lengths 668, 588, and 502 μμ. Values between 2148° and 2365° Abs. were obtained. The most probable value, 2210°, is compared with the values of Ladenburg and Nichols, 2115°, and of Féry, 2548° Abs. R. A. MORTON.

Complexity of the solid state. III. Behaviour of pure sulphur trioxide. II. A. SMITS and P. SCHOENMAKER (J.C.S., 1926, 1108—1127; cf. A., 1925, ii, 267).—The unary triple point observed in the work on the ice-like form of sulphur trioxide is at 16·8° and 158·5 mm. The low-melting, asbestos-like form is in inner equilibrium before intensive drying; for this form heat quantities can be calculated, and the unary triple point is at 32·5° and 398 mm. The intensively dried, low-melting, asbestos-like form cannot be prepared from the similarly dried ice-like form; instead of the low-, the high-melting form appears. This high-melting asbestos-like form after intensive drying is the form showing the most marked diminution of vapour pressure (*e.g.*, 59·1—3·7 cm. Hg) on distillation. At 18°, the velocity with which inner equilibrium is approached is imperceptible. At higher temperatures, the vapour pressure increases until inner equilibrium is reached. The unary sublimation curve, heat quantities, and the unary triple point at 62·2° and 174·3 cm. have been found. The high-melting asbestos-like form is shown to be a mixed crystal of at least two pseudo-components differing widely in volatility and m. p. The interpretation is made in terms of the senior author's theory of allotropy. R. A. MORTON.

Determination of gas density with the density balance. I. Efficiency and construction of different balances. A. STOCK and G. RITTER (Z. physikal. Chem., 1926, **119**, 333—367).—The construction and sources of error of gas density balances are discussed and the following new types are described. (I) A simple gas density balance suitable for general purposes and accurate to at least 1%. (II) A modification of I, with a magnetic zero-point adjustment. (III) A quartz precision density balance giving an accuracy of about 0·01%. (IV) A modification of III, with a magnetic zero-point adjustment. Type II has also been used in preliminary experiments on the magnetic weighing of gases.

L. F. GILBERT.

Variation of the density of a fluid with temperature. A. PREDVODITELEV (Z. Physik, 1926, **36**, 557—562).—The empirical formulæ of Saslavsky and Schaposchnikov can be deduced from van der Waals' equation. Comparison of the calculated values with experimental data for organic liquids shows slight deviations only, probably due to a factor being taken as constant over a certain range of temperature which is not rigidly a constant. The calculated value for neon is, however, less than half the experimental.

E. B. LUDLAM.

Density measurements with fused chlorides. W. KLEMM and J. ROCKSTROH (Z. anorg. Chem., 1926, **152**, 235—251).—Density measurements at a series of temperatures have been made with silver, potassium, rubidium, cuprous, beryllium, magnesium, zinc, mercurous, scandium, yttrium, lanthanum, thallous, thorium, and stannous chlorides in the fused state. Except with zinc chloride, the density is a linear function of the temperature. The following values of d_4^{25} are recorded: stannous chloride, 3·950; scandium chloride, 2·39; yttrium chloride, 2·67; lanthanum chloride, 3·82. The following m. p. have been determined: beryllium chloride, 416°; zinc chloride, 318°; mercurous chloride, 525°; thorium chloride, 765°; yttrium chloride, 700°.

R. CUTHILL.

Indium halides. I. W. KLEMM (Z. anorg. Chem., 1926, **152**, 252—266).—The density and conductivity of indium tribromide, tri-iodide, and mono-, di-, and tri-chlorides in the fused state have been determined at various temperatures, and are each found to be a linear function of the temperature. In the case of the trichloride and tribromide, the temperature coefficient of the conductivity is negative. For the mono-, di-, and tri-chlorides, d_4^{25} has the values 4·19, 3·62, and 3·46, respectively, whilst the m. p. are 225°, 235° (decomp.), and 586°. The m. p. of the tribromide and tri-iodide are 436° and 210°, respectively. R. CUTHILL.

Density and molecular state of fused salts. W. KLEMM (Z. anorg. Chem., 1926, **152**, 295—313).—An analysis of available data for the densities of salts in the fused state. The results, taken together with those obtained from a consideration of conductivities (this vol., 667), support the view that fused salts which are largely undissociated have larger molecular volumes in the fused state than those which are considerably dissociated. The former group also possess larger coefficients of expansion than the latter. R. CUTHILL.

Vapour-pressure curve and molecular heat of vaporisation of liquid carbon. H. HERBST (Physikal. Z., 1926, **27**, 366—371).—The temperature of the positive crater of a carbon arc increases with increasing current or voltage and other factors, until in free air a temperature of 5500—6000° Abs. is attained. The m. p. of graphite is 3800±100° Abs. (cf. A., 1925, ii, 759). The b. p. of liquid carbon under atmospheric pressure certainly exceeds 4700° Abs. and may be much higher. Assuming a b. p. of 4900°/1 atm. and 5720°/8 atm., the molecular heat of vaporisation is calculated as 141 Cal.; if the b. p. is 6000°, it is 211 Cal. The heat of sublimation of solid carbon, 216 Cal., diminished by the heat of fusion, gives a value 206 Cal., which corresponds well with the b. p. 6000°. R. A. MORTON.

Vapour pressure of hydrogen cyanide. H. SINOZAKI, R. HARA, and S. MITSUKURI (Bull. Chem. Soc. Japan, 1926, **1**, 59—61).—Results of two series of observations, between −16° and +46° (liquid) and between −86° and −14° (solid), are tabulated. For the former series, $\log p = -1460{\cdot}04/T + 0{\cdot}47647 \log T - 0{\cdot}0007344T + 6{\cdot}82130$, and for the latter, $\log p = -2014{\cdot}39/T + 1{\cdot}75 \log T - 0{\cdot}004077T + 6{\cdot}82130$, are suitable interpolation formulæ. W. A. CASPARI.

Critical constants and vapour tension of carbonyl chloride. A. F. O. GERMANN and Q. W. TAYLOR (J. Amer. Chem. Soc., 1926, **48**, 1154—1159).—The vapour pressures of nearly pure carbonyl chloride measured at both high and low temperatures agree with the measurements of Paternò and Mazzucchelli (A., 1920, ii, 309) and are given by $\log p$ (atm.) $= 4{\cdot}4659 - (1207{\cdot}9/T)(13{,}297/T^2)$. The observed critical temperature was 181·75° and, since Hackspill and Mathieu (A., 1919, ii, 446) found 183°, the round figure 182° is proposed, whence the calculated critical pressure is 55·6 compared with the observed value of 55·3 atm.; the round value 56 atm. is proposed. The critical density, calculated by the rule of Cailletet and Mathias, is 0·520. S. K. TWEEDY.

[Limits of validity of gas equations.] J. GEISSLER (Z. Elektrochem., 1926, **32**, 217; cf. Herz, this vol., 342).—Since it has been shown (A., 1918, ii, 220; Antonov, *ibid.*, 1925, ii, 865) that the pressure-temperature curves of saturated vapours are discontinuous, the relative merits of the Berthelot and Wohl equations can be tested only over the temperature range between two points of discontinuity. R. CUTHILL.

Internal pressure and free space. W. HERZ (Z. Elektrochem., 1926, **32**, 210—213).—The internal pressure, B, and free space, V_f, *i.e.*, the difference between the molecular volume at a particular temperature and that at 0° Abs. (cf. A., 1919, ii, 391), have been calculated for a number of liquids over a considerable temperature range. In general, the value of the product BV_f does not vary with the temperature, except near the critical point, where it falls somewhat. In ascending a homologous series, B falls and V_f rises at corresponding temperatures. R. CUTHILL.

Theory of the state of matter. V. Residual valency. VI. Critical volume. F. SCHUSTER (Z. Elektrochem., 1926, **32**, 188—191, 191—194; cf. this vol., 342).—V. It is suggested that for a series of substances with molecules of the same diameter, the greatest residual valency, as manifested, *e.g.*, by associative power, will be exhibited by that which has the smallest molecular volume and highest internal pressure. This view is supported by examples. Some substances possess several centres of residual valency, which saturate themselves by polymerisation, whilst others possess only one, and do not polymerise, although they form molecular compounds.

VI. By means of van Laar's equation ("Die Zustandsgleichung," Leipzig, 1924) $v_c/b = (3 + 0{\cdot}038\sqrt{T_c})/(1 + 0{\cdot}038\sqrt{T_c})$, where v_c is the critical volume, T_c the critical temperature, R the gas constant, and b van der Waals' constant, combined with the relation $b = RT_c/8p_c$, where p_c is the critical pressure, the value of v_c has been calculated for 66 substances. The results are in fair agreement with experimental data, and in general the property appears to be additive. R. CUTHILL.

Structure of the atomic magnet. Demonstration of the existence of a doublet in nickel. R. FORRER (Compt. rend., 1926, **182**, 1272—1275).—The atomic magnet for nickel consists of a right-angled doublet. This provides an explanation for many observations. R. A. MORTON.

Determination of surface tension by the method of ripples. P. N. GHOSH, D. BANERJI, and S. K. DATTA (Phil. Mag., 1926, [vii], **1**, 1252—1258).—A new stroboscopic method for the determination of the surface tension of liquids by the ripple method has been devised in which the measurements are made photographically. The values of the surface tension of water obtained by this method are in fair agreement with those of Weinstein and Volkmann, obtained by the capillary tube method, but are lower than those obtained by other workers employing different methods. A. E. MITCHELL.

Variation of surface tension of pure water with time. F. SCHMIDT and H. STEYER (Ann. Physik, 1926, [iv], **79**, 442—464).—A method of determining the surface tension of freshly-formed water surfaces has been devised, depending on the projection of an air current into a capillary and the carrying out of observations at intervals differing by $0{\cdot}25 \times 10^{-3}$ sec. after formation of the surface.

The graph showing surface tension against temperature when the former is measured $0{\cdot}5 \times 10^{-3}$ sec. after formation of the surface reaches a maximum at 13° with a value of 9·3 mg./mm., falling rapidly

to about 7·7 at 24°, much more slowly to 7·6 at 30°, and again rapidly to 7·15 at 36°. Similar but flatter curves are found when the time which elapses after formation of the surface is increased. The rapidity of the change may be judged from the values at 18°: $0{\cdot}5\times10^{-3}$ sec., 8·70; $1{\cdot}0\times10^{-3}$ sec., 8·33; $2{\cdot}0\times10^{-3}$ sec., 7·88; $6{\cdot}0\times10^{-3}$ sec., 7·43, to a limiting value of 7·395 mg./mm. R. A. MORTON.

Surface tension of solids. G. N. ANTONOV (Phil. Mag., 1926, [vii], **1**, 1258—1266).—A method for the determination of the surface tension of solids is described. It consists in varying the surface tension of some liquid, or suspension, the surface tension of which can be measured by a standard method, until it just wets the surface of the solid. The solid is then assumed to have the same surface tension as the liquid. By this method, glass has a surface tension of 120 dynes/cm., whilst rock salt exhibits the value of 315 dynes/cm. From the breaking stress of a crystal, rock salt gives a value of 1·4 dynes/cm., whilst that calculated from the molecular structure is 3000—4000 dynes/cm. A. E. MITCHELL.

Viscosity of gaseous mixtures. M. TRAUTZ and A. NARATH (Ann. Physik, 1926, [iv], **79**, 637—672).—The viscosity of mixtures of hydrogen chloride and hydrogen has been determined between 21° and 250°, and isotherms of viscosity/molar fractions have been plotted. Well-marked maxima occur in the isotherms corresponding with lower temperatures, whilst the curves for higher temperatures tend to flatten out until at 310° the maximum should disappear. The maxima on the isotherms lie on a straight line. At low temperatures, the increase in viscosity, due to addition of hydrogen, varies as the molar fraction, but the relationship breaks down at higher temperatures. The Sutherland constant (cf. this vol., 118) for hydrogen chloride is 362 and for hydrogen 83·7. The viscosity of air was determined as a control and earlier results were confirmed. Corrected values for the viscosities of hydrogen, oxygen, helium, argon, carbon monoxide, and ethylene are given. Kuenen's theory provides no satisfactory solution of the problem of the viscosity of mixtures. The hypothesis of polymerisation and formation of molecular complexes affords a promising, although so far only a qualitative, method of attack. R. A. MORTON.

Effect of temperature on viscosity of air. A. O. RANKINE (Proc. Roy. Soc., 1926, **A**, **111**, 219—223).—A criticism of the experiments of Williams (this vol., 234). R. CUTHILL.

Fusion curves and physical properties of the system benzene–toluene. S. MITSUKURI and A. NAKATSUCHI (Sci. Rep. Tôhoku, 1926, **15**, 45—52).—See this vol., 356.

Hardness of copper–tin alloys. A. MALLOCK (Nature, 1926, **117**, 787—788).—The hardness, as measured by the pressure which the material can withstand, of copper–tin alloys is maximal (220 tons/in.^{2}) at about 30 vol.% of tin. The values for copper and tin, respectively, are 48 and 6 tons/in.^{2} A. A. ELDRIDGE.

Miscibility, density, and refractive index in methyl alcohol–benzene–water mixtures. J. BARBAUDY (Compt. rend., 1926, **182**, 1279—1281).—The range of heterogeneity is more extended for the methyl alcohol–benzene–water mixtures than for the corresponding ethyl alcohol mixtures, confirming the relative insolubility of methyl alcohol in aqueous hydrocarbons. The mixtures methyl alcohol : benzene : water, 61·0 : 10·2 : 28·8, and 4·09 : 95·63 : 0·28 show the same density, d_4^{25} 0·870. The demarcation is, however, quite sharp, the mixture rich in benzene tending to become spherical in shape. The critical solution, d_4^{25} 0·8615, contains 30·8% of methyl alcohol, 65% of benzene, and 4·2% of water. R. A. MORTON.

Azeotropic properties of formic and acetic esters of saturated aliphatic alcohols. T. HANNOTTE (Bull. Soc. chim. Belg., 1926, **35**, 85—109).—The following temperatures are the b. p. at 760 mm. of the binary azeotropic mixtures examined, the numbers in parentheses giving the percentage of ester in the various mixtures: propyl formate–water, 71·6° (97·7); *iso*butyl formate–water, 80·4° (92·2); *n*-butyl formate–water, 83·8° (83·5); *iso*amyl formate–water, 90·2° (79); *n*-amyl formate–water, 91·6° (71·6); propyl acetate–water, 82·4° (86); *iso*butyl acetate–water, 87·4° (83·4); *n*-butyl acetate–water, 90·2° (71·3); *iso*amyl acetate–water, 93·8° (63·8); *n*-amyl acetate–water, 95·2° (59); propyl formate–propyl alcohol, 80·6° (90·2); *iso*butyl formate–*iso*butyl alcohol, 97·8° (79·4); *n*-butyl formate–*n*-butyl alcohol, 105·8° (76·3); *iso*amyl formate–*iso*amyl alcohol, 123·6° (74); *n*-amyl formate–*n*-amyl alcohol, 130·4° (57); methyl acetate–methyl alcohol, 54° (81·5); ethyl acetate–ethyl alcohol, 71·8° (69·4); propyl acetate–propyl alcohol, 94·2° (60); *iso*butyl acetate–*iso*butyl alcohol, 107·4° (45); *n*-butyl acetate–*n*-butyl alcohol, 117·2° (53).

The b. p. of the ternary azeotropic mixtures are given below, the numbers in parentheses giving the percentages of ester and alcohol, respectively, in the mixtures: propyl formate–propyl alcohol–water, 70·8° (82, 5); *iso*butyl formate–*iso*butyl alcohol–water, 80·2° (76, 6·7); *n*-butyl formate–*n*-butyl alcohol–water, 83·6° (68·7, 10); *iso*amyl formate–*iso*amyl alcohol–water, 89·8° (48, 19·6); *n*-amyl formate–*n*-amyl alcohol–water, 91·4° (41·2, 21·2); ethyl acetate–ethyl alcohol–water, 70·3° (83·2, 9); propyl acetate–propyl alcohol–water, 82·2° (59·5, 19·5); *iso*butyl acetate–*iso*butyl alcohol–water, 86·8° (46·5, 23·1); *n*-butyl acetate–*n*-butyl alcohol–water, 89·4° (35·3, 27·4); *iso*amyl acetate–*iso*amyl alcohol–water, 93·6° (24, 31·2); *n*-amyl acetate–*n*-amyl alcohol–water, 94·8° (10·5, 33·3).

The application of azeotropy to the preparation of esters is briefly discussed (cf. Wuyts, A., 1924, i, 710). J. S. CARTER.

Solubility of potassium halides in alcohol–water mixtures. S. M. ZEITLIN (Z. physikal. Chem., 1926, **121**, 39—44).—The solubility (in mol./litre) of potassium chloride, bromide, and iodide in methyl alcohol and in aqueous solutions of methyl and ethyl alcohols has been measured at 10·2° and

19·9°. The solubilities in methyl alcohol at 19·9° are 0·056, 0·142, and 0·735, respectively. R. CUTHILL.

[Solubility of potassium halides in alcohol–water mixtures.] A. E. BRODSKY (Z. physikal. Chem., 1926, **121**, 45).—Zeitlin's solubility data (cf. preceding abstract) are in agreement with Walden's rule $\varepsilon/\sqrt[3]{S}$=constant, where S is the solubility and ε is the dielectric constant of the solvent.

R. CUTHILL.

Solubility of alkaline-earth carbonates in aqueous hydroxylamine solutions. F. L. HAHN and K. BRUNNGÄSSER (Z. anorg. Chem., 1926, **153**, 77—87).—Solutions of hydroxylamine containing known volumes of 0·1N-barium chloride solution were titrated with 0·1N-sodium carbonate solution until precipitation occurred, and solutions containing sodium carbonate were similarly titrated with barium chloride. For a given volume of the first solution, whether barium chloride or sodium carbonate, the volume of titrating liquid required is the same. The product of the volumes of the two solutions is not constant, but diminishes with increasing volume of the solution first added. Precipitates are produced in clear solutions containing barium and carbonate by the addition of sodium hydroxide. The solubility of barium carbonate increases with increasing hydroxylamine concentration. Individual results are reproducible, but it is probable that supersaturation occurs, the amount of which depends on the conditions. A. GEAKE.

Solubility of glycine in aqueous and aqueous-alcoholic solutions at different p_H. K. SANO Biochem. Z., 1926, **171**, 277—286; cf. this vol., 345).—The solubility of glycine at the isoelectric point is depressed to $\frac{1}{2}$ in 20%, $\frac{1}{4}$ in 40%, 1/15 in 60%, 1/100 in 80% alcohol. Curves show the variation of relative solubility with p_H in 0, 20, 40, 60, and 80% alcohol. Such variation can be calculated by use of the mass law, agreement being rather better in aqueous than in alcoholic solution. P. W. CLUTTERBUCK.

Solubility of proteins in fat solvents. D. DEUTSCH (Magyar Orvosi Archiv., 1925, **26**, 525—526; cf. *ibid.*, 1924, **25**, 511).—Non-aqueous solutions of proteins were produced in the presence of certain electrolytes, *e.g.*, sulphuric or nitric acid.

CHEMICAL ABSTRACTS.

Supersaturation in turbidity titrations and a procedure for determining solubilities. F. L. HAHN and K. BRUNNGÄSSER (Z. anorg. Chem., 1926, **153**, 88—96).—When barium chloride solution is titrated with sodium carbonate, or *vice versa*, the volume required to produce turbidity is greater than corresponds with the solubility product of barium carbonate; no precipitate is formed until the supersaturation is such that nuclei can be formed spontaneously. This difficulty is avoided if the product of the concentrations at the point where the solutions first mix is considerably greater than it is after mixing is complete, and if this enhanced value is maintained for a sufficient time. In these circumstances, nuclei are formed which cause precipitation throughout the liquid if after mixing the solution is supersaturated. The first condition is best obtained by adding one drop of the titrating solution to a large volume, *e.g.*, 100—200 c.c. of the other solution, and the second condition by having the two solutions of the same concentration, so that the rate of diffusion is minimal. In practice, 0·03 c.c. of one solution is added to various volumes of the other, and the volume found for which a cloudiness is produced in 50% of the experiments. By this procedure, using 0·01N-solutions and assuming 85% dissociation, the solubility of barium carbonate is 0·025 g. per litre, in agreement with the accepted value. A. GEAKE.

Relative concentrations of various electrolytes required to salt out soap solutions. J. W. MCBAIN and A. V. PITTER (J.C.S., 1926, 893—898).—A study of the relative efficiency of various electrolytes in salting out 0·25N_w-solutions of sodium palmitate. At 90°, equimolecular proportions of different sodium salts produce the same effect irrespective of valency; although the concentration of sodium ion is important, the equilibria are not exclusively determined by it. It is possible to control the equilibria in any soap solution with any mixture of electrolytes with an accuracy of 5—10%. C. H. D. CLARK.

Narcosis. Partition coefficient of hypnotics between water and organic solvents, particularly those possessing ethylenic linkings. L. VELLUZ (Compt. rend., 1926, **182**, 1178—1180).—The partition coefficients of sulphonal, trional, dial, dipropylhydantoin, and mercuric chloride between water and a number of saturated and unsaturated oils and their corresponding fatty acids have been determined with reference to the mechanism of narcotic action. Solubility of the hypnotics is favoured by the carboxylic and hydroxyl groups and particularly by ethylenic linkings. It is greater in the glyceride than in the corresponding acid. F. G. SOPER.

Adsorption [at benzene–soap solution surfaces in the presence of electrolytes]. R. DUBRISAY (Compt. rend., 1926, **182**, 1217—1219).—Donnan's drop method is applied to the measurement of the number of drops of benzene passing through solutions containing pure soap, and soap in the presence of 1% of sodium chloride. By the use of a range of soap solutions of known titre, curves are plotted relating the concentration with the number of drops passing, and these are used in the determination of the variation in concentration of the soap solution in the above experiments. From these drop-numbers the ratio of the adsorptions per unit surface in the soap and soap-salt solutions are calculated, and values of 3·4 and 3·3 obtained using sodium laurate and glycocholate, respectively. The constancy of the ratio supports the author's theory that electrolytes which lower the concentration of the soap increase the amount adsorbed at the separating surface.

J. GRANT.

Adsorption of arsenious oxide by ferric hydroxide gels and ferric magnesium hydroxide gels. J. M. CLAVERA (Anal. Fís. Quím., 1926, **24**, 168—189).—The author has studied the adsorption of arsenious oxide from solutions of sodium arsenite by ferric hydroxide and ferric magnesium hydroxide gels, respectively. The preparations used were those

of the Spanish Pharmaceutical Codex. In the case of the ferric hydroxide gel, the adsorption follows the Freundlich adsorption isotherm. In the case of the ferric magnesium hydroxide gel, adsorption occurs only when the gel has been prepared without boiling. Gels prepared by adding ammonium hydroxide to ferric salts are more adsorptive than gels prepared by adding ferric salts to ammonium hydroxide. G. W. ROBINSON.

Adsorption and mobilisation of the potassium ion in colloidal clays. A. DEMOLON (Compt. rend., 1926, **182**, 1235—1238).—Adsorption of the potassium ion from potassium chloride solutions by brick-clay soils is almost unaffected by decarbonation, but considerably reduced by total decalcification. In the former case, the normal process occurs in which complex aluminosilicate clays react with the calcium carbonate and render it possible for the potassium to replace the calcium. In the latter case, these complex substances are removed. The effects of the oxide, sulphate, chloride, and nitrate of calcium in bringing potassium into solution show that this is independent of the nature of the anion. The capacity of brick-clays to take up potassium is thus regulated by the conditions of reciprocal exchange of the adsorbed potassium and calcium ions. J. GRANT.

Adsorption. XIII. Schultze-Hardy law and adsorption. N. R. DHAR and S. GHOSH (J. Physical Chem., 1926, **30**, 628—642; cf. A., 1924, ii, 737; Weiser, A., 1925, ii, 855; this vol., 242).—Previous work affords no support for the view that an ion which is highly adsorbed possesses a high coagulating power. Further, it is unjustifiable to assume that the greater the valency, and hence coagulating power, of an ion the greater is its adsorption. On the contrary, experiments with sols of mercury and antimony sulphides, of alumina and of manganese dioxide support the view that the greater the valency of an ion the less is it adsorbed, and the smaller the coagulating power the greater is the adsorption. Even with ions of the same valency, increased adsorption is not accompanied by greater coagulating power. New measurements of adsorption by a sol of manganese dioxide and by the carefully-purified, precipitated dioxide show the order of adsorption, in both cases, to be the same as previously found by Ganguli and Dhar (A., 1923, ii, 58), and by Chatterji and Dhar (*ibid.*, 615) viz., silver > potassium > copper > barium > aluminium, and support the view that the higher the valency of an ion the less the extent of its adsorption. Valency is probably a more important factor in coagulation than adsorbability. L. S. THEOBALD.

Adsorption of gases by activated charcoal at very low pressures. II. At −183°. H. ROWE (Phil. Mag., 1926, [vii], **1**, 1042—1054; cf. this vol., 345).—The adsorption, by activated coconut charcoal, of nitrogen, hydrogen, and carbon monoxide at very low pressures and −183° has been measured. The results are expressed better by an equation of the form suggested from the results obtained previously at higher pressures than by the usual Freundlich equation for adsorption. Saturation of the surface is characterised by a departure from the linear relationship between the quantity of gas adsorbed and the pressure. A. E. MITCHELL.

Absorption of hydrogen and carbon dioxide by pyrophoric iron, nickel, and cobalt. N. NIKITIN (Z. anorg. Chem., 1926, **154**, 130—143).—Iron, nickel, and cobalt, obtained by reduction of oxides and salts with hydrogen at the lowest possible temperature, give pyrophoric powders of very large surface. Since Sieverts (A., 1911, ii, 895) worked with strongly sintered powders, the surfaces of which were diminished by recrystallisation, the absorption was small. The surface area depends, not only on the specific properties of the metals, but also on the temperature of reduction. In these experiments, by using larger surfaces, the amount of absorption was much increased.

There is evidence for the existence of true gas-adsorption, in agreement with Freundlich's equation, at the surface of the crystalline powder at −180° for hydrogen with iron and nickel, and at 18° for carbon dioxide with iron.

Evidence is adduced for the formation of a nickel-hydrogen compound at the ordinary temperature which dissociates on either raising the temperature or lowering the pressure.

Pyrophoric iron absorbs large amounts of carbon dioxide at all the temperatures studied; nickel absorbs much less. Definite results could not be obtained with cobalt, but this showed singular power of absorbing hydrogen. M. CARLTON.

Adsorption on large molecules in solution. MARINESCO (Compt. rend., 1926, **182**, 1149—1151).—The viscosity of solutions of rhodamine in water and in a number of alcoholic solvents has been determined, and the molar volume V_E of the solute in volume V of solution calculated from the equation $\eta=\eta_0(1+2{\cdot}5V_E/V)$ (Einstein, Ann. Physik, 1911, **34**, 591). Owing to solvation, V_E is greater than V_S, the molar volume in the solid state (cf. Bancelin, Compt. rend., 1911, **152**, 1882), and may be expressed as a function of the molecular volume, ω, of the solvent, $V_E=C\omega+V_S$, where C is a constant $=12$. The thickness of the adsorption envelope is calculated from these values of V_E and lies between 2·3 Å. (for methyl and ethyl alcohols) and 3·5 Å. (for amyl alcohol), which corresponds with the diameters of the molecules of the solvents, assuming double molecules in the case of methyl alcohol. The number of molecules adsorbed per sq. cm. ($=C$/surface area of molecule) is $3{\cdot}8\times10^{14}$, in agreement with the values found by other workers. Solutions of eosin give similar results. In the presence of electrolytes, ions appear to be absorbed in preference to molecules of the solvent, for fluorescein in the presence of 3% sodium hydroxide in aqueous glycerol gives $V_E=500$, whilst $V_S=255$. This gives 1·3 Å. for the thickness of the adsorption envelope and corresponds with a unimolecular layer of ions. In mixtures of solvents, the thickness of the envelope indicates that the solvent with the higher dielectric constant is the more strongly adsorbed. F. G. SOPER.

Adsorption. III. Adsorption velocity. S. LIEPATOV (Kolloid-Z., 1926, **39**, 9—14).—The velocity of adsorption by starch and cellulose of alkali hydr-

oxides from alcoholic solutions is much smaller than that from aqueous solutions. In dilute solutions, the velocity is decidedly greater than in concentrated solutions. It increases with rise of temperature. The measured velocity corresponds with the rate at which the concentration at the boundary between two phases is adjusted. This adjustment is effected by diffusion. In the equation $K=1/t \log_e m/(m-\gamma Q)$, (cf. this vol., 577), K is proportional to the diffusion constant and to the total surface of the adsorbent, and inversely proportional to the thickness of the diffusion layer. N. H. HARTSHORNE.

Capillary condensation and adsorption. W. C. BRAY and H. D. DRAPER (Proc. Nat. Acad. Sci., 1926, **12**, 295—299; cf. Bachmann, A., 1917, ii, 562; Lowry and Hulett, *ibid.*, 1920, ii, 535; McBain, this vol., 467).—The sorption of water vapour at 25° by copper oxide, manganese dioxide, and mixtures of these oxides has been investigated. The chief feature of the isotherms is the rapid increase in sorption at high vapour pressures. Sorption involves two distinct phenomena, viz., true adsorption at low pressures and capillary condensation, the latter being negligible at pressures below 0·5 p_0, where p_0 is the vapour pressure of water, and capillary radii below 15 Å. This is contrary to the capillary theory of adsorption suggested by McGarvack and Patrick (A., 1920, ii, 417). Adsorption is a necessary precursor to capillary condensation, although the latter can occur only when the surface (covered with a unimolecular layer of adsorbed substance) is sufficiently curved. The structures of materials which are very adsorbent at low pressures consist of a very open or incomplete lattice, into the spaces of which the individual adsorbed molecules penetrate. J. S. CARTER.

Influence of electrical field on the adsorption of neutral molecules. A. FRUMKIN and A. OBRUTSHEWA (Nature, 1926, **117**, 790).—When to an acidified 0·5N-solution of silver nitrate containing n-octoic acid a similar solution of potassium iodide is gradually added, a sharp minimum value for the concentration of the octoic acid, as determined stalagmometrically, is observed near the point of complete precipitation. This point of maximum adsorption is somewhat displaced in the direction of an excess of potassium iodide. A. A. ELDRIDGE.

Surface activity of water. Surface activity and adsorptive forces. II. P. REHBINDER (Z. physikal. Chem., 1926, **121**, 103—126; cf. A., 1924, ii, 662).—Surface tension measurements by the method of maximum bubble pressure have been made with very concentrated aqueous solutions of silver ammonium nitrate, silver thallous nitrate, silver nitrate, potassium nitrite and carbonate, and ammonium nitrate. The surface tension, γ, of the solutions is given by the equation $\gamma=\gamma_0-b\log_e(ac+1)$, where γ_0 is the surface tension of the pure salt and c is the concentration of the water; which shows that water is a typical active substance in relation to the salts. In general, one of the two components of a solution is active, and if it be regarded as the solute, a relation similar to the above holds good. In the case of an aqueous solution of an active substance completely miscible with water, the elevation of the surface tension of the active substance is a linear function of the water concentration. Of the two components of a solution, the one with the smaller dielectric constant manifests surface activity. R. CUTHILL.

Spreading of dyes on the surface of water. A. FRUMKIN (Kolloid-Z., 1926, **39**, 8—9).—The following experiments illustrating the spreading of surface-active soluble substances on water are described. Particles of crystal-violet thrown on to a perfectly pure water surface show a lively movement, analogous to that of camphor, and leave coloured, spiral trails behind them. Eventually the whole surface becomes coloured. If at this stage a drop of oleic acid be added, the coloured layer is driven to the sides of the containing vessel and there sinks to the bottom. If a pure water surface is first touched with a drop of oleic acid and powdered crystal-violet then added, the particles of the latter show no movement, but send out coloured streamers below the surface of the water. A particle of crystal-violet added to a water surface previously "spread" with tetraiodofluorescein splits the latter by itself forming a cross-like pattern.
N. H. HARTSHORNE.

Surface tension. O. FAUST (Z. anorg. Chem., 1926, **154**, 61—68).—The surface tension of specially purified liquids and mixtures of which the viscosity and vapour pressure had previously (A., 1922, ii, 423) been determined was measured by a modification of Traube's method. Ignoring the deviations shown by the two aqueous solutions, Freundlich's comparison of physical properties may be extended to include viscosity, so that surface tension is directly proportional to intrinsic energy, critical pressure, latent heat, and viscosity and inversely proportional to compressibility and solubility. For the liquids tabulated, the ratio of the temperature at which the surface tension is 30 dynes/cm. to the critical temperature is constant, as was expected from previous experiments on viscosity (this vol., 343). M. CARLTON.

"Gas laws" in surface solutions. V. COFMAN (Nature, 1926, **117**, 755—756).—Delaplace's formula (A., 1925, ii, 772) $FA=kT$, where F is the pressure of surface films of oleic acid and A the area per mol., cannot be applied to concentrated films, but Marcelin's formula (this vol., 120; A., 1925, ii, 772) $FA=k$ may be correct under specified conditions. It is, however, more rational to express energy relations of films in terms of surface-pressure, surface, and the potential of the surface energy, $AF=kE$(or kE^2). Below a certain value of E, Adam's steep FA-curves will be obtained; above that value the curves will be similar to those of Marcelin and Langmuir. An "ideal film" or an "ideal colloid" may be defined as a system all surface and no volume, in a sense that its energy is a function of E only. A. A. ELDRIDGE.

Behaviour of neutral sodium caseinogenate in membrane hydrolysis. M. PÓLÁNYI (Biochem. Z., 1926, **171**, 473); also W. PAULI (*ibid.*, 474).—Replies to Starlinger (this vol., 631). P. W. CLUTTERBUCK.

Colloid absorption in quantitative analysis. E. EIGENBERGER.—See this vol., 701.

Rhythmic reactions of mercury salts in gelatin jellies. T. ORLOWSKI (Kolloid-Z., 1926, 39, 48—49).—By the action of ammonia solution on the white precipitate formed by treating gelatin sol with mercurous nitrate solution, coloured layers in the order of the colours of the visible spectrum and alternate white and dark grey spiral rings are observed in the upper and lower parts, respectively, of the containing vessel. The first effect is more marked the greater the concentration of the mercurous nitrate, whilst the second appears at low concentrations not at all, above a certain transition concentration only after some time, and at high concentrations almost simultaneously with the diffusion of the ammonia into the jelly. The gelatin concentration appears to exert no important effect on the phenomena. The substitution of sodium hydroxide solution for the ammonia solution results in no markedly coloured layers. N. H. HARTSHORNE.

Formation of the secondary systems of Liesegang rings. M. S. DUNIN and F. M. SCHEMJAKIN (Kolloid-Z., 1926, 39, 50—52).—The formation of silver dichromate rings in glass tubes has been studied. The usual system of rings was first formed, and at the end of these the silver dichromate separated in more or less equally distributed globules. Finally, these also ceased. After some further time a new system of rings started beyond the first system and went through the same stages of growth. Since the rings are themselves made up of systems of smaller rings, it is considered possible that the first and second systems observed are components of a ring in a "super"-system. N. H. HARTSHORNE.

Cryoscopic measurements with nitrobenzene. IV. Association in nitrobenzene solution. F. S. BROWN and C. R. BURY (J. Physical Chem., 1926, 30, 694—705).—The f.-p. depression of dry, wet, and partly saturated nitrobenzene by benzyl and *iso*-amyl alcohols, β-naphthol, and phenylacetic, propionic, benzoic, and cinnamic acids has been measured. These solutes fall into two groups (cf. Auwers, A., 1900, ii, 66); in the first the degree of association increases regularly with concentration as in the case of the alcohols and phenols; in the second it increases rapidly with concentration up to a limiting value (approx. 2), as in the case of the organic acids. The alcohols and phenols are apparently more associated in the wet than in the dry solvent, but with the organic acids the reverse holds good. With propionic acid, the curves for wet and dry solvent intersect and this probably occurs for other substances of this group. The change in the degree of association with concentration does not follow the law of mass action. The consequences of this are discussed, doubt being thrown on the existence of association in many cases. Preliminary calculations of the activities in dry and wet nitrobenzene have been made.

L. S. THEOBALD.

Densities of aqueous solutions of certain perchlorates. A. MAZZUCCHELLI and D. PRÒ (Gazzetta, 1926, 56, 99—111; cf. A., 1922, ii, 376; 1925, ii, 963).—Aqueous solutions of sodium perchlorate follow the general rule, that the apparent volume of the salt increases with increase in the concentration and also with rise of temperature; further, the apparent volume of the salt is markedly increased by the presence of the free acid, but always remains below the volume of the anhydrous salt. That of ammonium perchlorate is increased so much by addition of the free acid that, at the higher temperatures, it exceeds the specific volume of the anhydrous salt. The apparent volume of perchloric acid itself increases little with the concentration, but considerably with rise of temperature.

The values of the ratio of the coincidence pressure, K, at which water expands similarly to the solution considered (cf. Tammann, "Innere Kräfte und Eigenschaften der Lösungen") to the molecular concentration, are not equal for solutions of equal concentration of perchloric acids and its ammonium and sodium salts, and for each of these substances increase linearly with the concentration.

T. H. POPE.

Viscosity of aqueous solutions of the sodium silicates. V. R. MAIN (J. Physical Chem., 1926, 30, 535—561).—The relative viscosities of solutions of commercial sodium silicate have been measured at 25°. The values obtained with an Ostwald viscosimeter are lower than those obtained with a variable pressure type of instrument (Ubbelohde), but the resulting curves with the former are smoother. With the latter, the relation between the time of flow, t, and the pressure, p, is given by the equation $p^n t=\alpha$ (constant), and the relative viscosity by α/α_{H_2O}. The value of n is independent of the instrument used, the proportion of silica in the solution, and concentration. The viscosity–concentration curves are typical of emulsoid or lyophile sols. When the concentration is low, the viscosity increases slowly with the concentration, but there is subsequently a rapid increase at a point which depends on the silica content of the solution. The slope of the viscosity curve at a given concentration depends on the ratio $Na_2O : SiO_2$ in the solution. For large values of this ratio the change of slope is gradual, but it increases with the silica content, until the ratio $Na_2O : SiO_2$ approaches 1 : 4, when the curves rise steeply with increasing concentration, becoming almost vertical.

Temperature and viscosity are connected by the equation $\eta_t=\eta_0-kT$, and the temperature coefficient is greater the greater the proportion of silica. Below the ratio 1 : 2, the change in η_t is small.

Solutions for which the above ratio is less than 1 : 2 are chiefly non-colloidal, and an increase in the proportion of silica is accompanied by the formation of a solvated colloidal aggregate, the size and nature of which depend on the ratio and on the absolute concentration. L. S. THEOBALD.

Colloidal bismuth hydroxide. C. PAAL and L. DI POL (Ber., 1926, 59, [*B*], 874—877).—Solid, colloidal bismuth metahydroxide is prepared by the addition of bismuth nitrate dissolved in aqueous glycerol to an aqueous solution of sodium protalbate or lysalbate containing sodium hydroxide; after being centrifuged, the solutions are dialysed against water and subsequently evaporated in a vacuum at 50°, and finally over concentrated sulphuric acid.

Sodium protalbate is the more efficient protective agent. The preparations contain 20% of bismuth as metahydroxide under the most favourable conditions. Pre-treatment of the protective colloid with warm sodium hydroxide enables more concentrated bismuth hydroxide sols to be produced, which, when dried, pass more or less completely into non-reversible gels. H. WREN.

Colloidal bismuth. C. PAAL and L. DI POL (Ber., 1926, **59**, [*B*], 877—882).—Bismuth hydrosols are readily obtained by the reduction of technical "bismon" or colloidal bismuth hydroxide (cf. preceding abstract) with hot formaldehyde. The preparations are treated with acetic acid, which precipitates the adsorption compound of bismuth and the acids of the protective colloid; the precipitates are centrifuged and dissolved in dilute sodium hydroxide. Evaporation of the solutions in the absence of air yields solid adsorption compounds of colloidal bismuth and the sodium salts of the protective acids, which retain their colloidal solubility for months if protected from air, whereas the corresponding preparations containing the protective acid rapidly pass into irreversible gels. H. WREN.

Preparation of colloidal manganese dioxide by the reduction of potassium permanganate solution with organic reducing gases. I. Reduction with ethylene. A. STEOPOE (Kolloid-Z., 1926, **39**, 35—37).—Colloidal solutions of manganese dioxide have been prepared by passing ethylene through potassium permanganate solutions, the particular advantage of this method being that the removal of electrolytes is unnecessary, since the oxidation product of the ethylene, viz., glycol, is electrochemically indifferent, and the potassium hydroxide formed is without influence on the stability of the sol. The sol is more stable in stoppered than in unstoppered vessels owing in the latter case to the action of atmospheric carbon dioxide. In a series of sols containing from 2·2125 to 0·0470% of manganese dioxide, those of intermediate concentration showed the maximum stability, the dilute sols being almost as unstable as the concentrated ones. After preparation, the sols separate into two or three transparent, yellow to brown layers, which on stirring do not reseparate. On long keeping, the layers disappear of their own accord and they are not formed at all in the presence of protective colloids. The phenomenon is explained by assuming that the separation into layers indicates a separation of particles according to their size, and that the final homogenisation represents the disappearance of the smaller particles to the advantage of the larger, since, according to Jablczyński's classification (cf. A., 1924, ii, 157), manganese dioxide is a sparingly soluble colloid. N. H. HARTSHORNE.

Preparation and conditions of formation of the two possible types of emulsion in the system cresol-gelatin-water. R. M. WOODMAN (J. Physical Chem., 1926, **30**, 658—672; cf. J. Pomol. Hort. Sci., 1925, **4**, 184).—Both types of emulsion are possible in this system and marked excess of one liquid phase determines the type formed, the liquid in excess becoming the external phase, *e.g.*, a relatively large amount of water favours the cresol-in-water type. Previous suspension or solution of the emulsifier in one of liquids has no apparent effect on the type of emulsion formed. When the constituents of the system are present in the same amounts, the type formed depends on the mode of preparation, gentle shaking or partial rotation favouring the cresol-in-water type and prolonged shaking the reverse type, which is generally more stable than the former. The water-in-cresol type was the only one possible at 52°, when 10 c.c. of 0·4% aqueous gelatin and 10 c.c. of cresol were the amounts used. Under conditions such that both types are possible, there are indications that a new gelatin solution would give only the water-in-cresol type, medium-aged solutions, both types, and old solutions, the reverse type. Different samples of cresol behaved similarly, and inorganic impurities in the gelatin had no effect on the type. Where the proportions admit the possibility of both emulsions, a cresol-in-water emulsion which had broken gave the same type on re-emulsification by hand shaking in all cases, but in some cases a creamed water-in-cresol emulsion was reversed by any method of re-shaking, particularly in the cold. L. S. THEOBLAD.

Formation of nuclei in supersaturated media. M. VOLMER and A. WEBER (Z. physikal. Chem., 1926, **119**, 277—301).—The views of Gibbs are discussed and expanded. The rate of formation of nuclei is a function of the number already present. The influence of various solid substances (*i.e.*, with different surface energies) on the formation of nuclei from supersaturated mercury vapour and solutions of salts is described. Experiments show that crystals deposited from solution on the surface of another crystalline substance tend towards a geometrically orderly arrangement. The factors governing crystal growth are examined. L. F. GILBERT.

Organogels of silicic acid. Replacement of water in the hydrogel by alcohol. J. B. FIRTH and W. L. PURSE (J. Physical Chem., 1926, **30**, 617—619; cf. Graham, J.C.S., 1864, **17**, 318; Neuhausen and Patrick, A., 1922, ii, 144).—The replacement by alcohol of the water of four silicic acid gels prepared under different conditions and containing from 7·53 to 33% of water has been investigated by a static and a dynamic method. The latter, in which dry air saturated with alcohol vapour was passed over the gel for 3 days, gives the more complete replacement. Complete elimination of water, although not regarded as impossible, was not obtained.
L. S. THEOBALD.

Formation of gels of vanadium pentoxide and [stannic hydroxide]. S. GHOSH, D. N. CHAKRAVARTI, and N. R. DHAR (Z. anorg. Chem., 1926, **152**, 399—404).—Gels of vanadium pentoxide can be obtained by dialysis of sols, or by addition to them of small quantities of electrolytes. Stannic hydroxide gels can be obtained by the latter method. Ability to form stable gels is considered to run parallel with the possession of high viscosity and a high degree of hydration. R. CUTHILL.

Viscosity of some sols in presence of potassium chloride. D. N. CHAKRAVARTI and N. R. DHAR (Z. anorg. Chem., 1926, **152**, 393—398).—Addition of increasing quantities of potassium chloride to sols of vanadium pentoxide, antimony sulphide, mastic, and gum dammar causes the viscosity first to fall, then to pass through a minimum and rise again. The viscosity of mastic sols decreases with increasing age. It is suggested in explanation that sols are less hydrated than the uncharged substances, and that the viscosity increases with the hydration, so that the viscosity of a sol is reduced by adsorption of ions with charges of the same sign. R. CUTHILL.

Colloid-chemical study of the photo-polymerisation product of vinyl chloride. G. FLUMIANI (Z. Elektrochem., 1926, **32**, 221—230).—Mol. wt. determinations of the polymerisation product of vinyl chloride, obtained by the action of light on the simple compound in the presence of uranyl nitrate (cf. Plotnikov, A., 1922, i, 419) have been made by the f.-p. method in nitrobenzene, acetophenone, phenanthrene, and naphthalene. Solutions in the first two solvents have also been studied ultramicroscopically. Contrary to expectation, the degree of dispersion was greater in the more concentrated solutions than in the more dilute, but was not directly proportional to the concentration. The degree of dispersion also depends on the method of formation, *e.g.*, a solution prepared directly has a smaller degree of dispersion than one of the same concentration prepared by dilution of a more concentrated solution or gel. By previously heating the solution to various temperatures for different periods of time, the depression of f. p., *i.e.*, the degree of dispersion, increases with increase of temperature and time of heating, reaching a maximum at about 110°. The degree of dispersion also depends on the solvent. The phenomena observed are discussed with reference to the forces between the colloidal particles and the solvent medium. M. S. BURR.

Properties of alkaline silicic acid sols. H. FREUNDLICH and H. COHN (Kolloid-Z., 1926, **39**, 28—35).—The sensitisation of silicic acid sols caused by the addition of alkalis (Flemming, A., 1902, ii, 646) has been confirmed by measurements of the coagulation of different sols made alkaline with potassium hydroxide or ammonia, by lithium, sodium, potassium, and barium chlorides, calcium nitrate, and magnesium sulphate. The change from a hydrophile sol to one with distinctly hydrophobe properties was observed and shown to be due to the presence of the alkali. The charge on the silica particles in alkaline sols was measured by means of a new cataphoresis apparatus which eliminates any effects due to the migration of silicate ions. The gradual transformation from sol to silicate solution brought about by the addition of alkali has been followed by means of conductivity and p_H measurements and dialysis experiments. The alkali sensitisation is considered to be due to dehydration of the silica particles: viscosity measurements, observations of the appearance and condition of the coagulate, and the fact that some other hydrophile sols exert a strong protective action on the sensitised sol contribute to this conclusion. The flocculation observed sometimes when silicic acid and albumin sols are mixed (Mylius and Groschuff, A., 1906, ii, 160) occurs with certainty only if the sols are neutral. N. H. HARTSHORNE.

Viscosity anomalies in cellulose sols. W. VON NEUENSTEIN (Kolloid-Z., 1926, **39**, 88—90).—Cellulose nitrate and acetate solutions become less viscous with age, but subsequent mechanical treatment raises the viscosity again. The diminution is assumed to be due to the arrangement of the rod-like micelles to form larger secondary particles which are broken up by mechanical treatment into an irregular structure of higher viscosity. N. H. HARTSHORNE.

Reactions between a dissolved substance and contiguous colloidal particles. K. F. HERZFELD (Z. physikal. Chem., 1926, **119**, 377—381).—Theoretical. L. F. GILBERT.

Determination of mol. wts. by centrifuging. T. SVEDBERG (Z. physikal. Chem., 1926, **121**, 65—77).—By means of the centrifugal method (this vol., 340), the mol. wt. of highly purified egg-albumin is found to be 33,000—35,000. R. CUTHILL.

Action of heat on the complex calcium caseinate + calcium phosphate. Greater sensitivity of the phosphate micelles. C. PORCHER (Compt. rend., 1926, **182**, 1247—1249; cf. A., 1925, i, 846).—If a neutral or almost neutral caseinate (p_H 7—7·03) is heated for 30 min. to a temperature ranging from 40° to 100°, its p_H and the rate of coagulation of its neutral calcium phosphate complex by rennin are not substantially altered. At 125°, however, coagulation will not occur, but if fresh quantities of calcium phosphate are added and neutrality is restored, coagulation may be produced again. Consequently the calcium phosphate is the component of the complex which determines its coagulation by rennin. J. GRANT.

Infra-red absorption spectra of cellulose in the region of the dispersion of fluorite. R. O. HERZOG and G. LASKI (Z. physikal. Chem., 1926, **121**, 136—142).—Measurements have been made over the range of wave-lengths 2—8 μ. The absorption spectrum of cellulose nitrate differs from that of cellulose, but in neither case does mercerisation cause any alteration in the spectrum. It appears that if any of the atoms or radicals in a molecule are replaced by others, the amplitudes of the system of bands corresponding with the remaining radicals change. R. CUTHILL.

Structure of cellulose and its significance in chemical transformations. R. O. HERZOG (J. Physical Chem., 1926, **30**, 457—469; cf. Herzog and Jancke, A., 1921, ii, 531).—The *X*-ray data for cellulose agree well with those calculated from the quadratic equation for rhombic symmetry assuming the unit-cell to consist of four $C_6H_{10}O_5$ groups. The progress of mercerisation can be followed by *X*-ray spectography. Cellulose fibres after treatment with strong sodium hydroxide solution show a point diagram different from that of the original cellulose, the difference becoming more pronounced with complete mercerisation. A quadratic equation for mercerised cellulose is given as well as the dimensions of crystal-

lites of natural cellulose fibres. The behaviour of bast fibres in both magnetic and electric fields corresponds closely with the results of optical measurements and *X*-ray investigations (cf. Kolloid-Z., 1924, **35**, 201).

X-Ray examination of nitrated and acetylated hemp fibre indicates that these derivatives of cellulose probably crystallise in the rhombic system and that the dimensions of the crystallites are practically the same as for the untreated cellulose (cf. Herzog and Londberg, A., 1924, i, 373). Fibres obtained by denitration of a cellulose nitrate and by hydrolysis of an acetate give the diagram of the original, untreated cellulose, but cellulose regenerated from the esters prepared from a mercerised cotton gives the diagram of cellulose hydrate.

The size of particles in colloidal solutions of cellulose nitrate, as found by the diffusion method, corresponds exactly with the dimensions of the crystallites computed from the *X*-ray analysis.

L. S. THEOBALD.

Flow of an elastic liquid through a capillary. Theory of viscosity measurements. M. REINER (Kolloid-Z., 1926, **39**, 80—87).—On the assumption that the variations in the viscosity constant (η) of certain sols when measured at different shear gradients are due to elastic properties, the following equation, giving the quantity of liquid (Q') which flows through a capillary in unit time, has been deduced: $Q'=R^4\pi p/8\eta l[1-2\cdot667\theta l/pR+5\cdot333/p^4(\theta l/R)^4]$, where R is the inner radius of the capillary, l its length, p the driving pressure, and θ the "flow-solidity." When $\theta=0$, the equation becomes that of Poiseuille and has therefore a general application. It has been verified by measurements with a benzopurpurin sol which have shown that sufficiently accurate results are obtained without the third term in the square brackets. N. H. HARTSHORNE.

Mechanism of coagulation. W. W. LEPESCHKIN (Kolloid-Z., 1926, **36**, 41—47).—The difference between irreversible and reversible coagulation lies in the formation of adsorption compounds by the colloid particles and in their non-hydration, in the first case. Arsenious sulphide may, by dialysis and cataphoresis, be made to show reversible coagulation. The irreversible coagulation of this sol is caused by the formation of adsorption compounds with salts, which are not decomposed by water. Dilute nitric acid in the cold and dilute potassium hydroxide at high temperatures, however, decompose them without destroying the colloid. The addition of alcohol by lowering the dielectric constant of the water accelerates the coagulation of the sol, whilst greater concentrations of alcohol retard it on account of the depression of the ionisation of the coagulating salt. Ether emulsion in the presence of salts brings about a rapid coagulation of the sol, due to adsorption on the drop surfaces. Dissolved ether causes no alteration in the coagulation velocity, but if mixed with alcohol diminishes it. The raising of the inner friction of the sol by the addition of agar-agar completely stops coagulation, whilst the addition of glycerol or sugar retards or stops it according to the quantity added. N. H. HARTSHORNE.

Influence of lyophilic colloids on the precipitation of insoluble salts, gelatin, and silver chromate. I and II. T. R. BOLAM and (Miss) M. R. MACKENZIE (Trans. Faraday Soc., June 1926, advance proofs).—I. The ability of gelatin to prevent the precipitation of silver chromate is not dependent on the presence of calcium, but is much increased by increasing the acidity of the solution. The results of Williams and MacKenzie (J.C.S., 1920, **117**, 844) for the diffusion of silver chromate, upon which doubt was cast by Sen and Dhar (A., 1924, ii, 730), have been verified, and the chromate ion is found to diffuse more rapidly than the silver ion. Gelatin gels containing silver chromate appear to contain no colloidal particles when examined with the ultra-microscope, nor are they coagulated by sodium, potassium, and zinc nitrates.

II. The effect of added substances on the silver-ion concentration in solutions of silver chromate has been examined electrometrically. The results indicate that in presence of gelatin much higher concentrations can be obtained than in pure aqueous solution. This is supported by conductivity measurements. It seems that the gelatin combines with some of the silver chromate, and keeps the rest in a supersaturated state. R. CUTHILL.

[Structure of] precipitates. III. S. ODÉN (Arkiv Kemi, Min., Geol., 1926, **9**, No. 23, 1—38; cf. A., 1920, ii, 600, 675).—The formation of precipitates is said to take place in five stages, which, however, are not all invariably passed through in every case. (i) The formation of nuclei consisting of a condensation of ions and molecules which ultimately change into the more stable unit-cell; (ii) the growth of these nuclei to form primary particles, (iii) which are reversible aggregates, and, in a manner analogous to the coagulation of colloids, further aggregate to form (iv) irreversible aggregates, which may either be spherulitic or possess a definite structure. The final stage (v) consists in the growth of larger crystals at the expense of smaller ones.

The relation between the total number, n, of primary nuclei and the concentration of the reacting ions c_1 and c_2 is $n=\text{const.}\ (c_1c_2)^a$, where a depends on the number of ions constituting the unit cell. The growth of the nuclei follows the law $-dc/dt=D/\delta\times O_t(c_t-c_\alpha)$, where $-dc/dt$ is the velocity of growth, D the coefficient of diffusion, δ the thickness of the layer of adhesion, O_t the total surface of the primary particles, c_t the concentration at the time t, and c_α the saturation concentration after infinite time. When the growth is completed, $c_t=c_\alpha$ and the primary particles are formed. The formation of the primary particles may be much delayed by the presence of other substances; this has been investigated experimentally in the case of the precipitation of strontium sulphate in presence of 0·2 g. per litre of sodium citrate.

The primary reversible aggregates of stage (iii) retain a certain electrical charge, and show a difference of potential towards the solution; the time required for their complete formation is great compared with the formation and growth of the nuclei, but is in most cases less than 1 minute. The distribution of the

various sizes of these primary particles has been studied experimentally in the cases of the precipitation of silver chloride, lead sulphate, barium carbonate, antimony sulphide, and barium sulphate; in the last case, the presence of hydrochloric acid during precipitation has a marked influence on the size of the grains. In the above cases, a "disperser" or stabilising ion, negatively or positively charged according to the particular case, must be present to prevent aggregation. An improved form of the author's automatic sedimentation balance, employed in this work, is described. The last stage (v) may in certain cases proceed exceedingly slowly. It is dependent, not only on a difference in solubility with size, but also on a variation in size of the original particles, and takes place more quickly the greater the initial variation of these is. Experimental evidence in support of this for the case of the precipitation of calcium carbonate is adduced. H. F. HARWOOD.

Rhythmic phenomena in the precipitation of suspensions of red mercuric sulphide. N. I. MOROSOV (J. Trans. Russian Chinese Polytech. Inst. Harbin, 1925, No. 4, 135—139).—When an aqueous suspension of red mercuric sulphide is prepared by rubbing with lactose and shaking with water, stratification is observed. CHEMICAL ABSTRACTS.

Number of electrical quanta on colloid particles. W. KISTIAKOVSKI (Kolloid-Z., 1926, **39**, 26—27).—When the size of a colloid particle does not differ greatly from those of the accompanying ions it can be shown that $r=K'\rho u$, where r is the number of electrical quanta on the particle, ρ its radius, u its migration velocity, and K' a constant. The value of K' can be obtained from a comparison of diffusion equations (Einstein, Stokes–Millikan) with migration equations (Kohlrausch, Burton) which lead to the equation $(r \,.\, r_1/M)(F \,.\, dE/dl)=6\pi N\rho\eta u/(1+A'\lambda/\rho)$, in which r_1 is the valency of the accompanying ions, M the common divisor of r and r_1, dE/dl the strength of the electric field in the determination of u, η the inner friction coefficient of the disperse phase, N Avogadro's constant, F Faraday's constant, A' a constant (Millikan, Physikal. Z., 1923, **13**, 173), and λ/ρ the ratio of the mean free path of a molecule to its radius. The equation is found to give results in agreement with the experimental work of Svedberg (A., 1909, ii, 645), and of Galecki (Z. physikal. Chem., 1909, **67**, 200).
N. H. HARTSHORNE.

Anomalous flocculation of clay. W. O. KERMACK and W. T. H. WILLIAMSON (Nature, 1926, **117**, 824).—The clay used by Joseph and Oakley (this vol., 576) may have lost the coating of colloidal silica on which the anomalous flocculation may depend. With suspensions of kaolin, marked anomalous precipitation has been obtained in alkaline solution by calcium ions after the addition of small quantities of colloidal silica. Cæsium, ammonium, and potassium salts give similar, although delayed, results. The nature of the precipitate obtained under the prescribed conditions differs from that obtained at other ionic concentrations, and other values of p_H of the medium.
A. A. ELDRIDGE.

Peptisation and formation of complex ions. N. R. DHAR and S. GHOSH (Z. anorg. Chem., 1926, **152**, 405—412).—Peptisation experiments indicate that in such processes as the dissolution of metallic sulphides in yellow ammonium sulphide, the formation of complex ions is preceded by the formation of a colloidal solution. The formation of such a colloidal solution is probably due to the affinity of the peptising agent for the insoluble substance. R. CUTHILL.

Periodicity of colloidal reactions. W. KOPACZEWSKI and W. SZUKIEWICZ (Compt. rend., 1926, **182**, 1276—1278).—The capillary rise and flocculating power of sodium oleate and certain other colloids exhibit periodic rise and fall over a period of days. Similar variations occur concomitantly in physical properties, *e.g.*, surface tension, viscosity, electrical conductivity, and hydrogen-ion concentration. The hydrosol of tin chloride behaves similarly in passing to the state of gel. Colloids do not in general age in a continuous manner, but the periodicity cannot as yet be explained. The age of colloids appears to be important for all reactions in which they participate, including those occurring in the living organism.
R. A. MORTON.

Application of the Tyndall effect in the measurement of the cataphoresis of colourless sols. A. DUMANSKI and A. KNIGA (Kolloid-Z., 1926, **39**, 40—41).—The application of the Tyndall effect to make visible the boundary of colourless sols in macroscopic cataphoresis measurements has been made by the authors quite independently of the work of Kruyt (cf. this vol., 122), who used the same method. N. H. HARTSHORNE.

Cataphoresis of colloidal solutions at small electrolyte concentrations. A. IVANITZKAJA and M. PROSKURNIN (Kolloid-Z., 1926, **39**, 15—26).—Measurements of the cataphoresis of the negative sols, carbon, arsenious sulphide, and vanadium pentoxide, have shown that the lowering of charge brought about by the progressive addition of electrolytes is almost always preceded by an increase of charge at very small electrolyte concentrations. The electrolytes used were hydrochloric, sulphuric, and phosphoric acids and potassium hydroxide for the carbon sol, hydrochloric acid for the arsenious sulphide sol, and hydrochloric and sulphuric acids, potassium hydroxide, and aluminium, barium, and potassium chlorides for the vanadium pentoxide sol. In the salts used, the effect of the cations increases with their valency, whilst of the acids the monobasic hydrochloric acid was the most active and was practically equalled in this respect by potassium hydroxide. Analogous results were obtained with platinum, cadmium, and zinc hydrosols, prepared by Bredig's method, and a similar series of electrolytes, but here the cataphoretic maximum was observed at much smaller electrolyte concentrations. Positively charged alumina suspensions behave similarly.
N. H. HARTSHORNE.

Electrostatic capacity of vegetable tissues and organic colloids. L. PETRI (Kolloid-Z., 1926, **39**, 63—67).—In contrast to inorganic substances which when attached to the leaf system of a charged

electroscope show a normal discharge curve, vegetable tissues in similar circumstances show a more or less marked increase of potential before discharging. The phenomenon has been studied by means of a micro-electroscope which is described. Tissues killed by boiling show the increase much more markedly than when living; further, in dry air, it is much more marked than in moist air, and if the leaves etc. be coated with glycerol or paraffin, it is completely absent. It is greatly decreased by "fixing" the tissues in mercuric chloride solution. The conclusions arrived at are that it is connected with the evaporation of water from the tissue and the consequent diminution of its electrostatic capacity, and that the capacity is greater in living than in dead tissues. Further experiments on the same lines are described and the results are discussed, principally from a botanical point of view. N. H. HARTSHORNE.

Dissociation of the hydrogen molecule. M. BODENSTEIN and G. JUNG (Z. physikal. Chem., 1926, **121**, 127—135).—Further measurements of the rate of combination of hydrogen and bromine at the ordinary temperature in sunlight, and at 302° in the dark (cf. A., 1925, ii, 218), indicate that the heat of activation of the reaction $H+HBr=H_2+Br$ is probably zero. It is then calculated, from the results previously obtained, that the heat of dissociation of the hydrogen molecule at 0° is 106,700±3000 cal.
R. CUTHILL.

New mass action law. III. Theoretical calculation of isotherms. R. LORENZ and M. MANNHEIMER (Z. anorg. Chem., 1926, **152**, 314—323; cf. this vol., 355).—The application of the new law to the calculation of the isotherms of the system $Pb-Cd-PbCl_2-CdCl_2$ (A., 1924, ii, 258) gives results which, unlike the ideal isotherms, are in good agreement with the experimental results. R. CUTHILL.

Active molecules in chemical equilibria. D. ALEXÉEV (J. Chim. phys., 1926, **23**, 415—446).—An equation for the equilibrium constant of a reaction is deduced on the assumption that the velocity of a unimolecular reaction depends on the rate of formation of active molecules the velocities of which exceed a certain limit, u, the transformation itself being instantaneous. For a general reaction of the type $n_1A_1+n_2A_2\ldots\rightleftharpoons n_1'A_1'+n_2'A_2'\ldots$, the equation deduced from the equilibrium constant, K, is $\log K=-\Sigma n\log\varepsilon+\Sigma(n\log u)+Q_0/4{\cdot}57T$, where ε is a factor common to all reactions, and Σn is the difference of the numbers of reacting molecules on the two sides of the equation, and the term $\Sigma(n\log u)$ refers to the numbers and critical velocities of each reacting molecular species. Q_0 is the heat of reaction at absolute zero and is equal to the difference between the kinetic energies of the reacting molecules at their critical velocities, *i.e.*, to a series of the type $\frac{1}{2}n_1'M_1'u_1'^2\ldots-\frac{1}{2}n_1M_1u_1^2\ldots$ The critical velocities have been calculated for a number of substances from the known heats of dissociation, and used in comparing the calculated and experimental equilibria constants; the agreement is generally good. The reactions considered are the decomposition of hydrogen chloride, bromide, iodide, and sulphide, the Deacon process ($2H_2O+2Cl_2\rightleftharpoons4HCl+O_2$), the formation of methane ($CH_4\rightleftharpoons2H_2+C$), the water-gas equilibrium, and the dissociation of carbon dioxide, carbonyl chloride, sulphur trioxide, sulphuryl chloride, and nitrosyl chloride. The critical velocities for the different molecular species are as follows, the figures being for $\log_{10}u$: H_2, 6·2643; Cl_2, 5·4214; Br_2, 5·1902; I_2, 5·0192; S_2, 5·5484; O_2, 5·3718; HCl, 5·6746; HBr, 5·4523; HI, 5·2932; H_2S, 5·7851; H_2O, 5·9224; CH_4, 5·9869.
W. HUME-ROTHERY.

Thermochemical equilibrium from the kinetic and photochemical points of view. W. KUHN (J. Chim. phys., 1926, **23**, 369—393).—The kinetic and photochemical theories require respectively a definite energy of collision or an absorption of a definite frequency for reaction to occur, and the expressions for the velocity constants $Ae^{-u_1/kt}$ and $Ae^{-h\nu_1/kT}$ are strictly analogous. Calculations show that at 500° the velocity constants calculated by the kinetic theory are much greater than those obtained by the radiation theory, but both are roughly of the correct order of magnitude. Kinetic excitation is favoured by low temperature, high concentration, large molecular diameter, low critical energy, and small coefficient of absorption. At high temperatures, reactions may become purely photochemical. The Bohr theory, that each absorbing molecule takes up energy $h\nu$, when combined with the law of Kirchhoff, $K_\nu\alpha_\nu=\beta_\nu$, where K is the intensity of radiation, and α and β are the absorption and emission coefficients, respectively, leads to the conclusion that at equilibrium the numbers of molecules absorbing and emitting radiation in a given time are equal, the condition being analogous to the kinetic conception of equilibrium. In this way, by introducing Beer's law, expressions are obtained relating the equilibrium constants with the optical properties of the substances. The relation between the optical properties and chemical constants is discussed and the author's equations are compared with those of the Nernst theory. Whilst in this way general expressions can be obtained for chemical equilibria, the velocities of reaction can be considered only in special cases.
W. HUME-ROTHERY.

Influence of the capacity of the discharge circuit on the decomposition of carbon dioxide under reduced pressure by spark discharge. P. JOLIBOIS, H. LEFEBVRE, and P. MONTAGNE (Compt. rend., 1926, **182**, 1145—1146; cf. this vol., 586).—The limiting dissociation of carbon dioxide by spark discharge depends on the nature of the tube and on the capacity of the discharge circuit. The limiting dissociation first increases slowly from about 25% without condenser until a capacity C_0 is used, after which there is a rapid increase in the dissociation to a capacity C_1, followed by a region of slow increase. At the same time, the nature of the discharge changes from one with definite dark and luminous regions below C_0 to a continuous luminous spark band above C_1. With a tube of 110 c.c. volume, filled with carbon dioxide at 3·4 mm. pressure, a 22 cm. spark gap, and a platinum disc cathode and point anode, the results were 27, 52, 83, 90, 90, 94% limiting dissociation for $1{\cdot}1\times10^{-3}$, $1{\cdot}15\times10^{-2}$, 5×10^{-2}, $5{\cdot}2\times$

10^{-1}, 2·26, and 10·8 microfarads capacity of the discharge circuit, respectively. F. G. SOPER.

Influence of boric acid on the electrolytic dissociation of electrolytes. I. M. KOLTHOFF (Rec. trav. chim., 1926, **45**, 394—399).—Böeseken and Verkade (A., 1916, ii, 595; 1925, ii, 128) consider that the decreased conductivities of solutions of acids which do not form complexes with boric acid in presence of 0·5*M*-boric acid are indicative of a diminution in the degree of ionisation. This and other conclusions are not warranted, as these authors do not take into account the repression of the dissociation of boric acid by the stronger acid. In the present investigation, the conductivities at 18° of solutions of potassium chloride, barium chloride, and hydrochloric, sulphuric, succinic, acetic, fumaric, and adipic acids, in general over the concentration range 0·001—0·1*N*, in pure water and in presence of 0·5*M*-boric acid have been measured. Assuming that the mobilities of the borate, H_2BO_3', and acetate ions are the same (Abegg and Cox, A., 1904, ii, 256), the conductivity at 18° of a 0·5*M*-solution of boric acid corresponds with a value of the dissociation constant, $K_a=8·45\times10^{-9}$, no correction being made for the viscosity of the solution. Using this value of K_a, the conductivity due to the borate ion in the various acid–boric acid mixtures has been calculated and the necessary corrections have been applied to the measured conductivities. In the case of the salts, the conductivity of the 0·5*M*-solution of boric acid itself was subtracted from the measured values. Comparison of the ratios of the corrected conductivities in presence of boric acid and the corresponding observed conductivities in pure water shows that in the cases of the strong electrolytes the decrease in conductivity is of the order 5—6% and independent of dilution. The decrease is due solely to the higher viscosity of the medium. With the weak acids, the percentage decrease is also independent of dilution, being 5, 7, 7, and 9% for succinic, acetic, adipic, and fumaric acids, respectively. There appears to be a slight decrease in the dissociation of these weak acids, boric acid probably diminishing the dielectric constant, and hence the dissociating power, of water by a very small amount. J. S. CARTER.

Use of boric acid for determining the structure of various organic compounds. I. Dissociation constants of various acids in the presence of boric acid. J. BÖESEKEN and J. COOPS (Rec. trav. chim., 1926, **45**, 407—413; cf. A., 1921, i, 843, and preceding abstract).—The only classes of carboxylic acids which show an increased electrical conductivity in the presence of 0·5*M*-boric acid are α-hydroxy- and *o*-hydroxy-acids. In all other cases, a 10—20% diminution in conductivity is observed which is attributed to the formation of a partly dissociated compound with boric acid having a weakly acidic character. The ionic equilibria which are involved in the solutions on this hypothesis are discussed in detail, and from the published data for thirteen mono- and di-carboxylic and hydroxy-acids the dissociation constants of the boric acid complexes are calculated. G. M. BENNETT.

Constitution of magnesium acetate solutions. A. C. D. RIVETT (J.C.S., 1926, 1063—1070).—The system magnesium acetate–water has been studied. The eutectic temperature cannot be determined owing to the high viscosity of concentrated solutions at low temperatures, whilst on the salt-solution side, hydrolysis fixes an upper limit. The solid phase is a tetrahydrate, m. p. about 68°, the solubility curve passing through a maximum value near this temperature. A solution saturated at 14·9° contains 37·97% of anhydrous salt. The viscosity at 25° increases at first with concentration in a more or less normal manner, but then increases from about 7 (water=1) at $2·5M_w$ to 155 at $5·4M_w$. The relative viscosities of $1·59M_w$ and $5·97M_w$ solutions fall from 3·40 to 2·93 and from 188 to 78, respectively, on increasing the temperature from 35·1° to 55°. The conductivity passes through a maximum value at about M_w. Approximate measurements of surface tension at 25° are recorded. It is suggested that magnesium acetate exists as simple ionisable salt in dilute solutions, but that association occurs in more concentrated solutions. The polymerisation is supposed to be a consequence of chelate ring-formation, the magnesium atom exerting a co-ordination number of 4 towards oxygen in the acetate radicals. Such polymerisation is of a type similar to that shown by basic beryllium acetate (Bragg and Morgan, A., 1924, i, 7). J. S. CARTER.

Hydrolysis of the acetals of pentaerythritol. A. SKRABAL and M. ZLATEWA (Z. physikal Chem., 1926, **119**, 305—318).—The rates of hydrolysis of the diformal, diacetal, dipropional, diisobutylal, monoacetonal, and diacetonal derivatives in presence of hydrochloric acid were determined at 25°. The large variations in the velocity coefficients are correlated with differences of chemical constitution. Experimental details are given for the preparation of the above compounds. L. F. GILBERT.

Dissociation of multivalent substances. I. Relation of constants to titration data. II. Relation of constants to chemical structure. H. S. SIMMS (J. Amer. Chem. Soc., 1926, **48**, 1239—1250, 1251—1261).—I. The "classical" dissociation constants of a dibasic acid in solution are given by $K_1'=f_{H^·}.HA'/H_2A$ and $K_2'=f_{H^·}.A''/HA'$, $f_{H^·}$ representing the activity of the hydrogen ion. The corresponding "titration" constants, *i.e.*, the constants obtained by calculating the titration data on the assumption that the dibasic acid is a mixture of two monobasic acids, are $G_1'=f_{H^·}.\alpha_1/1-\alpha$, and $G_2'=f_{H^·}.\alpha_2/1-\alpha_2$, α representing the probability of dissociation. Since the first stage ionisation may not be complete when the second stage begins, G' and K' are not identical. It is shown that $1/K_2'=1/G_1'+1/G_2'$ and $K_1'/K_2'=G_1'/G_2'+G_2'/G_1'+2$, similar formulæ holding for any multivalent acid, base, or ampholyte. The corresponding constants G and K, *i.e.*, G'' and K' corrected for interionic attraction, are connected by the same formulæ, which for ampholytes are valid only at very small ion concentrations. An accurate general method of calculating dissociation constants is thus obtained. Formulæ are also derived for isoelectric points, hydrogen-ion activity, and the concentration of multivalent substances.

II. The influence of (*a*) the nature of the ionisable groups, (*b*) the character of the substituents, and (*c*) the electrostatic forces between the ionisable groups on the dissociation constants of multivalent acids, bases, or ampholytes is considered. The order of magnitude of each constant is determined by (*a*); the effect of (*b*) varies with the nature and position of the substituent. The effect of (*c*) is expressible by equations which enable the distance between the two charges on a bivalent ion or the distance between the positive and negative charges on a univalent ion to be calculated. Isomeric *cis*- and *trans*-acids have nearly identical "intrinsic" constants, K_0, *i.e.*, constants computed without regard to electrostatic forces. Formulæ are given for calculating the dissociation constants of higher multivalent acids, bases, and ampholytes. Relationships between K, K_0, G, and a characteristic constant, K_c, are also deduced. S. K. TWEEDY.

Thermodynamics of surface actions. II (cont.) Variation of surface tension with pressure. L. GAY (J. Chim. phys., 1926, **23**, 394—414; cf. this vol., 578).—Theoretical. The variation of surface tension with pressure is discussed for the case in which one of the fluid phases is near a critical point (either liquid–vapour or bi-liquidal point). Variations of both total pressure and of the pressure of one phase alone are considered, on the assumption that in general the pressure of a phase depends on the nature of its surfaces of contact with other phases. The modification of the phase rule to meet the above assumption is discussed with regard to the critical points. In the region of the critical point, the interfacial tension between the two phases is practically zero, and if x_1 and x_2 are the compositions of the two phases, the partial differentials $\delta x_1/\delta T$, $\delta x_1/\delta P$, $\delta x_1/\delta s$, $\delta x_2/\delta T$ . . ., are infinitely great at the critical point, T, P, and S being the temperature, pressure, and interfacial area, respectively. W. HUME-ROTHERY.

Fusion curves of the systems benzene–*m*-xylene, toluene–*m*-xylene, and *m*-xylene–*p*-xylene. A. NAKATSUCHI (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 53—59; cf. this vol., 356).—The f.-p. curves of the binary systems, benzene–*m*-xylene, toluene–*m*-xylene, and *m*-xylene–*p*-xylene show well-marked minima at −60·2° (21·74% of benzene), −105·5° (77·56% of toluene), and −57° (85·95% of *m*-xylene), respectively; in each case, the longer branch of the liquidus is a curve concave to the axis of composition and the shorter branch a straight line. The heats of fusion of the individual substances calculated from the f.-p. data are: benzene 2400, toluene 1150, *m*-xylene 2400, and *p*-xylene 4100 cal. A. R. POWELL.

Binary system barium iodide–water. J. PACKER and A. C. D. RIVETT (J.C.S., 1926, 1061—1062).—The solid phases in equilibrium with saturated solutions between −33·5° (eutectic) and +25·7°; 25·7° and 98·9°; 98·9° and 120° are $2BaI_2,15H_2O$, $BaI_2,2H_2O$, and BaI_2,H_2O, respectively. The transition temperatures, 25·7° and 98·9°, were measured thermometrically. At 15°, the saturated solution contains 65·75% of anhydrous salt. J. S. CARTER.

System: benzamide–bromine. W. FINKELSTEIN (Z. physikal. Chem., 1926, **121**, 46—64; cf. A., 1925, ii, 546).—The conductivity of solutions of benzamide in bromine at 18° passes through a maximum with increasing concentrations of bromine and also increases on keeping. F.-p. depression measurements give a maximum mol. wt. equal to five times that of the compound $Ph{\cdot}CO{\cdot}NH_2Br_2$. The transport number of the cation is 0·054, a value which is ascribed to the presence in the solution of ionised polymerised molecules. R. CUTHILL.

Palladium–hydrogen equilibrium and palladium hydride. L. J. GILLESPIE and F. P. HALL (J. Amer. Chem. Soc., 1926, **48**, 1207—1219).—Data for the equilibrium were obtained at 0°, 30°, 80°, 160°, and 180°. Apparently two solid solutions exist, the saturated one richer in hydrogen having approximately the composition Pd_2H at 80°, 160°, and 180°, but containing larger quantities of hydrogen at lower temperatures. The existence of a hydride, probably Pd_4H_2, at high temperatures is inferred. The heat evolved at 1 atm. by the reaction $H_2(g.)+4Pd=2(Pd_2H)$ (decomposed) is calculated as 8780, 8700, and 8450 cal./mol. of hydrogen at 0°, 30°, and 80°, respectively, in approximate agreement with the figure of Mond, Ramsay, and Shields (A., 1898, ii, 600). S. K. TWEEDY.

Chlorine tensions of metallic chlorides. Chemical constants of chlorine. K. JELLINEK and R. ULOTH (Z. physikal. Chem., 1926, **119**, 161—200).—Equilibria of the type $MCl_2+H_2 \rightleftharpoons M+2HCl$ have been investigated between 300° and 750° and at 1 atm. pressure by a dynamic method. The salts studied were silver, cuprous, nickel, cobalt, lead, cadmium, and manganese chlorides. From the data obtained the vapour pressures of diatomic chlorine were calculated with the help of Nernst's formula for the dissociation of hydrogen chloride (Z. Elektrochem., 1909, **15**, 687). These vapour pressures and those for gold, mercurous, and zinc chlorides were also calculated from the *E.M.F.* of cells containing the molten or dissolved salts. Wohl's formula for the dissociation of diatomic chlorine (A., 1925, ii, 395) was used to determine the partial pressures of monatomic chlorine. The partial pressure of molecular chlorine over gold chloride is much greater than that of monatomic chlorine; for silver and mercurous chlorides these pressures are of the same order, whilst that of monatomic chlorine is the greater for the other chlorides in the temperature interval concerned. The chemical constants of molecular and of monatomic chlorine as calculated from the published data for silver, mercurous, and lead chlorides are $1{\cdot}99\pm0{\cdot}18$ and $1{\cdot}68\pm0{\cdot}26$, respectively. L. F. GILBERT.

Organic molecular compounds. XVIII. Calculation of molar fraction. G. WEISSENBERGER, R. HENKE, and F. SCHUSTER (Z. anorg. Chem., 1926, **152**, 325—332; cf. this vol., 465).—Examination of binary systems consisting of one liquid component and one solid component shows that Konovalov's vapour-pressure functions are applicable only in a limited number of cases, which include systems in which molecular compounds are formed as well as systems in which these are not

formed. It is suggested that in a system consisting of a volatile liquid and a non-volatile liquid, which form a compound, the expression Δ/p' gives the fraction of the volatile liquid which has entered into combination, Δ being the deviation of the observed vapour pressure, p', from the rectilinear relationship. Using this relation to calculate the molar fractions of the various molecular species, the observed behaviour of a number of systems of this type is shown to be in good agreement with the requirements of the mass law. If either of the liquids is associated, the results are not so satisfactory. R. CUTHILL.

Binary liquid mixtures. XX. Systems with substituted hydronaphthalenes. XXI. Systems with butyric acid. G. WEISSENBERGER, R. HENKE, and H. KATSCHINKA (Z. anorg. Chem., 1926, **153**, 33—40, 41—46; cf. Sitzungsber. Akad. Wiss. Wien, 1925, [ii], **134**, 483).—XX. The vapour-pressure curves of mixtures of volatile liquids with α-chlorotetrahydronaphthalene are similar to those with tetrahydronaphthalene (Sitzungsber. Akad. Wiss. Wien., 281, 295), and in both cases only chloroform shows evidence of compound formation. The effect of the chlorine atom is to accentuate the differences between the calculated and actual vapour pressures, without changing their sign. The vapour pressures of mixtures of benzene with α-chlorotetrahydronaphthalene are slightly less than the calculated values, corresponding with the strong absorption of benzene vapour by tetrahydronaphthalene. There is no evidence of compound formation between mono- or di-methyldecahydronaphthalenes and volatile hydrocarbons. The vapour pressures are slightly higher than calculated, the deviations for the α-monomethyl derivative being greater than for the β-derivative. The conclusion is confirmed that hydrocarbons have little or no residual affinity. In general, the differences between the calculated and actual vapour pressures are greater the greater the dissimilarity between the two constituents of a mixture.

XXI. The vapour pressures of binary mixtures of butyric acid with acetone, methyl acetate, and chloroform are less than correspond with their contents of the volatile constituent. Butyric acid has two centres of residual affinity, the oxygen atom of the carbonyl group and the hydrogen atom of the hydroxyl. Union with acetone and methyl acetate occurs through the hydroxyl hydrogen atom; with acetone, equal numbers of molecules of the two constituents take part, but the residual affinity of methyl acetate is less than that of acetone and the compound contains excess of butyric acid. Union takes place between equal numbers of molecules of butyric acid and chloroform, and the carbonyl and the trichloromethyl are the active groups. Butyric acid does not combine with carbon disulphide or with benzene. A. GEAKE.

Properties of ternary liquid mixtures. P. BRUN (Compt. rend., 1926, **182**, 1219—1221).—For mixtures of ethyl alcohol and water with a third liquid (propyl alcohol, *iso*butyl alcohol, and *iso*amyl alcohol—representing decreasing degrees of miscibility), measurements have been made of the density and refractive index. Thence the specific refractivities (r_L) and variations in volume of the mixtures are calculated. From the corresponding trilinear graphs it is shown geometrically that (as with binary liquid mixtures) the specific properties of the mixtures are continuous at the critical point. J. GRANT.

Ternary diagram of the system iron–carbon–copper. T. ISHIWARA, T. YONEKURA, and T. ISHIGAKI (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 81—114).—The ternary diagram of the system iron–carbon–copper has been constructed, for the iron corner and for alloys containing up to 30% Cu, from phase-rule considerations based on the known binary diagrams, iron–cementite and iron–copper and on a somewhat hypothetical diagram for the system cementite–copper. The positions of the most important lines and points have then been checked by thermal and micrographical analysis of the corresponding alloys, and found to agree reasonably well with the theoretical positions. At 1100°, there is an invariant point corresponding with a concentration of 4·3% C and 3·3% Cu at the intersection of the eutectic and monotectic lines. The maximum concentration of the γ solid solution is about 3·5% C and 3·8% Cu. The eutectoid line starts from the binary iron–copper eutectoid point at 2·3% Cu and 833° and gradually descends, the copper content decreasing as the carbon increases. Addition of copper to steel lowers the A1 transformation point 20° with 2% Cu; the eutectoid invariant point corresponds with a composition of 0·9% C, 1·75% Cu, and 97·35% Fe at 700°. Saturation of iron with copper to give a uniform solid solution lowers the A2 point by about 10°. A. R. POWELL.

System ferric sulphate–base.—A. KRAUSE (Rocz. Chem., 1926, **6**, 45—58).—The products of the reaction at 15° between aqueous ferric sulphate and sodium and potassium hydroxides, carbonates, and hydrogen carbonates, ammonia, and aniline have been analysed. The composition of the precipitates changes continuously in such a way that the ratio $Fe_2O_3 : SO_3$ is proportional to the p_H of the solution, due to adsorption by the precipitate. The relation between the composition of the latter and the p_H of the solution is given by $K^x=yd$, where y is the ratio $Fe_2O_3 : SO_3$ in the precipitate, and K and d are constants. R. TRUSZKOWSKI.

System ammonium acetate–acetic acid–water. (MISS) R. SUGDEN (J.C.S., 1926, 960—961).—A study of the equilibria of this system at 0°, 16°, and 25° yields no evidence of the complex $2CH_3{\cdot}CO_2NH_4,3CH_3{\cdot}CO_2H,H_2O$ described by Berthelot (Bull. Soc. chim., 1864, **22**, 440). The existence of the acid acetate, $CH_3{\cdot}CO_2NH_4,CH_3{\cdot}CO_2H$, is confirmed. C. H. D. CLARK.

System sodium thiosulphate–sodium sulphate–water. R. R. GARRAN (J.C.S., 1926, 848—855).—The system has been examined at 0°, 18°, 25°, and 40°. Mixed crystals are formed at the three lower temperatures by the decahydrates and at all temperatures by the pentahydrates. At 25° and 40°, mixed crystals of the anhydrous salts probably occur. The Glauber's salt transition point is lowered to 20° by the addition of sodium thiosulphate. C. H. D. CLARK.

System sodium sulphide–sodium sulphate–water. A. R. HOGG (J.C.S., 1926, 855—862).—The equilibrium has been studied at 0·1°, 18°, 25°, 31°, and 40°. A new decahydrate, $Na_2S,10H_2O$, is described which changes to the nonahydrate at 4·7°; the transition point is lowered to 2·3° by saturated sodium sulphate. Mixed crystals of the two decahydrates are formed at 0·1°. At 18°, sodium sulphide nonahydrate dissolves some sulphate, but neither Glauber's salt nor anhydrous sodium sulphate shows any appreciable tendency to include sodium sulphide. At higher temperatures, mixed crystal formation is absent. The Glauber's salt transition point is lowered by sodium sulphide from 32·4° to 20·6°.

C. H. D. CLARK.

Diagrams of state of some silver and alkali salts. S. F. SHEMTSCHUSHNI (Z. anorg. Chem., 1926, **153**, 47—61).—Silver bromide forms a continuous series of solid solutions with sodium bromide, and silver chloride with sodium chloride. The rates of diffusion of the silver salts into the solid solutions are not sufficient to keep the interiors of the crystals first formed at the changing equilibrium concentrations. The cooling curves are therefore somewhat different from the normal type. The curves obtained by plotting the temperature when crystallisation is complete against the molecular percentage composition are not true solidus curves, but run nearly parallel to the concentration axis from the m. p. of the silver salt until the concentration of the sodium salt is about 50%. The solid solutions slowly decompose at low temperatures and become opalescent. In agreement with Sandonnini (A., 1912, ii, 941), the m. p. diagram of silver bromide and potassium bromide is found to consist of two branches with a eutectic point at 285°. The eutectic mixture contains, however, 67 mol.-% of silver bromide, instead of 56 mol.-% as found by Sandonnini. No solid solutions are formed. The m. p. of the individual halides are: silver bromide 419°, silver chloride 451°, sodium bromide 766°, sodium chloride 816°, potassium bromide 748°. These systems were examined microscopically by fusing a fragment of the mixed salts on a slide, covering with a heated cover-glass, and cooling. Mixtures melting above 650—675° could not be examined; at higher temperatures glass softens and quartz is attacked by the salts. The solid solutions crystallise in polyhedra with fairly sharp dividing lines. The systems containing up to 75 mol.-% of sodium bromide or 60 mol.-% of sodium chloride are optically anisotropic, although the four pure halides concerned are isotropic. This is probably due to internal pressure set up in the crystals during the formation of the solid solution. The structure of mixtures of silver and potassium bromides is in accordance with the m. p. diagram. A. GEAKE.

Equilibrium between carbon monoxide, carbon, and carbon dioxide, and the reactions between ferrous oxide and carbon, and between carbon monoxide and iron. V. FALCKE and W. FISCHER (Z. Elektrochem., 1926, **32**, 194—201; cf. A., 1921, ii, 511).—The equilibrium $C+CO_2 \rightleftharpoons 2CO$ has been investigated between 600° and 750°, using as catalysts iron, cobalt, and nickel which had been previously heated in a current of carbon monoxide until they took up about 50% of carbon. The log. equilibrium constant plotted against the temperature gives a straight line, on which lie also the values previously obtained for temperatures above 700°. The use of iron without previous treatment as a catalyst gives slightly lower values. R. CUTHILL.

System calcium oxide–ferric oxide–silica. W. C. HANSÉN and R. H. BOGUE (J. Amer. Chem. Soc., 1926, **48**, 1261—1267).—The above system was investigated in the three regions concerned with Portland cement. Optical examination affords no evidence of ternary compounds. Dicalcium silicate, $2CaO,SiO_2$, is inverted to the γ-form in slowly-cooled mixtures, but whereas in the lime–alumina–silica system small amounts of alumina prevent this inversion, it is inhibited only by a high ferric oxide concentration (45%). This supports the theory that it is the glass present in the clinker which prevents the conversion into the γ-form, since absence of glass in this system was observed. Evidence for the compound $3CaO,SiO_2$ was found (Day and Shepherd, A., 1906, ii, 770). Probably only part of the ferric oxide in Portland cement clinker is present as the crystalline compounds, $2CaO,Fe_2O_3$ or CaO,Fe_2O_3. S. K. TWEEDY.

Equilibrium in the reaction $NiO+H_2 \rightleftharpoons Ni+H_2O$. Free energy of nickelous oxide. R. N. PEASE and R. S. COOK (J. Amer. Chem. Soc., 1926, **48**, 1199—1206).—The above equilibrium, approached from either side of the equation, was investigated at 485° and 600° by a flow method. The equilibrium ratios of steam to hydrogen were 330 and 240 at the respective temperatures. The free energy of the reaction (at constant pressure) is given by $-3647-6{\cdot}722T$, whence the heat of formation of nickelous oxide is −3647 cal. and its free energy of formation −56,497 cal. The calculated partial pressure of oxygen over nickel oxide at 1100° was 10^{-6} mm., in disagreement with the observations of Foote and Smith (A., 1908, ii, 847). Some abnormalities, observed in the initial stages of the reduction and oxidation, are explicable on the assumption that the free energies of a metallic film on the metal oxide and of an oxide film on the metal are higher than those of the metal and oxide, respectively, in the massive state. S. K. TWEEDY.

Energy of solution of gaseous ions in relation to the effect of a charge on the dielectric. W. M. LATIMER (J. Amer. Chem. Soc., 1926, **48**, 1234—1239).—The energies of solution in water of some gaseous metallic ions are calculated, and the ionic radii derived from Born's formula (A., 1920, ii, 527). The results indicate that the energy of combination of the various ions with water is small in comparison with the effect of the ion as a charged particle on water as a dielectric. The electron affinities of chlorine, bromine, and iodine are also calculated. The Debye theory of strong electrolyte solutions is strongly supported by the results obtained.

S. K. TWEEDY.

Thermal decomposition of siderite, rhodochrosite, and dolomite. J. A. HEDVALL (Verh. Geol. Verein Stockholm, 1925, **47**, 1—8; from Chem. Zentr., 1926, I, 810).—The thermal decomposition

of these natural carbonates has been examined by two methods: (*a*) slowly heating in an electric oven and constructing the temperature-time curve; (*b*) heating in a current of nitrogen, the issuing gases being led into a solution of barium hydroxide. Siderite commences to decompose at 195—200°, the dissociation pressure reaching 1 atm. at 490°. The corresponding temperatures for rhodochrosite are 435° and 540°, respectively. The temperature-time curve for dolomite shows breaks at 580°, 623°, 643°, 675°, and 910°, the last temperature being that at which the dissociation pressure of calcium carbonate is 1 atm. (A., 1917, ii, 208). It is hence concluded that dolomite contains free calcium carbonate, free magnesium carbonate being absent, since there is no corresponding break in the curve. Free calcium carbonate appears as a result of the reaction $CaO+CaMg(CO_3)_2=2CaCO_3+MgO$ (A., 1922, ii, 766).

J. S. CARTER.

Thermionic properties of some mixtures used as catalysts in the synthesis of ammonia. C. H. KUNSMAN (J. Physical Chem., 1926, **30**, 525—534).—The catalysts studied were made by fusing a mixture of pure artificial magnetite with about 1% of alumina and about 0·5% of alkali or alkaline-earth salt, usually the nitrate. These mixtures are good emitters of positive ions, the reduced mixtures being much more active than the unreduced mixtures. The positive emission satisfies Richardson's equation; the electron emission under similar conditions is negligible. From an iron–aluminium–cæsium oxide mixture, the positive currents obtained are largely due to positively charged cæsium ions. The magnitude of the current at a given temperature depends on the alkali or alkaline-earth metal or oxide added as promoter, and on the previous heat treatment. The temperature at which the first positive ion current, 1×10^{-10} amp., was detected was lowest for a cæsium-promoted catalyst, followed successively by rubidium, potassium, sodium, magnesium, and calcium.

The surface of the fused mixture is defined in terms of φ_+, the equivalent work function, in volts, of the vaporised positive ions. For potassium and cæsium ions, respectively, φ_+ equals 2·10 and 2·37 volts.

The structure of the catalyst mixtures and the cause of emission of positive ions are discussed.

L. S. THEOBALD.

[Heat of formation of calcium cyanamide.] V. EHRLICH (Z. Elektrochem., 1926, **32**, 187—188).—On the author's view (A., 1923, i, 309) that calcium cyanamide is formed by the consecutive reactions $CaC_2=(CaC)+C$ and $(CaC)+N_2=CaCN_2$, the heat of the former reaction is calculated to be 8600 ± 3000 cal., if Franck and Hochwald's value of 84,000 cal. (B., 1926, 88) be taken for the heat of formation of the cyanamide.

R. CUTHILL.

Thermal decomposition of nitrous oxide. E. BRINER, C. MEINER, and A. ROTHEN (Helv. Chim. Acta, 1926, **9**, 409—414).—When nitrous oxide is circulated through a silica vessel heated by an electric furnace, nitric oxide is formed in amounts which reach a maximum with rise of temperature and with increasing velocity of circulation. At 1300°, 25% of nitrous oxide is transformed into nitric oxide when 9 litres of gas are circulated per hour. The highest proportions of nitric oxide are formed at higher temperatures, and since the rate of decomposition of this oxide into its elements is less at the lower temperatures considered (about 700°), it is suggested that nitrous oxide breaks down simultaneously in two ways according to the schemes $N_2O\longrightarrow N_2+0{\cdot}5O_2+20{\cdot}6$ Cal. and $N_2O\longrightarrow NO+0{\cdot}5N_2-0{\cdot}9$ Cal. Rising temperature favours the more endothermic of these reactions. The maximum observed in the amount of nitric oxide formed with increase of temperature is ascribed to the increasing rate of decomposition of nitric oxide, which eventually counterbalances the effect of temperature in promoting its formation. The percentage of nitric oxide produced is much lowered at all temperatures by the presence in the reaction vessel of powdered quartz or of platinum. To this cause is ascribed the fact that Hinshelwood and Prichard (A., 1925, ii, 310) did not observe the formation of this oxide in the decomposition of nitrous oxide by a heated platinum wire.

M. CLARK.

Investigations at high temperatures. XVIII. Pure calcium carbide and its heat of formation. O. RUFF and B. JOSEPHY (Z. anorg. Chem., 1926, **153**, 17—32).—Calcium carbide was prepared as pure as possible by heating a pure soot and redistilled calcium at 1250° in argon. The product thus obtained contained approximately 1% of free calcium, 2·5% of calcium oxide, 0·5% of iron, and 16% of uncombined carbon. The mean corrected heat of dissolution of this carbide in 0·5*N*-hydrochloric acid (previously saturated with acetylene) at 18·5° and constant pressure is 60·8 Cal. By utilising the known values of the heat of formation of acetylene and of the heat of dissolution of calcium in aqueous hydrochloric acid, the heat of formation of calcium carbide from solid calcium and diamond is calculated to be 14·5 Cal. and 14·1 Cal. from graphite. Calculation by means of Nernst's equation from the dissociation pressure of calcium carbide gives 117 Cal. as the heat of formation from gaseous calcium and graphite, and the more exact reaction isochore of van 't Hoff gives 70·5 Cal. For the latter calculation, the mean molecular heat of calcium carbide over the range 0—2773° Abs. was calculated from the atomic frequency by Koref's formula; molecular heats thus calculated for the temperature ranges 20—325°, 20—500°, and 20—725° are 14·3, 15·5, and 16·4, respectively, in satisfactory agreement with experimentally determined values of 14·15, 15·28, and 17·6. The heat of formation in the condensed system cannot be calculated, as the heat of evaporation of calcium at 18° is uncertain.

A. GEAKE.

Thermochemistry of some ethoxides and thallous salts. R. DE FORCRAND (Compt. rend., 1926, **182**, 1191—1194).—The heats of solution of thallium and sodium in water, certain weak acids, and alcohols, according to the equation MH (solid or liquid)+Tl (or Na solid)=MTl (or MNa solid)+H, are given. These are obtained by the combination of the values for the heats of solution of the solid acid or alcohol and of the solid thallous compound in water and sulphuric acid; the heat of fusion of the

alcohol or acid, and the heat of neutralisation of the dilute aqueous solution. The differences between the values for sodium and thallium are less constant than those obtained for the acid or alcohol in the state of solution (cf. this vol., 476). The compound TlOH may be prepared in the solid state by dilution of thallous ethoxide with a large excess of water. This is due to the small amount of heat evolved in the reverse reaction and the solubility in the water of the ethyl alcohol produced. J. GRANT.

Two rapid and accurate methods in calorimetry. W. P. WHITE (J. Amer. Chem. Soc., 1926, **48**, 1146—1149).—The classical Regnault-Pfaundler formula for the cooling correction is rearranged so that one of the usual two blank experiments is rendered unnecessary with no sacrifice in precision. Fewer observations of rise of temperature are necessary if their summation is carried out by Simpson's rule; the accuracy, also, is thereby increased. S. K. TWEEDY.

Calorimetric researches. X. Heats of combustion of successive terms of homologous series. Dicarboxylic acids of the oxalic acid series. P. E. VERKADE, H. HARTMAN, and J. COOPS (Rec. trav. chim., 1926, **45**, 373—393; cf. A., 1925, ii, 364).—The heats of combustion of the first twelve members of the oxalic acid series have been determined, the values being based on those of benzoic and salicylic acids, 6324 and 5241·8 cal.^{15}/g. (air), respectively (A., 1925, ii, 39). Berner's value for the heat of combustion of salicylic acid (this vol., 116) is held to be incorrect. The following numbers give the molecular heats of combustion (Cal. 15°) at constant volume, Q_v, the figures in parentheses being the corresponding values at constant pressure, Q_p: oxalic acid, 61·0, (60·1); malonic acid, 207·1, (206·5); succinic acid, 357·4, (357·1); glutaric acid, m. p. 98°, 514·9, (514·9); adipic acid, m. p. 153°, 668·6, (668·9); pimelic acid, m. p. 105°, 827·1, (827·7); suberic acid, m. p. 141°, 982·4, (983·2); azelaic acid, m. p. 107—108°, 1140·4, (1141·7); sebacic acid, m. p. 133°, 1295·9, (1297·3); nonanedicarboxylic acid, m. p. 110°, 1453·8, (1455·6); decanedicarboxylic acid, m. p. 126·5°, 1608·2, (1610·7); undecanedicarboxylic (brassylic) acid, m. p. 113°, 1766·3, (1768·6). As stated (*loc. cit.*), the results of Stohmann are in agreement. The values of Luginin (Ann. chim. phys., 1891 [vi], **23**, 179) deviate considerably. Leaving aside the values for oxalic and malonic acids, a consideration of the Q_p values shows that on introduction of a methylene group into an acid with an even number of carbon atoms the resulting mean increase in the heat of combustion is 158·3±0·2 Cal., whilst in the case of an acid with an odd number of carbon atoms the corresponding increment is 155·1±0·4 Cal. The acids thus fall into two thermal homologous series, the odd and even series. The almost constant increments between successive higher terms of these two series indicates that although the heat of combustion is also influenced by structural considerations, the additive nature here predominates. The heats of combustion of oxalic and malonic acids are abnormally high, due to the fact that these two initial terms have abnormally high energy contents, the structural element of the heat of combustion here becoming appreciable.

In the course of preparation of some of the acids, the m. p. and/or b. p. of a number of intermediates were determined: *N*-benzoylpiperidine, m. p. 48°, b. p. 172—173°/9 mm.; *n*-pimelonitrile, b. p. 171—172°/12 mm.; λ-bromo-undecoic acid, m. p. 57°, ethyl ester, b. p. 169—170°/7 mm.; λ-hydroxy-undecoic acid, m. p. 70°. The dicarboxylic acids containing 8—13 carbon atoms were all obtained starting from castor oil. For details as to the technique, which is rather involved, the original must be consulted. J. S. CARTER.

Hydrogen. III. Electro-affinity of hydrogen. G. JOOS and G. F. HÜTTIG (Z. Elektrochem., 1926, **32**, 201—204; cf. this vol., 254).—From the heats of formation of the hydrides of the alkali metals, it is calculated that the electro-affinity of hydrogen is about 10 Cal., less than half the molecular energy of dissociation of the molecule; hence the value of the former is calculated to be 23 Cal. R. CUTHILL.

Densities, equivalent conductivities, and relative viscosities at 25° of solutions of hydrochloric acid, potassium chloride, and sodium chloride, and of their binary and ternary mixtures of constant chloride-ion content. C. E. RUBY and J. KAWAI (J. Amer. Chem. Soc., 1926, **48**, 1119—1128).—The densities of mixtures of the above solutions of concentration up to 4*M* with respect to the chloride ion closely follow the mixture rule; where appreciable differences do exist (concentrated solutions) the observed values are always the greater. The analogous mixture rule for relative viscosity, η, gives values consistently greater than those observed, except for mixtures approximately 0·1*M* and less, which conform to the rule. A corresponding mixture rule for $\Lambda\eta$ holds fairly well, the agreement being better than that between the observed and similarly calculated values of Λ. The composition–conductivity curves, however, indicate that $\Lambda\eta$ is not a linear function of the composition. S. K. TWEEDY.

Factors influencing the accuracy of measurements of the electrical conductivity of liquids and solutions. II. Discussion of the bridge assembly for the measurement of electrical conductivity with particular reference to the Vreeland oscillator as a source of current of constant frequency. J. L. R. MORGAN and (MISS) O. M. LAMMERT (J. Amer. Chem. Soc., 1926, **48**, 1220—1233; cf. A., 1923, ii, 604).—The factors which affect the constancy of the high-frequency current given by Vreeland oscillators (Types A and D) are discussed. S. K. TWEEDY.

Conductivity and catalytic activity of hydrogen halides in *n*-butyl alcohol. H. GOLDSCHMIDT and E. MATHIESEN (Z. physikal. Chem., 1926, **121**, 153—158).—The conductivities of hydrogen chloride, bromide, and iodide in *n*-butyl alcohol solution at 25° increase in this order. Gradual addition of water to the first solution causes the conductivity first to fall, then to pass through a minimum and rise again. In the esterification of phenylacetic acid in butyl alcohol solution, the catalytic activities of hydrogen bromide

and iodide are about the same and rather greater than that of hydrogen chloride. This reaction does not obey the unimolecular law, possibly because the real catalyst, the complex ion $(C_4H_{10}O,H)^{\cdot}$, is decomposed by the water formed. This view is supported by the fact that the addition of water retards the reaction. R. CUTHILL.

Transference numbers of hydrochloric acid in glycerol–water mixtures. W. W. LUCASSE (J. Physical Chem., 1926, **30**, 562—565; cf. A., 1925, ii, 399).—Measurements at 25° of cells of the form Ag|AgCl|HCl (m)|HCl (0·01M)|AgCl|Ag, in which m varied from 0·01 to 1M in solvents of 1 and 5 mol. % glycerol are given. From these data and the results for corresponding cells without liquid junction, the transference numbers have been calculated by the method of MacInnes and Beattie (A., 1920, ii, 466). L. S. THEOBALD.

Electrolytic transport of water in solutions of alkali chlorides. J. VELÍŠEK (Chem. Listy., 1926, **20**, 242—251).—The transport numbers and electrolytic transference of water have been determined for solutions of alkali chlorides by the method of Baborovský (A., 1923, ii, 288). With M-solutions of potassium or lithium chlorides the results are affected by electro-osmosis only at extreme dilutions. The values for the electrolytic transport of water are 0·5, 1·0, and 1·6 for M-solutions of potassium, sodium, and lithium chlorides, respectively. The true transport numbers of potassium, sodium, and lithium ions in chloride solutions are 0·498, 0·395, and 0·316. The results obtained are in good agreement with those of Washburn (A., 1908, ii, 1009). The assumption that the degree of hydration of a given ion is constant in different solutions in which its concentration is the same is unjustified. W. HUME-ROTHERY.

Significance of electrode potential. J. HEYROVSKÝ (Proc. Roy. Soc., 1926, **A**, **111**, 201—202).—A reply to the criticism of Butler (*ibid.*, 1923, **A**, **104**, 667). R. CUTHILL.

Electrochemistry of chromium. II. Equilibrium potentials $Cr/Cr^{\cdot\cdot}$ and $Cr^{\cdot\cdot}/Cr^{\cdot\cdot\cdot}$. G. GRUBE and L. SCHLECHT (Z. Elektrochem., 1926, **32**, 178—186; cf. this vol., 362).—The normal electrode potential $Cr/Cr^{\cdot\cdot}$ referred to the hydrogen electrode is found to be −0·55 volt, using a solution of chromous sulphate and an activated chromium electrode. The potential $Cr^{\cdot\cdot}/Cr^{\cdot\cdot\cdot}$ varies with the nature of the salt and the electrode used, and with the acidity and total concentration of the solution. For a solution containing 0·02 g.-atom of chromium per litre in the form of equimolecular quantities of chromic and chromous acetates the value is $-0·403\pm0·003$ volt. R. CUTHILL.

Electrochemical behaviour of chromium. E. LIEBREICH and W. WIEDERHOLT (Z. Elektrochem., 1926, **32**, 261–262, 263). G. GRUBE (*ibid.*, 262).—Polemical (cf. Liebreich and Wiederholt, A., 1925, ii, 44; Grube, Heidinger, and Schlecht, this vol., 362). M. S. BURR.

Manganese dioxide–permanganate electrode. D. J. BROWN and R. F. TEFFT (J. Amer. Chem. Soc., 1926, **48**, 1128—1132).—From *E.M.F.* measurements of the cell $H_2|HClO_4(m_1)|HClO_4(m_2),KMnO_4(m_3)|MnO_2$ at 25° the oxidation potential of the reaction $MnO_4' + 4H^{\cdot} + 3e = MnO_2 + 2H_2O$ was found to be 1·586 volts (cf. Ruby, A., 1921, ii, 246). This value decreases with decreasing acid concentration exactly as required by theory. Pure manganese dioxide could not be obtained electrolytically. S. K. TWEEDY.

Oxidation-reduction potentials of reversible oxidising systems, and oxidation of organic molecules by these systems. C. FROMAGEOT (Compt. rend., 1926, **182**, 1240—1242).—The fall in potential of a reversible oxidising system 30 mins. after the introduction of an organic molecule is taken as a measure of the oxidisability of the latter. If the system contains metallic ions (*e.g.*, $Ce^{\cdot\cdot\cdot\cdot}/Ce^{\cdot\cdot\cdot}$), ethyl alcohol and acetaldehyde produce no fall in potential and pyruvic acid only a very slight one. In a peroxide system ($HClO_3/Cl_2$), these molecules are all oxidised. The speed of oxidation is independent of the oxidation potential of the systems if these are of different types, but rises with rise of potential in systems of the same type. The nature of an oxidising system rather than its potential decides its oxidising capacity, the order of oxidisability of different molecules differing according to the type of system used. J. GRANT.

Oxidation potential of the system selenium dioxide–selenium. S. R. CARTER, J. A. V. BUTLER, and F. JAMES (J.C.S., 1926, 930—937).—The half-element $Pt|yN\text{-}SeO_2 + zN\text{-}Se$ in 11·6 N-HCl gives constant and reproducible oxidation potential unaffected by light. Tenfold changes in concentration of either selenium dioxide or of selenium while the other is kept constant lead to changes of *E.M.F.* of 0·022—0·028 volt. In the lower concentrations of selenium, however, a gradual falling off of potential with time is observed, which may be attributed to occurrence of the reaction: $SeO_2 + 4HCl = Se + 2H_2O + 2Cl_2$. The oxidising character of selenium dioxide may be attributed to the amphoteric nature of selenium, whereby positively charged selenium ions are formed, with the possible intermediate formation of selenium tetrachloride. Selenium is compared and contrasted with sulphur and tellurium in this connexion. C. H. D. CLARK.

Reactive nature of aldehydes from the point of view of the apparent *E.M.F.* S. B. ARENSON, P. E. ROLLER, and D. J. BROWN (J. Physical Chem., 1926, **30**, 620—627; cf. Bugarszky, A., 1904, ii, 551).—Measurements have been made, at 25°, of the apparent *E.M.F.* of acetaldehyde and of chloral hydrate in sodium hydroxide solution, and of acetaldehyde in sulphuric acid solution. In agreement with Baur (A., 1902, i, 77), the *E.M.F.* changes rapidly for M-solutions of acetaldehyde and chloral hydrate in N-sodium hydroxide. The addition of sodium acetate and of potassium oxalate to solutions of acetaldehyde in sodium hydroxide has no effect on the apparent *E.M.F.* The velocity of condensation of the acetaldehyde in alkaline solution is apparently a reaction

of the first order. Further, the velocity of reduction for aldehydes is inversely proportional to the hydrogen-ion concentration. The velocity of decomposition of chloral hydrate in dilute alkaline solutions was also studied.

A theory is advanced to account for the changes in *E.M.F.* observed. L. S. THEOBALD.

Electromotive force and the solvent. A. E. BRODSKY (Z. physikal. Chem., 1926, **121**, 1—25).—A development of a thermodynamic theory of the influence of the solvent on chemical equilibrium in solution. The *E.M.F.* of cells of the type $Hg|Hg_2X_2,KX|KY,Hg_2Y_2|Hg$, where X, Y=Cl, Br, I, has been determined in water, methyl alcohol, and aqueous solutions of methyl and ethyl alcohols at various temperatures. The results show that, for equal initial concentrations of potassium halides as theory requires, $E-E'=RT/F \cdot \log_e (L_1L_2'/L_2L_1')$, where E and E' are the *E.M.F.* of the same cell in two solvents, in one of which the solubilities of the potassium halides are L_1 and L_2, and in the other L_1' and L_2', and R, T, and F have their usual significance. For saturated solutions, the *E.M.F.* is independent of the solvent. R. CUTHILL.

Electrode potentials and the solvent. A. E. BRODSKY (Z. physikal. Chem., 1926, **121**, 26—38).—Combination of the previously developed theory of the influence of the solvent on chemical equilibrium (cf. preceding abstract) with Nernst's theory of *E.M.F.* shows that for a given substance the electrolytic solution tension is proportional to the solubility in the particular solvent used, and for saturated solutions the *E.M.F.* is independent of the solvent. This is shown to be in agreement with the results of *E.M.F.* measurements with the electrodes $Hg|Hg_2Cl_2,KCl$ and $Hg|Hg_2Br_2,KBr$ in water, methyl alcohol, and aqueous solutions of methyl and ethyl alcohols combined with the 0·1*N*-calomel electrode in water. There appears to be in general a linear relationship between the dielectric constant of the solvent and the electrode potential. R. CUTHILL.

Liquid boundaries and diffusion potentials. S. R. CARTER and F. M. LEA (J.C.S., 1926, 834—836; cf. A., 1925, ii, 300, 403).—Methods which lead to the most constant and reproducible diffusion potentials at boundaries involving hydrochloric and sulphuric acids and potassium chloride solutions, are explained on the basis of results previously obtained. An acid|acid boundary gives smaller variation with time than an acid|salt boundary at corresponding concentrations. C. H. D. CLARK.

Thermodynamic potential differences at boundary of two liquid phases. IV. S. VOSNESSENSKI, K. ASTACHOV, and K. TSCHMUTOV (Z. physikal. Chem., 1926, **121**, 143—152; cf. this vol., 129).—The *E.M.F.* at the surface of separation of an aqueous solution of an electrolyte and a solvent (completely miscible with pure water) with which the aqueous solution is in equilibrium, has been determined by experiments with cells of the type *N*-calomel electrode|aqueous solution|non-aqueous solution|*N*-calomel electrode. Using methyl or ethyl alcohol as solvent and potassium carbonate or ammonium sulphate as electrolyte, the *E.M.F.* measured are very small, but with potassium chloride and acetone they are much larger and increase on keeping. Experiments have also been made with a flowing aqueous phase, separated from the other phase by a porous membrane. R. CUTHILL.

Sulphate solutions. Cells without liquid junction. G. ÅKERLÖF (J. Amer. Chem. Soc., 1926, **48**, 1160—1176).—The *E.M.F.* of the cells: (I) $Hg,Hg_2SO_4|M_2SO_4(c)|M_xHg|M_2SO_4(c_2)|Hg_2SO_4,Hg$; (II) $H_2|H_2SO_4(c_1),M_2SO_4(c)|Hg_2SO_4|Hg$; and (III) $H_2|M_2SO_4(c),MOH(c_1)|M_xHg|MOH(c_1)|H_2$ were measured by an improved experimental method, c_1 being the reference, and c the salt concentration. The activity coefficients of (α) potassium, sodium, and lithium sulphates (cell I), (β) of sulphuric acid in solutions of these sulphates (cell II), and (γ) of potassium and sodium hydroxides in the corresponding sulphate solutions (cell III) were calculated from the results and, in the cases of (β) and (γ), from approximation equations similar to those of Debye and Hückel (A., 1923, ii, 459, 724). The agreement between the calculated and observed values is generally good. The ion activity coefficient of water is greater in potassium sulphate than sodium sulphate solutions; the ionic product of water increases rapidly on addition of sulphates, the potassium salt being less effective than the sodium salt, with which the product attains a maximum at 1·5*M*. Indications were obtained that the Debye–Hückel theory may be inapplicable to dilute sulphuric acid solutions.

S. K. TWEEDY.

Eppley unsaturated standard cells at high temperatures. W. C. VOSBURGH (J. Opt. Soc. Amer., 1926, **12**, 393—395).—Data are given for twenty well-aged, representative Eppley cells at high temperatures; ten of these were made with 13% cadmium amalgam, and ten with the usual 12·5% amalgam. Cells with 13% amalgam can be used up to 60° without appreciable error, whilst those with 12·5% amalgam can probably be depended on up to about 55° for purposes not requiring a degree of accuracy greater than 0·01%. With increasing time, the maximum temperature at which a cell may be used without error becomes lower, but it is likely that with fair treatment the change in two or three years would be hardly appreciable. W. CLARK.

Temperature formula for the Weston standard cell. W. C. VOSBURGH (J. Opt. Soc. Amer., 1926, **12**, 511—517).—The *E.M.F.* of a number of normal Weston cells, some with neutral and some with slightly acid electrolytes, were measured at 5° intervals over the range 15—40° by use of the standard cell potentiometer of Eppley and Gray (*ibid.*, 1922, **6**, 859), and a number of cells at 25° as reference standards. Cells with electrolytes containing 0·02—0·08 mol. of sulphuric acid per litre were also measured at 25° and 35°. Wolff's temperature formula (Bull. Bureau of Standards, 1908, **5**, 326) was found to hold for all, the presence of acid having little or no effect on the temperature coefficient. A. B. MANNING.

Evidence for a film theory of hydrogen overpotential from surface tension measurements. A. L. McAulay and F. P. Bowden (Proc. Roy. Soc., 1926, **A**, **111**, 190—200).—The electrode potential and surface tension of mercury serving as the cathode in the passage of the current through solutions of various electrolytes have been simultaneously measured. With solutions containing ions of the noble metals, increase of the current density up to a certain point has little effect on either the potential or the surface tension, and no hydrogen is liberated, but further increase causes the potential suddenly to become more negative, whilst at the same time there is a sudden increase in the surface tension, and formation of a film of hydrogen. Addition of ions more noble than copper reduces the surface tension again, the film being destroyed by replacement. In the absence of noble metal ions, the film is established by very small currents, and the surface tension rises rapidly with the current density to an almost constant value. Conditions under which no overpotential is obtained in absence of a film on the cathode give rise to overpotential if a film has been previously formed. Up to a certain point in the growth of the film the single electrode potential measured above the reversible potential of mercury is proportional to the surface tension of the film; beyond this point the potential increases, but the surface tension remains nearly constant.

R. Cuthill.

Deposition of metallic zinc on the positive pole of a simple voltaic cell. S. R. Humby and M. W. Perrin (J.C.S., 1926, 959—960).—The more electro-positive metal may be deposited on the other electrode when a simple voltaic cell is left in action for some time. In the cell $Zn|H_2SO_4|Cu$, zinc is deposited while the solution is still acid, but when the poles are disconnected the zinc dissolves.

C. H. D. Clark.

Explosive reactions in gaseous media. Explosive reactions considered generally. W. E. Garner (Trans. Faraday Soc., June 1926, advance proof).—A summary of the history of, and recent work on, the subject, the difficulties due to the complexities of the systems investigated being emphasised. Mallard and Le Chatelier's equation connecting the explosion temperature and the initial and maximum pressures enables the specific heats and degrees of dissociation of gases at high temperatures to be obtained. Abnormalities are due to the formation of unknown and unstable molecules. The discontinuities in radiation observed in flames are due to the lack of uniformity of temperature throughout the reacting gaseous mixtures, resulting from loss of energy by radiation etc. Dixon and Higgins established definite pressures at which the ignition temperature of a gas mixture is a maximum. This result is not in accord with the Arrhenius equation, which also fails to account for the specific effect of diluent gases on the explosion temperature. Since also, diluents do not change the position of equilibrium, their nature is that of negative catalysts. Mallard and Le Chatelier's theory of the velocity of uniform movement of flame, based on the raising to ignition temperature of the unburnt gas by the burning gas, is substantiated by the work of Ellis. Their quantitative expression of this (and also that of Nusselt) does not account for the finite value of the velocity when the ignition temperature equals the maximum temperature reached in the flame. Ionisation and catalytic theories of "anti-knock" compounds, and the effect of the mode of confinement of the gases on the nature of the explosion, are also discussed.

J. Grant.

Explosive reactions in gaseous media. "Uniform movement" during the propagation of flame. W. Payman and R. V. Wheeler (Trans. Faraday Soc., June 1926, advance proof).—Curves relating the speed of uniform movement of a flame in a horizontal glass tube and the percentage of combustible gas in the air used show marked maxima. Wide differences are found between these maxima for different combustible gases, between their ranges of inflammability, and between the speeds of flames in different air mixtures with the same gas. The speed is proportional to the ratio $(T-t)/(t-0)$, where T, t, and 0 are the combustion, ignition, and initial temperatures, respectively. Coward and Hartwell have shown that the effect of replacing a particular combustible gas by one of higher specific heat is to lower the speed, but to raise the range of inflammability. Owing to a mass action effect, the greatest speeds are obtainable where the inflammable gas is present in excess. For air containing complex gas mixtures the "law of speeds" provides that if the component gases have the same speed, then the mixture will also have this speed so long as an excess of inflammable gas is present. The combustion can then be regarded as that of independent simultaneous combustions of simple mixtures of air and the individual gases. The rate of development of pressure with different mixtures of air and inflammable gas is also directly proportional to the maximum speed of the flame produced, and the law of speeds also applies here.

J. Grant.

Explosive reactions in gaseous media. Ignition-point of gases. H. B. Dixon, J. Harwood, and W. F. Higgins (Trans. Faraday Soc., June 1926, advance proof).—Nernst's falling piston method of adiabatic compression for the determination of the ignition-points of gases has been improved by causing the piston to be arrested when the ignition compression is reached, and by preventing the recoil of the piston at this stage. Lower values of the ignition-points of oxygen–hydrogen mixtures are then obtained which decrease with the proportion of oxygen present. For methane–oxygen mixtures the reverse applies, the fall and rise respectively being greatest in the improved machine. The lags between the completion of the piston-stroke and the recoil due to the explosion are shortest with the highest compressions. These results suggest the need for improvement in the concentric tube method. The whole furnace is enclosed in a steel case, which ensures more uniform heating throughout the cylinder, the interval between the turning on of the gas and its inflammation being timed by a pendulum and metronome. Lags of 0·5 and 0·6 sec. give most

concordant results for air with hydrogen and methane, respectively. Below atmospheric pressure, the rapid ignition-points of hydrogen and methane fall and rise, respectively, and conversely above atmospheric pressure. For each gas tested there is a crucial pressure at which the ignition-point is a maximum. The results obtained by this method are in good agreement and may be correlated with those obtained by compression. J. GRANT.

Explosive reactions in gaseous media. Ionisation and gaseous explosions. S. C. LIND (Trans. Faraday Soc., June 1926, advance proof).—Recent evidence in favour of the thermal in place of the ionic propagation of gaseous explosion is summarised. Wendt and Grimm's theory of the reduction of ionisation, and consequently of the speed of propagation of the flame, produced by "anti-knock" substances, is not confirmed. The actual rate of slow oxidation of methane, normally dependent on the influence of external α-rays, is unaffected by the presence of an "anti-knock" compound (diethyl selenide). Ionisation is probably an accompaniment of, rather than a cause of, detonation. J. GRANT.

Velocity of [gas] reactions involving atoms. M. BODENSTEIN (Sitzungsber. Preuss. Akad. Wiss., 1926, **13**, 104—114).—From a consideration of data previously published (A., 1925, ii, 135, 218) it is concluded that, in so far as bimolecular reactions between atoms or between an atom and a molecule are concerned, every collision is operative. As a result of various influences, only a definite proportion of the reacting substances is converted into products of reaction. The number of collisions must, therefore, be multiplied by a factor which is independent of temperature (cf. Herzfeld, A., 1919, ii, 503).
J. S. CARTER.

Gaseous combustion in electric discharges. I. Combustion of electrolytic gas in direct current discharges. G. I. FINCH and L. G. COWEN (Proc. Roy. Soc., 1926, **A**, **111**, 257—280).—Electric discharges have been passed through electrolytic gas at pressures between 20 and 100 mm. in such a way as to eliminate as far as possible any chemical combination, including that due to heat, other than that caused by ionisation of the gas. Up to a certain current strength, the rate of combustion increases with the current strength at a rate which is constant, and depends only on the material of the cathode, and not on the pressure or distance apart of the electrodes. This is taken to represent combustion in the cathode zone only. Beyond this point, combustion suddenly commences in the zone between the electrodes as well, and proceeds at a rate which is proportional to the current, and is independent of the material of the electrodes, but dependent on their distance apart and on the gas pressure. In no case does any appreciable combustion seem to occur in the anode zone. R. CUTHILL.

Limits of inflammability of firedamp in atmospheres which contain blackdamp. H. F. COWARD and F. J. HARTWELL.—See B., 1926, 426.

Rate of the reaction between ethylene and chlorine. T. D. STEWART and R. D. FOWLER (J. Amer. Chem. Soc., 1926, **48**, 1187—1194).—The combination in glass vessels of gaseous ethylene and chlorine mixed with air is a purely surface reaction. At 17°, it is only one tenth as rapid as the corresponding reaction between ethylene and bromine vapour at 0° (Stewart and Edlund, A., 1923, ii, 304). The reaction may be to some extent autocatalytic.
S. K. TWEEDY.

Velocity of the gas reaction $2NO+Cl_2=2NOCl$ in a magnetic field. F. A. HENGLEIN (Z. Elektrochem., 1926, **32**, 213—215).—A magnetic field of 20,000 gauss does not affect the rate of the above reaction at 15·2°, in spite of the claim of Pinkus and de Schulthess (A., 1921, ii, 368) that the reaction involves ionisation. R. CUTHILL.

Ignition of gases by sudden compression. H. T. TIZARD and D. R. PYE (Phil. Mag., 1926, [vii], **1**, 1094—1105).—Experiments on the compression of mixtures of ethyl ether, pentane, hexane, heptane, and octane with air, in which the time of compression was maintained constant at 0·14 sec., have confirmed the previous conclusions of the authors (*ibid.*, 1922, [vi], **44**, 79) that the reaction between the compounds and oxygen proceeds at a rate conditioned by the temperature and that the ignition or non-ignition depends on the rate of loss of heat at this temperature. If the rate of loss of heat is measured, the ignition temperature under one set of conditions can be calculated, with fair accuracy, from the observed ignition temperature under other conditions. With the paraffin hydrocarbons, the ignition temperatures decrease with increasing mol. wt., which is in agreement with the observation that paraffin hydrocarbons tend to detonate the more readily in internal combustion engines the higher are their b. p.
A. E. MITCHELL.

Explosion regions. IX. Explosion space $EtBr-NH_3-O_2-N_2$. W. P. JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1926, **45**, 400—406; cf. this vol., 359).—The explosion range for ethyl bromide–oxygen–nitrogen mixtures has been examined. The ratio outside the parentheses represents the ratio $[O_2]/[N_2]$, whilst l and u represent the lower and upper limiting percentages, respectively, of ethyl bromide in explosive mixtures: 90/10 ($l=10$); 60/40 ($l=10·7$); 43/57 ($l=10·7$, $u=32·5$); 28/72 ($l=14·2$, $u=21·1$); 25/75 (no inflammation). In a number of these cases, the upper limit lies above the saturation point (41·3% of vapour at 14°). The explosion space for the four-component mixture was investigated. The ratio has the same significance and l and u represent the lower and upper limiting percentages of ethyl bromide in presence of the amount of ammonia indicated: 95/5, 10% NH_3 ($l=4·7$), 50% NH_3 ($u=17·8$), 41·3% EtBr (upper limit of ammonia, 23·5%); 62·5/37·5, 4% NH_3 ($l=8·9$), 12% NH_3 ($l=5·2$), 30% NH_3 ($u=25·5$); 43/57, 14% NH_3 ($l=4·5$), 20% NH_3 ($u=18·3$), 30% NH_3 ($u=9·4$); 28/72, 2% NH_3 ($l=14·3$, $u=19·8$), 10% NH_3 ($l=9·8$, $u=13·2$), top of curve is situated at 8% EtBr and 15% NH_3; 25/75, mixtures do not inflame. The space figure has been constructed. The explosion

space contains a metastable region corresponding with supersaturated vapour. J. S. CARTER.

Thermal decomposition of acetone in the gaseous state. C. N. HINSHELWOOD and W. K. HUTCHISON (Proc. Roy. Soc., 1926, **A**, **111**, 245—257).—The above process, which has been followed at temperatures between 506° and 632° by observing the increase in pressure, is a homogeneous unimolecular reaction. The heat of activation is 68,500 cal., and the relation between the velocity coefficient, k, and the temperature (Abs.), T, is $\log_e k = 34{\cdot}95 - 68{,}500/RT$. It is calculated that the number of molecules reacting per sec. is about 10^5 times as great as the maximum number that could be activated by collision. Nitrogen and carbon monoxide do not affect the rate of reaction. The products of decomposition are about one half saturated hydrocarbons and hydrogen, one third carbon monoxide, and the remainder carbon dioxide and ethylene.

R. CUTHILL.

Reduction of ferric salts with hydrogen sulphide. W. MOLDENHAUER and E. MISCHKE (Z. Elektrochem., 1926, **32**, 252—261).—In neutral or in very feebly acid solution, the velocity of reduction of ferric salts by hydrogen sulphide is too large to be measured. The velocity has been determined, however, in sulphuric, hydrochloric, and phosphoric acid solutions of varying concentrations. In sulphuric acid at 0° and 20° and in hydrochloric at 0°, it is a termolecular reaction. In hydrochloric and phosphoric acid solutions at 20° it is a bimolecular reaction. In all cases, the velocity diminishes rapidly with increase in concentration of acid, the velocity constant being a logarithmic function of the normality of the acid. The inhibiting influence of phosphoric acid on the rate of reaction is very much greater than that of either of the other acids, and when these are added to the former they influence the velocity only to a slight extent. It is suggested that the inhibiting action of acids is due to the formation of a complex compound the nature of which also influences the order of the reaction. The precipitate of iron sulphide formed in feebly acid, neutral, or slightly alkaline solution contains only ferrous iron, thus suggesting that the reduction proceeds with even greater rapidity than precipitation. By the action of hydrogen sulphide on freshly precipitated ferric hydroxide, or of strongly ammoniacal ammonium sulphide on ferric sulphate solution, exactly two thirds of the iron appears to be reduced to the ferrous state. This is probably accounted for by the formation of a ferrous sulphoferrite, $4FeS,Fe_2S_3$.

M. S. BURR.

Kinetics of the oxidation of tervalent titanium by iodine. D. M. YOST and S. ZABARO (J. Amer. Chem. Soc., 1926, **48**, 1181—1187).—The rate of the reaction: $2Ti^{\cdot\cdot\cdot} + I_2 + 2H_2O = 2TiO^{\cdot\cdot} + 2I' + 4H^{\cdot}$ is proportional to the concentrations of the tervalent titanium and of the tri-iodide ion ($I_2 + I' = I'_3$) and inversely proportional to those of the hydrogen and iodide ions. The results, which do not support the intermediate formation of hypoiodous acid, indicate that an additive product is slowly formed by the interaction of iodine and the ion $Ti(OH)^{\cdot\cdot}$, which reacts rapidly with more of the latter to give the final reaction products. The results both of this reaction and of that studied by Bredig and Michel (A., 1922, ii, 359) may also be interpreted by assuming the production of quinquevalent titanium as the first stage of the reaction. S. K. TWEEDY.

Velocity of addition of sulphites to maleic and fumaric acids. J. M. VAN DER ZANDEN (Rec. trav. chim., 1926, **45**, 424—427; cf. Hägglund and Ringbom, this vol., 363).—The reaction between fumaric and maleic acids and a sulphite has been studied at 25° in solutions containing 1 mol. of sulphurous acid and 1, 2, or 3 mols. of sodium hydroxide per mol. of unsaturated acid. Similar bimolecular constants are obtained when the course of the reaction is followed by titrating the change of acidity or by titrating the sulphite iodometrically. Maleic acid reacts faster than fumaric acid in all cases, but the effect of various proportions of alkali is different for the two acids, as is shown by the following figures for 1, 2, and 3 mols., respectively, of sodium hydroxide: fumaric acid, 59×10^{-5}; 19×10^{-4}; 53×10^{-5}; maleic acid, 112×10^{-5}; 40×10^{-4}; 60×10^{-3}. G. M. BENNETT.

Rate of reaction between formic acid and iodine in aqueous solution. D. L. HAMMICK and M. ZVEGINTZOV (J.C.S., 1926, 1105—1108).—The reaction between iodine and formic acid is bimolecular; its velocity is inversely proportional to the concentration of iodine ion and directly proportional to the concentration of formyl ion. The figure obtained for the ratio of the two velocity constants of the reaction in the presence of an excess of potassium iodide agrees with that obtained by Dhar, but it is shown that this does not support Dhar's views (*ibid.*, 1917, **111**, 726) that the potassium iodide acts as a retarding catalyst. A. R. POWELL.

Reactivity of alkyl iodides with sodium benzyl oxide. A criticism. L. J. GOLDSWORTHY (J.C.S., 1926, 1102—1104).—Experiments are described which show that sodium benzyl oxide undergoes almost complete alcoholysis in 0·1*N*-solutions in absolute alcohol and consequently Haywood's figures (*ibid.*, 1922, **121**, 1904) for the velocities of the reactions between alkyl iodides and sodium benzyl oxide are really velocities of the reactions between the iodides and sodium ethoxide. Even in *N*-solutions of sodium benzyl oxide only traces of benzyl ethyl ether are formed. A. R. POWELL.

Benzylation of amines. III. D. H. PEACOCK (J. Physical Chem., 1926, **30**, 673—679).—The alterations in the velocity constant for the reaction between amines and benzyl chloride are discussed. (cf. A., 1925, i, 1399). L. S. THEOBALD.

Reduction of nitrous oxide. M. L. NICHOLS and I. A. DERBIGNY (J. Physical Chem., 1926, **30**, 491—506; cf. Bancroft, A., 1924, ii, 745; Dhar, *ibid.*, 1925, ii, 315; Coblens and Bernstein, *ibid.*, 804).—The reduction of nitrous oxide by aqueous solutions of titanous chloride, stannous chloride, and sodium sulphite has been studied at 25°. The products are ammonia, hydroxylamine, and nitrogen, respectively. The rate of reduction increases with increasing con-

centration of the reducing agent, decreases with a rise in temperature, and, in the case of stannous chloride and titanous chloride, decreases with increased (hydrochloric) acid concentration. Variation in these three factors changes only the percentage amount of reduction, but not the nature of the final product with a given reducing agent. Reduction of nitrous oxide by titanous chloride is catalysed by platinum. The probable mechanism of reduction based on the initial formation of hyponitrous acid, according to the equation $N_2O+H_2O=(NOH)_2$, is discussed (cf. Milligan and Gillette, A., 1924, ii, 605). Determinations of *E.M.F.* for solutions of the reducing agents used and for a saturated solution (20°) of nitrous acid, all with varying amounts of hydrochloric acid, gave results in agreement with those of Neumann (A., 1894, ii, 373). L. S. THEOBALD.

Reactions in the solid state. VI. D. BALAREV (Z. anorg. Chem., 1926, **153**, 184—190; cf. A., 1925, ii, 893).—The majority of the reactions between intimate mixtures of solid substances at high temperatures studied by Tammann and his pupils are shown to be due to the presence of a gaseous phase caused by dissociation or vaporisation of one of the constituents, or to the formation of a small amount of a liquid phase, *e.g.*, a eutectic between the two constituents of the mixture or between one constituent and the reaction product. The temperature at which the reactions proceed at an appreciable velocity is always sufficient to produce one new phase, otherwise the action ceases. In the case of the reaction between tungsten or molybdenum trioxide with an alkaline-earth oxide, if the temperature of the mixture is kept above a certain minimum, depending on the degree to which the powder has been pressed together, and one spot is then heated further until the reaction starts, the whole mass is soon glowing throughout; the temperature obtained is sufficient, not only partly to vaporise the acid oxide, but also to cause the formation of fusible eutectics between the salt formed and the remaining acid oxide. Lead oxide and molybdenum trioxide react vigorously only above 700°, at which temperature lead oxide has an appreciable vapour pressure. The interchange of sulphur and oxygen when zinc or lead sulphide is heated with cadmium or copper oxide at 600° is due to the presence of gaseous sulphur derived from the dissociation of the metal sulphide, which, in the case of zinc, cadmium, and copper, is appreciable above 300°. Several other alleged reactions in the solid state are discussed. A. R. POWELL.

Hydrogen-ion concentration [of water] and corrosion. J. R. BAYLIS.—See B., 1926, 493.

Factors other than dissolved oxygen influencing the corrosion of iron pipes. J. R. BAYLIS.—See B., 1926, 493.

Thermal decomposition of carbonates. B. BRUŽS (J. Physical Chem., 1926, **30**, 680—693).—The decomposition of ferrous, lead, cobalt, zinc, and mercurous carbonates has been investigated at various constant temperatures and at constant pressure. The rates of decomposition agree with the unimolecular formula. For ferrous carbonate, as siderite, the Arrhenius formula holds between 491° and 581°. The critical increment calculated from the velocities at 501° and 561° is 85,500 cal. At 491°, the velocity constant is abnormal, and between 445° and 495° the velocities are low. It is suggested that within this range the velocity constant remains unchanged, whilst the "active mass" increases with temperature. At 760 mm. pressure, synthetic ferrous carbonate decomposes at 340° as compared with 495° for the mineral form. Between 427° and 477°, cobalt carbonate decomposes according to the scheme $CoCO_3 \longrightarrow CoCO_3,CoO+CO_2$, followed by $CoCO_3,CoO \longrightarrow CoO+CO_2$, and the corresponding critical increments are 72,000 and 82,200 cal., respectively. Between 407° and 452°, zincspar decomposes to the extent of 65% at an almost constant rate, after which the reaction slows down and stops abruptly. Cerussite forms the compound $PbO,PbCO_3$ between 320° and 350°, but no indication of the compound $3PbO,5PbCO_3$ (cf. Centnerszwer, Falk, and Awerbuch, A., 1925, ii, 400) was obtained. The critical increments for zincspar and cerussite are 95,000 and 69,600 cal., respectively. Synthetic mercurous carbonate gave curves similar to those obtained by Lewis (A., 1905, ii, 578) for silver oxide, and the reaction is autocatalytic in character. L. S. THEOBALD.

Tarnishing of copper in sulphur vapour. K. FISCEBECK (Z. anorg. Chem., 1926, **154**, 261—266; cf. Tammann and Bredemeier, A., 1924, ii, 613).—The tarnishing of copper in sulphur vapour at constant sulphur vapour pressure follows a logarithmic law. The law holds if the gas phase be eliminated, but the fraction by which the concentration falls from film to film becomes very small: change of pressure, 100—1000 atm., has little effect. Temperature influences the reaction enormously; at 40°, heat evolution is very great, the temperature of the reaction mixture rising very much above that of the electrically heated bath. M. CARLTON.

High-temperature oxidation of metals. J. S. DUNN (Proc. Roy. Soc., 1926, **A**, **111**, 203—209).—The rate of oxidation of alloys of copper and zinc between 600° and 900° is equal to $Ae^{-Q/RT}$, where T is the temperature (Abs.) and A and Q are constants. This expression can be deduced theoretically if the mechanism of oxidation be assumed to be the diffusion of oxygen in solid solution in a protective film of cuprous oxide. This diffusion does not appear to occur by intermediate formation of cupric oxide. R. CUTHILL.

Low-temperature oxidation of copper. J. S. DUNN (Proc. Roy. Soc., 1926, **A**, **111**, 210—219).—The progress of oxidation between 200° and 300° has been followed by conductivity measurements. For short intervals of time, the rate of oxidation of ordinary copper can be represented by the expression $W^2=Kt$, where W is the oxygen absorbed as oxide, t is the time, and K is a constant. This equation can be deduced on the assumption that the rate is determined by the diffusion of oxygen through a surface layer of oxide. Catalytically active copper oxidises more rapidly than ordinary copper, and does not follow the above law unless it is annealed above 400°.

The known anomaly in the rate of oxidation of activated copper near 210° (cf. Palmer, A., 1923, ii, 474) is probably due to some change in the surface film of oxide, this view being supported by the fact that the rate of oxidation is reduced by annealing the oxide film in a vacuum. It is suggested that the surface of activated copper consists of a colloidal aggregate of atoms. R. CUTHILL.

Thermal decomposition of formic acid. W. L. NELSON and C. J. ENGELDER (J. Physical Chem., 1926, **30**, 470—475; cf. Muller and Peytral, A., 1921, i, 156, and following abstract).—When slowly passed through tubes of silica, pyrex, porcelain, or copper (3 c.c. per hr.) heated at 350—550°, formic acid decomposes mainly according to the reaction $H{\cdot}CO_2H=CO_2+H_2$ (i). An amount, usually small, decomposes thus $2H{\cdot}CO_2H=CO_2+H_2O+H{\cdot}CHO$. The carbon monoxide found is accounted for by the ordinary dehydration reaction and the reaction $H{\cdot}CHO=CO+H_2$. At 450°, the decomposition reaches 90% or more, the pyrex glass tube being the least and the copper tube the most active. Etching the silica tube increases activity. With copper, reaction (i) occurs almost exclusively and reaches more than 99% at 450° and 550°. On account of complications in the gas volume relations, exact calculations cannot be made. L. S. THEOBALD.

Catalytic decomposition of formic acid. B. B. WESCOTT and C. J. ENGELDER (J. Physical Chem., 1926, **30**, 476—479; cf. Sabatier and Mailhe, A., 1911, i, 515; Hinshelwood and Topley, J.C.S., 1923, **123**, 1014; Adkins, A., 1923, ii, 309).—The catalytic effects of small amounts of alumina, titania, and nickel on the decomposition of formic acid between 200° and 500° have been studied. Up to temperatures slightly above 300°, the reaction $H{\cdot}CO_2H=CO+H_2O$ (i) predominates when alumina and titania are the catalysts, whilst with nickel up to 353° the dehydrogenating reaction $H{\cdot}CO_2H=CO_2+H_2$ (ii) occurs almost exclusively. Alumina and titania also catalyse this last reaction to some extent. The reaction tube of unglazed clay decomposed the formic acid mainly according to (ii), its effect being marked above 350°. Decomposition according to the equation $2H{\cdot}CO_2H=CO_2+H_2O+H{\cdot}CHO$ occurred to a slight extent in all the runs, and is attributed solely to the walls of the reaction vessel (cf. preceding abstract). L. S. THEOBALD.

Catalytic action of iron ores in decomposing carbon monoxide. P. FARUP.—See B., 1926, 490.

Thermal decomposition of cellulose and lignin in presence of catalysts and hydrogen under pressure. A. R. BOWEN and A. W. NASH.—See B., 1926, 474.

Catalytic action of metals of the platinum group and their degree of subdivision. II. G. R. LEVI and R. HAARDT (Atti R. Accad. Lincei, 1926, [vi], **3**, 215—223).—Investigations similar to those on platinum (this vol., 365) have now been made on various preparations of palladium, rhodium, iridium, ruthenium, and osmium in the spongy and "black" forms. The results show that the granules of metals of the platinum group obtained as "black" have dimensions comparable with those of colloidal metals, often of high dispersion. Thus, for the cubic metals, platinum, palladium, rhodium, and iridium, the sides of the cell of base a are 3·903, 3·873, 3·795, and 3·823 Å., respectively, and the sizes of the granule Λ, 4·80—11·27, 4·98—11·10, 2·20, and 1·60 μμ, respectively; for the hexagonal metals, ruthenium and osmium, a is 2·680 and 2·714 Å., Λ_a 1·92—2·27, and 1·70 μμ, and Λ_c 3·06—3·61, and 2·70 μμ, respectively. The fact that the granules of the spongy metals are large compared with those of metallic blocks explains the advantage of subdividing the catalyst on a diluent substance such as asbestos, porcelain, etc. T. H. POPE.

Cathodic sputtering. I. Electrochemical sputtering. A. GÜNTHER-SCHULZE (Z. Physik, 1926, **36**, 563—580).—The sputtering of 24 elements in hydrogen has been examined; carbon, selenium, tellurium, arsenic, antimony, and bismuth behave in a manner which suggests the formation of hydrides, the diffusion of these away from the cathode, and then their decomposition; this is called electrochemical sputtering. The normal and electrochemical effects are compared for different distances between anode and cathode, and for different values of the cathode fall of potential, a high value favouring the normal effect. E. B. LUDLAM.

Radiation in gaseous explosions. W. T. DAVID (Trans. Faraday Soc., June 1926, advance proof).—Gaseous mixtures emit radiations strongly after explosion, especially during the cooling period. In the case of coal gas and air, 1% of the total radiation is luminous and is emitted entirely during the explosion period, the infra-red spectrum being, on the whole, the same as that of a Bunsen flame. It is inferred that the emission is due chiefly to chemical activity, since the stronger emission is accompanied by rapid combustion and cannot be explained in terms of temperature. Hydrogen–air mixtures do not show this effect, presumably because the influence of chemical activity on the radiation is masked as a result of the relatively simple and rapid process by which hydrogen is oxidised compared with hydrocarbons. The distribution of the energy of combination of molecules during combustion depends on the degree of violence with which this takes place. As combustion becomes more violent, high-frequency vibrations begin to take a share of the energy from low-frequency vibrations, and an increasing proportion of infra-red radiation is emitted. Infra-red radiation will also preactivate certain gaseous mixtures in closed vessels, provided nitrogen is present and the radiation can be absorbed by the combustible gas. There is evidence for the formation of oxides of nitrogen during combustion, the effect of radiation being probably to provide vibratory energy which inhibits that interplay between molecules of oxide and gas which retards combustion. J. GRANT.

Photo-sensitiveness of dyes. G. KÖGEL and A. STEIGMANN (Kolloid-Z., 1926, **39**, 52—56).—A general discussion. N. H. HARTSHORNE.

Spectral distribution of sensitivity of photographic materials. L. A. JONES and O. SANDVIK (J. Opt. Soc. Amer., 1926, **12**, 401—416).—An automatic monochromatic sensitometer is described in which the sector wheel apertures are spaced spirally round the centre of rotation. The sector rotates with uniform angular velocity and also longitudinally, and the plate is moved forward one step after exposure through the successive apertures; twelve exposures increasing by consecutive powers of two are obtained. To reduce the percentage of stray radiation to a minimum, two monochromatic illuminators in series were used. In some cases, when a single monochromator was used, stray radiation amounted to 50% of the total radiation. The amount of spectral energy per cm.^{2} necessary to give unit density for development to unit "gamma" with metol–quinol was determined for four different emulsions. The maximum sensitivity was found to be in the ultra-violet. An apparent drop in sensitivity found below 3500 Å., may be due to reciprocity failure. "Gamma" increases with wave-length in the region of 3000—5500 Å., the increase being more marked for longer development times. "Gamma" for maximum development is a minimum in the ultra-violet and increases generally towards the red. The velocity constant of development is a maximum for exposures in the ultra-violet and decreases towards the red. W. CLARK.

Hydrolysis of starch grains by light polarised by small particles. E. S. SEMMENS (Nature, 1926, **117**, 812—822).—A suspension of potato starch in water, immersed in a colloidal solution of taka-diastase, was exposed to morning and evening sunlight, so that the starch was irradiated by polarised light reflected vertically upwards. The cells were disrupted, with slow crystallisation of the contents; on prolonged exposure the empty shells yielded a fatty substance. The liquid distinctly affected Fehling's solution. It would appear that there is an orientation factor in the action of certain enzymes. A. A. ELDRIDGE.

Hydrogen. IV. Copper hydride. G. F. HÜTTIG and F. BRODKORB (Z. anorg. Chem., 1926, **153**, 235—245; cf. this vol., 686).—The hydrogen–copper ratio of freshly-prepared moist copper hydride corresponds with the formula CuH, but the compound appears to contain in addition a certain amount of water. After drying in a vacuum desiccator at the ordinary temperature, the preparation invariably contains less hydrogen than is required by the above formula. The dry substance slowly loses hydrogen when heated to 110°, at which temperature the remainder of the gas is evolved with explosive violence; the rate of decomposition of the moist substance at the ordinary temperature in a vacuum decreases gradually with the time. The rate of decomposition of the moist substance increases rapidly with rise of temperature, and at 85° the substance is completely decomposed without explosion. *X*-Ray examination shows copper hydride to have a face-centred cubic lattice with a parameter of 4·33 Å., corresponding with a molecular volume of 12·18 and *d* 5·30 compared with the respective values of 7·12 and 8·93 for pure copper. A. R. POWELL.

Silver carbonate. G. H. JEFFREY and A. W. WARRINGTON (Chem. News., 1926, **132**, 373—375).—The composition of "pure" silver carbonate and its decomposition by heat have been quantitatively studied. Prepared in the cold and dried to constant weight over sulphuric acid or phosphorus pentoxide, silver carbonate still contains from 0·043 to 0·246% of water. Other methods in which heat is applied likewise do not give the pure carbonate. The product obtained by heating silver carbonate to constant weight at 180° contains the oxide, undecomposed carbonate, and water. The product now prepared, in red light, is sage-green in colour, and after drying is only slowly affected, and to a slight extent, by strong sunlight. When damp, however, rapid darkening with little, if any, decomposition occurs. Nine experiments at a temperature sufficient to effect decomposition, but not to fuse the silver formed, are recorded and give the value 107·86 for the atomic weight of silver. L. S. THEOBALD.

Action of oxalic acid on alkali chlorides and nitrates. N. A. TANANAEV (Z. anorg. Chem., 1926, **154**, 186—188).—A 0·1*N*-solution of lithium, sodium, potassium, rubidium, or cæsium chloride or nitrate was treated with *N*-oxalic acid solution, the ratio of chloride or nitrate to oxalic acid being 1 : 4. The residue on evaporation and ignition was the corresponding carbonate, free from chloride or nitrate.

This method, when modified, can be used as a sensitive means of detecting the alkali metals in the presence of the alkaline earths. Since the conversion of chloride or nitrate into carbonate is quantitative, the former may be used for standards in acidimetry. M. CARLTON.

Compounds of metallic salts and carbon monoxide. XIV. Compound of potassium cobaltocyanide and carbon monoxide and the valency of the central atom in complex salts. W. MANCHOT and H. GALL (Ber., 1926, **59**, [*B*], 1056—1059).—A concentrated aqueous solution of potassium cyanide, potassium acetate, and cobalt acetate rapidly absorbs carbon monoxide at −10°, yielding the *compound* $K_3Co(CN)_5,CO$.

Weinland's statement ("Einführung in die Chemie der Komplexverbindungen," 1919, p. 34) that molecules such as carbon monoxide and nitric oxide play the same part in complex salts as acid residues or ammonia is incorrect, since acid residues influence the valency of the central atom, whereas the other groups do not. H. WREN.

Complex compounds of beryllium. III. R. FRICKE and O. RODE (Z. anorg. Chem., 1926, **152**, 347—356; cf. A., 1925, ii, 886).—When heated, beryllium chloride combines with *o*-toluidine to form the *compound* $BeCl_2,2C_6H_4Me\cdot NH_2$ (red), with propionitrile to form $BeCl_2,2Et\cdot CN$ (colourless), with *iso*hexonitrile to form $BeCl_2,2C_5H_{11}\cdot CN$ (white, with benzyl cyanide to form $BeCl_2,2CH_2Ph\cdot CN$ (white), and with *p*-toluonitrile to form $BeCl_2,2C_6H_4Me\cdot CN$ (colourless). The following complex *compounds* are

obtained by mixing the ethereal solutions of their constituents: with quinoline, $BeCl_2,2C_9H_7N$ (yellow); with succinonitrile, $BeCl_2,C_2H_4(CN)_2$ (white); and with α-naphthonitrile, $BeCl_2,2C_{10}H_7{\cdot}CN$ (yellow). By adding liquid hydrogen cyanide to an ethereal solution of beryllium chloride, a white *compound*, $BeCl_2,4HCN$, is produced. Dicyanogen appears to form a very unstable *compound*. All the above compounds are solids. R. CUTHILL.

Complex compounds of beryllium. IV. R. FRICKE and L. HAVESTADT (Z. anorg. Chem., 1926, **152**, 357—367; cf. preceding abstract).—The following solid complex *compounds* of beryllium chloride have been obtained by mixing ethereal solutions of their constituents: with phenylhydrazine, $BeCl_2,4NHPh{\cdot}NH_2$ (pale yellow); with hydrazine, $BeCl_2,3N_2H_4$ (white); with ethylenediamine, $BeCl_2,2C_2H_4(NH_2)_2$ (white), and with benzidine, $2BeCl_2,3(C_6H_4)_2(NH_2)_2$ (white). In preparing these substances, moisture must be carefully excluded. R. CUTHILL.

Interchange of radicals between solid phases. V. Reactions of alkaline-earth oxides with sulphides, carbides, silicides, and phosphides. J. A. HEDVALL and E. NORSTRÖM (Z. anorg. Chem., 1926, **154**, 1—29; cf. A. 1922, ii, 766; 1923, ii, 860; 1924, ii, 484; 1925, ii, 125, 306).—Alkaline-earth oxides will not react with metallic sulphides in the absence of oxygen even when heated. Zinc, copper, or silver sulphide mixed with an alkaline-earth oxide and heated in air or oxygen reacts as follows: $CaO+ZnS+2O_2=CaSO_4+ZnO$; with silver the action continues: $Ag_2O=2Ag+0{\cdot}5O_2$. The definite reaction temperature for each oxide rises in the order: barium, strontium, calcium. Magnesium oxide usually reacts at a higher temperature than calcium oxide, but with silver sulphide the reaction temperature is 100° lower than with calcium oxide. Cuprous sulphide shows abnormalities with strontium, calcium, and magnesium oxides which are in agreement with the sudden oxidation of cuprous sulphide at 383°.

Gaseous sulphur dioxide can play no part in any of these reactions. Only with barium oxide is there any evidence for peroxide formation. Experiments with the compounds Cr_5C_2, $FeSi_2$, and Ca_3P_2 give results similar to those with the sulphides. Barium oxide and iron silicide react almost explosively at 329°, whereas calcium oxide reacts at 811°. M. CARLTON.

Basic salts. A. BENRATH (Z. anorg. Chem., 1926, **154**, 436—438).—A discussion of the criteria of basic salts, together with a suggested formulation of basic salts of zinc, copper, and mercury. M. CARLTON.

Iodomercurates of potassium which crystallise from acetone solution. (MLLE.) M. PERNOT (Compt. rend., 1926, **182**, 1154—1156).—The isothermal equilibrium diagram of the system potassium iodide–mercuric iodide–acetone has been constructed at 56°. At this temperature, five iodomercurates can exist as solid phases in equilibrium with acetone solutions and correspond with the formulæ: $HgI_2,2KI$, $2HgI_2,3KI$; and three *isomeric* salts, HgI_2, KI, $0{\cdot}25C_3H_6O$. These latter salts are compared with that isolated from aqueous solution which has the formula HgI_2,KI,H_2O (Pavlov, A., 1900, ii, 101) in which water and acetone replace each other in equal volumes (cf. Tourneux and Pernot, A., 1925, ii, 380). F. G. SOPER.

Rate of decomposition and reducing power of aluminium amalgam. F. L. HAHN and R. SCHLEIPEN (Z. anorg. Chem., 1926, **153**, 97—114; cf. A., 1924, ii, 412).—Activation in an alkaline solution containing cyanide results in a particularly reactive amalgam. Frequently a silver-like amalgam is thus obtained which does not react immediately with water; the reaction is, however, very regular and complete and, by measuring the hydrogen evolved, it is shown to be autocatalytic in form. In the presence of cinnamic acid, the autocatalytic nature of the reaction disappears, the amounts of hydrogen evolved and utilised for reduction being each approximately proportional to the time. More hydrogen is utilised when the aluminium is activated in an alkaline than in a neutral solution. When solutions of zinc salts are added to activated aluminium, a portion of the hydrogen is evolved very rapidly, but the greater part of the aluminium does not react with water. If reducible substances or substances which form insoluble zinc salts are added, the formation of such "dead" aluminium is partly or wholly prevented. A. GEAKE.

Thallium meta- and ortho-silicates. K. A. VESTERBERG and C. U. WILLERS (Arkiv Kemi, Min., Geol., 1926, **9**, No. 26, 1—8).—The existing statements in the literature concerning thallium silicates are untrustworthy, as the preparations described were not homogeneous. Two definite silicates have now been prepared. *Thallium metasilicate*, Tl_2SiO_3, is obtained as a white, amorphous precipitate when a 4% solution of sodium metasilicate is slowly added to a solution containing 2% of thallous nitrate and 4% of thallous hydroxide. An excess of thallous hydroxide must always be present, as the silicate readily undergoes hydrolysis. *Thallium orthosilicate*, Tl_4SiO_4, is prepared (i) by adding a concentrated solution of sodium metasilicate to a boiling 16·5% solution of thallous hydroxide, when a crystalline, canary-yellow precipitate is obtained which consists of the orthosilicate together with a little metasilicate, (ii) by boiling thallium metasilicate with an excess of 0·75*N*-thallous hydroxide solution, (iii) by shaking finely-divided, precipitated silica with an excess of thallous hydroxide solution. Both the above thallium silicates are anhydrous, in contradistinction to the metasilicates of sodium and lithium, which contain 9 mols. and 1 mol. of water, respectively. H. F. HARWOOD.

Germanium. II. Germanium tetrachloride and its ammonia compounds. W. PUGH and J. S. THOMAS (J.C.S., 1926, 1051—1061).—Unsatisfactory yields of germanium tetrachloride are obtained by passing a chlorine over a strongly-heated mixture of germanium dioxide and carbon, but

quantitative conversion of the dioxide into the tetrachloride ensues if the former is heated in a stream of carbonyl chloride. A very pure chloride is obtained by distilling a solution of germanium dioxide in concentrated hydrochloric acid in a current of hydrogen chloride at 90°, passing air through the well-cooled distillate to remove excess of hydrogen chloride, and redistilling with the addition of sulphuric acid. At 0°, germanium tetrachloride floats below concentrated sulphuric acid, but at 50° the position of the two layers is suddenly reversed and the chloride floats on the acid. Dry ammonia reacts with anhydrous germanium chloride or with an ethereal solution of the chloride to give a light, white powder of *hexammingermanic chloride*, $GeCl_4,6NH_3$, which is slowly hydrolysed in aqueous solution or on keeping in moist air to germanic hydroxide. When hexamminegermanic chloride is treated with ammonia at 0° at 3 atm., further adsorption of ammonia occurs with the formation of a second *ammine*, $GeCl_4,16NH_3$, which is stable at the ordinary pressure only below −4°, at which temperature its vapour pressure is 760 mm. This compound is a colourless liquid smelling strongly of ammonia, whereas the hexammine has no appreciable ammonia pressure at the ordinary temperature and suffers no loss in weight when kept over concentrated sulphuric acid for some days. Analogous compounds to the hexammine have been prepared with mono-, di-, and tri-ethylamine, with propylamine, and with butylamine. A. R. POWELL.

Double sulphates of rare earth and alkali metals. V. Cerous ammonium sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1926, [vi], **3**, 178—183).—Investigation of the system, $Ce_2(SO_4)_3$–$(NH_4)_2SO_4$–H_2O at 25°, indicates the existence of the compounds: (i) $Ce_2(SO_4),(NH_4)_2SO_4,8H_2O$, which has d^{15} 2·523 and is stable at 25° in contact with solutions containing from 0·8% to 5% of cerous sulphate and from 28% to about 1% of ammonium sulphate (cf. Wyrouboff, Bull. Soc. franç. Min., 1891, **14**, 84; Kraus, A., 1901, ii, 453); (ii) $Ce_2(SO_4)_3,5(NH_4)_2SO_4$ (cf. Barre, A., 1911, ii, 42). T. H. POPE.

Oxidation of ammonia. J. R. PARTINGTON (Nature, 1926, **117**, 756—757).—Although the second equation previously suggested (this vol., 487) is erroneous, nitrohydroxylamic acid is still regarded as a possible intermediate product. From a consideration of hitherto unpublished experimental records, a reaction scheme must conform with the following conditions: (*a*) Reactions of order higher than bimolecular are improbable; (*b*) hypothetical intermediate compounds should not be capable of rapid direct decomposition into nitrous oxide; (*c*) oxygen in excess of the amount required to form nitric oxide is necessary; (*d*) reactions between gases condensed on or dissolved in the platinum, or between labile platinum oxides and dissolved gases, seem not improbable. The following schemes are suggested: *A* (i) $NH_3+O_2=NH(OH)_2$; (ii) $NH(OH)_2+O=N(OH)_3$; (iii) $4N(OH)_3=4NO+6H_2O+O_2$. *B* (i) $NH_3=NH+H_2$; (ii) $NH+O_2=HNO_2$, etc. *C* (i) $NH_3+O_2=NH(OH)_2$; (ii) $NH(OH)_2+O_2=HNO_3+H_2O$ etc. A. A. ELDRIDGE.

Action of red phosphorus on iodine in organic solvents. R. N. TRAXLER and F. E. E. GERMANN (J. Amer. Pharm. Assoc., 1925, **14**, 476—477).—See A., 1925, ii, 1087. A. A. ELDRIDGE.

Complex metal phosphites and pyrophosphates. A. ROSENHEIM, S. FROMMER, H. GLÄSER, and W. HÄNDLER (Z. anorg. Chem., 1926, **153**, 126—142). The highly-complex phosphites are very similar to the corresponding pyrophosphates, and this has led to the conclusion that in such compounds the phosphorous acid is dimeric, so that the P_2O_7 radical of pyrophosphates is replaced by a $H_2P_2O_6$ radical in phosphites. *Potassium*, *sodium*, and *ammonium uranyl phosphites*, $M_2[UO_2(HPO_3)_2]$, are obtained as crystalline precipitates when uranyl sulphate or nitrate is added to the concentrated solution of the alkali phosphite, and the solution boiled. Sodium and *lithium* uranyl pyrophosphates, $M_2[UO_2P_2O_7]$, are similarly obtained. The solubilities of both these series of salts diminishes in the order K, NH_4, Na, the potassium and ammonium uranyl pyrophosphates being too soluble to be precipitated. Crystalline *ammonium* ($+8H_2O$), *potassium* ($+12HO$), *sodium* ($+14H_2O$), and *guanidine* ($+8H_2O$) *chromic phosphites*, $M[Cr(HPO_3)_2],xH_2O$, are obtained when chromic chloride is added to the corresponding alkali phosphites. They are similar in properties and crystal form to the corresponding complex pyrophosphates (Rosenheim and Triantaphyllides, A., 1915, ii, 463). *Sodium* ($+20H_2O$), *potassium* ($+20H_2O$), and *ammonium* ($+8H_2O$) *ferric phosphites*, $M_2[Fe(OH)(HPO_3)_2],xH_2O$, are similarly formed. The corresponding sodium ferric *pyrophosphate*, $Na_2[Fe(OH)P_2O_7],xH_2O$, was not obtained pure, but a more basic *salt*, $Na_3[Fe(OH)_2P_2O_7],4H_2O$, was obtained by oxidising sodium ferrous pyrophosphate with air. Complex *ammonium* ($+18H_2O$) and *potassium* ($+32H_2O$) *nickelous phosphites*, and *cobaltous phosphites*, $M_2[X_3(HPO_3)_4],xH_2O$, are formed, but no complex manganous, ferrous, stannous, plumbic, cupric, or cadmium phosphites could be prepared. On the other hand, complex nickelous and cobaltous pyrophosphates could not be obtained, but sodium ($+4H_2O$), *potassium* ($+3H_2O$), and *ammonium* ($+H_2O$) *cadmium pyrophosphates*, *sodium manganous pyrophosphate* ($+4H_2O$), sodium ($+2·5H_2O$), and *ammonium* ($+2H_2O$) *ferrous pyrophosphates*, and *potassium plumbic pyrophosphate* ($+5H_2O$), of the general formula $M_2^I[M^{II}P_2O_7],xH_2O$ were prepared. *Sodium plumbic pyrophosphate* has the formula $Na_4[Pb_4(P_2O_7)_3],6H_2O$. The alkali double salts of the phosphites and pyrophosphates of bivalent metals are thus not analogous, and there is no reason to assume the existence of a dimeric phosphite radical. It is therefore probable that in the corresponding compounds of tervalent metals such a radical does not exist. A. GEAKE.

Union of phosphorus and nitrogen under the influence of electric discharges. W. MOLDENHAUER and H. DÖRSAM (Ber., 1926, **59**, [*B*], 926—931).—Yellow phosphorus, distributed as evenly as possible over the inside of a glass tube, readily absorbs nitrogen at 180—200 mm. pressure when exposed to electric discharges between aluminium

electrodes. The product is a mixture of unchanged white phosphorus, red phosphorus, and *phosphorus nitride*, PN. It is extracted with carbon disulphide, and the residue is heated in a porcelain boat in a slow current of nitrogen at 500—550°/12 mm.; the nitride thus acquires some impurities from the porcelain. It is a voluminous, yellowish-brown powder, extraordinarily resistant to chemical agents. H. WREN.

Formation of ozone and hydrogen peroxide in the oxy-hydrogen flame. E. H. RIESENFELD and H. VON GÜNDELL (Z. physikal. Chem., 1926, **119**, 319—332; cf. A., 1924, ii, 543, 603; 1925, ii, 147).—A continuation of previous work (A., 1925, ii, 148) with the use of improved apparatus. The more efficient method employed of cooling the flame causes a decrease in the amount of ozone formed under otherwise similar conditions. The yield of ozone can even be reduced to zero, only water and hydrogen peroxide being formed. As low temperatures are favourable to the stability of hydrogen peroxide, it is deduced that the ozone results from the decomposition of hydrogen peroxide, and not from a side reaction, as was previously thought. It is considered that part of the atomic oxygen liberated in this decomposition combines with molecular oxygen to form ozone, the other part forming molecular oxygen by mutual interaction; excess of oxygen therefore favours the production of ozone. The mechanism of the hydrogen-oxygen-hydrogen peroxide-water reaction is discussed. L. F. GILBERT.

Oxides of chromium. A. SIMON and T. SCHMIDT (Z. anorg. Chem., 1926, **153**, 191—218).—When heated, chromium trioxide melts just below 200° and a portion begins to distil; at 265°, evolution of oxygen begins and the substance slowly solidifies to a dark brownish-violet mass of a new *oxide*, Cr_5O_{13}. Between 285° and 329°, evolution of oxygen ceases, to recommence again just above 320° and ceases once more at 360—365°; finally, rapid and complete decomposition to chromium sesquioxide takes place at 410°. The composition of the residue between 365° and 410° corresponds with that of the known intermediate oxide, Cr_5O_{12}; both this oxide and Cr_5O_{13} are shown to be chromates of chromium and their mode of decomposition is in agreement with the theory that heating first eliminates chromium trioxide, which is then further decomposed according to the temperature into Cr_5O_{12} or Cr_2O_3. No other intermediate oxides are formed during the thermal decomposition of chromium trioxide; in fact, the other known oxides between Cr_5O_{12} and Cr_2O_3 are all, with the exception of Cr_5O_9, shown to be less stable than Cr_5O_{12} at high temperatures. The magnetic oxide, Cr_5O_9, however, does not begin to decompose below 460° and is not completely decomposed until 660°; it is therefore the most stable chromium oxide containing more oxygen than the sesquioxide, although it cannot be prepared by heating the trioxide.

A. R. POWELL.

Hydrates of chromic nitrate. J. R. PARTINGTON and S. K. TWEEDY (J.C.S., 1926, 1142—1145).—Slow crystallisation at the ordinary temperature of a solution of chromic hydroxide in the minimum quantity of nitric acid results in the deposition of red-dish-violet, octahedral crystals of $Cr(NO_3)_3,12{\cdot}5H_2O$, m. p. 104—105°, which appear to be identical with those obtained by Halse (Chem.-Ztg., 1912, **36**, 962), who ascribed to them the formula $Cr(NO_3)_3,7{\cdot}5H_2O$. The nonahydrate may be prepared by the slow evaporation over sodium hydroxide of a solution of violet chromic chloride containing a little more than the requisite amount of nitric acid. The crystals melt at 66—66·5°, and not at 36·7°, as previously recorded (Ordway, Amer. J. Sci., 1850, **9**, 30). On cooling, the fused salt passes through a pasty stage between 37° and 20°, but the crystals ultimately obtained are again the nonahydrate. The solution obtained by heating chromic acid with nitric acid in a bomb tube slowly deposits brown crystals of $Cr(NO_3)_3,7{\cdot}5H_2O$, which lose water over sodium hydroxide and appear to be converted into the hexahydrate. The viscosities of solutions of chromic nitrate nonahydrate have been determined for varying concentrations at 18° and at 25°; the values in each case lie on smooth curves. A. R. POWELL.

Complex cobaltic salts with nonovalent ions. F. M. JAEGER and P. KOETS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 59—83).—By the action of triaminotriethylamine·[=triam] on the compound $\{Co(en)_2ClH_2O\}Cl_2$ a red salt, $\{Co_3(en)_6(triam)_2\}Cl_9,6H_2O$, has been obtained. By the action of sodium iodide on this compound, the iodide is formed along with crystals of $Co(en)_3I_3,H_2O$. A sulphate has been prepared of composition $\{Co_3(en)_6(triam)_2\}_2(SO_4)_9,8H_2O$. Both cryoscopic and electrical conductivity determinations indicate the possibility of the dissociation of the sulphate into 11 ions, showing that the complex cobalt ion has a valency of 9. The sulphate mother-liquors gave compounds of the probable composition $\{Co(en)_3\}_2(SO_4)_3,2H_2O$, $\{Co(triam)_2\}(SO_4)_3,2H_2O$, and the sulphate of the nonovalent ion with $6H_2O$. Certain chlorosulphates have also been obtained, $\{Co_3(en)_6(triam)_2\}_2Cl_{12}(SO_4)_3,10H_2O$, $\{Co(en)_3\}_2Cl_4SO_4,5H_2O$, and $\{Co(triam)_2\}ClSO_4,xH_2O$. By double decomposition of the sulphate of the nonovalent ion with barium nitrate, chlorate, perchlorate, iodate, thiocyanate, and dithionate, the corresponding salts have been prepared. Detailed descriptions of the crystalline forms of most of these salts are given. No indications of the presence of isomeric salts were obtained in any case, and attempts to resolve the complex ion into optically active isomerides with the help of *d*-tartaric acid, *d*-bromocamphorsulphonic acid, or optically active malic acid were unsuccessful. This is explained by supposing that the complex ion has the configuration $[triam{:}(Co\,en_2)_3{:}triam]^{IX}$ and is a derivative of a *trans*-compound of the constitution $\{Co(en)_2ClH_2O\}X_2$ or $\{Co(en)_2Cl_2\}X$, although either the *cis*- or *trans*-salt may be used as the starting point. M. S. BURR.

General method of preparation of nitrites. C. DUVAL (Compt. rend., 1926, **182**, 1156—1158).—Nitrites are conveniently prepared by the action of sodium or potassium nitrites in the presence of ammonium acetate on the requisite acetates, using preferably ammonia, alcohol, or acetone as solvent. *Cobalt nitrite* is yellow and slightly soluble in water. *Nickel nitrite* forms first a double nitrite with ammon-

ium nitrite from which the simple nitrite is deposited. *Hexamminecobaltic nitrite* is yellowish-brown, very soluble in water, and hydrolyses to the hexamminecobaltinitrite with liberation of ammonia: $2[Co(NH_3)_6](NO_2)_3 \longrightarrow [Co(NO_2)_6][Co(NH_3)_6]+6NH_3$. *Aquopentammine-*, *nitropentammine-*, cis- and trans-*dinitrotetrammine-*, trans-*dichlorotetrammine-*, cis- and trans-*dibromo-* and *di-iodotetrammine-*, *chloronitrotetrammine-*, *diaquotetrammine-*, *chloroaquotetrammine-*, *sulphato-*, *carbonato-*, and *oxalato-pentammine-cobaltic nitrites* have also been isolated. F. G. SOPER.

Black nickel oxide. M. LE BLANC and H. SACHSE (Z. Elektrochem., 1926, **32**, 204—210; cf. this vol., 373).—The dark-coloured substance obtained by heating nickel carbonate at temperatures up to 550° in presence of oxygen consists of the oxide NiO, water, and active oxygen, and possibly contains a higher oxide of nickel. Attempts to prepare NiO_2 (Vaubel, A., 1922, ii, 875), and Ni_3O_4 (Baubigny, A., 1879, 299) have failed. Nickelous oxide readily takes up oxygen, forming a product identical with that obtained by heating the carbonate. The *X*-ray diagram of this substance contains only the lines corresponding with nickelous oxide. R. CUTHILL.

Compounds of metallic salts and carbon monoxide. XV. Metallic carbonyls. Carbonyl compound of univalent nickel. W. MANCHOT and H. GALL (Ber., 1926, **59**, [*B*], 1060—1063).—Solutions of red potassium nickelocyanide, $K_2Ni(CN)_3$ (cf. Bellucci, A., 1914, i, 260), rapidly absorb carbon monoxide at −9°, yielding, probably, the salt $K_2Ni(CN)_3,CO$. Nickel monocyanide (Bellucci, *loc. cit.*) and carbon monoxide afford an intermediate compound, $Ni(CN)(CO)_x$, which rapidly decomposes into nickelous cyanide and nickel carbonyl. H. WREN.

Ruthenium tetrachloride. S. AOYAMA (Z. anorg. Chem., 1926, **153**, 246—252; cf. A., 1925, ii, 816).—When a solution of hydroxytetrachlororuthenic acid in concentrated hydrochloric acid is saturated with chlorine for 5 hrs. at 100° and then allowed to evaporate spontaneously at the ordinary temperature, first over sulphuric acid, then over phosphorus pentoxide, a current of chlorine being passed through the solution during the whole time, very hygroscopic, reddish-brown, monoclinic crystals of *ruthenium tetrachloride*, $RuCl_4,5H_2O$, are deposited. The crystals melt at 25° and lose $2{\cdot}5H_2O$ at 57°, $4H_2O$ at 78°, and $4{\cdot}5H_2O$ at 100°. The concentrated solution is stable at the ordinary temperature, does not liberate iodine from potassium iodide, gives a black precipitate with silver nitrate, and yields crystalline double salts with potassium and ammonium chlorides. The dilute solution slowly hydrolyses with the formation of a black, colloidal solution, yields silver chloride on the addition of silver nitrate, liberates iodine from potassium iodide, and first a colloidal, brown solution, then a yellowish-brown precipitate of ruthenium trisulphide is obtained on saturation with hydrogen sulphide. A. R. POWELL.

Ternary salts of rhodium. O. E. SWJAGINZEV (Z. anorg. Chem., 1926, **153**, 143—148).—When silver nitrate is added to a fresh solution of "rhodium chloro-nitrate," actually $Rh_2Cl_6,6NH_4Cl,2NH_4NO_3$, the precipitate obtained is not silver chloride, but a complex silver *salt* in which for each atom of rhodium three ammonium groups are replaced by three atoms of silver. It is concluded that the salts contain no ionisable chlorine, but have the constitution $[RhCl_6]M_3,NH_4NO_3$. When the ammonium salt is heated, halts occur at about 290° and 420°, in concordance with the temperatures at which halts occur when ammonium nitrate and chloride, respectively, are heated; the loss in weight after the first halt agrees approximately with the loss of 1 mol. of ammonium nitrate. When the silver salt is heated, there is a halt at the lower temperature only. It is concluded that these complex salts contain three shells and may be formulated as $\{[RhCl_6]M_3,NO_3\}NH_4$, the $RhCl_6$ group behaving as an atom of a metal such as cobalt. A similar mercurous *salt* is formed, but is not stable; a lead salt was less stable, and mercuric nitrate gave no precipitate. A. GEAKE.

Compounds of metallic salts and carbon monoxide. XIII. Compound containing palladium and carbon monoxide. W. MANCHOT and J. KÖNIG (Ber., 1926, **59**, [*B*], 883—886; cf. this vol., 139).—The *compound* $PdCl_2,CO$ is obtained when carbon monoxide is passed into a well-shaken suspension of (pure) palladous chloride in anhydrous methyl or ethyl alcohol at 0° or, preferably, by passing carbon monoxide, charged with the vapour of methyl alcohol, over palladous chloride at the ordinary temperature. The compound readily yields palladium and carbon dioxide. Consideration of the properties of the compounds of the platinum metals with carbon monoxide indicates generally that the primary addition of oxidising agent and oxidisable substance does not necessarily occur in the ratio according to which the subsequent oxidation takes place. H. WREN.

Potassium and sodium pallado-oxalate. G. LANDESEN (Z. anorg. Chem., 1926, **154**, 429—435).—According to Vèzes (A., 1899, i, 672) potassium pallado-oxalate contains 3 mols. of water of crystallisation; the corresponding sodium salt contains 2 mols. Usually bivalent palladium has a co-ordination number four, but this may be higher in some circumstances, the higher compounds generally being less stable than the lower. The sodium salt may be formulated $Na_2[Pd(H_2O)_2(C_2O_4)_2]$, in which palladium has a co-ordination number six, but the potassium salt (if $+3H_2O$) admits of two possible formulæ: (1) the two oxalic acid radicals each have one co-ordination position, but the palladium consequently has a co-ordination number five, or (ii) one of the oxalic acid radicals has two places which gives palladium its saturation co-ordination number. However, a potassium salt ($+4H_2O$) was obtained which may be formulated $K_2[Pd(C_2O_4)_2(H_2O)_4]$. The sodium salt ($+2H_2O$) was, as expected, more stable than the potassium salt. Two modifications of the potassium salt were observed: yellow needles, obtained below 51°, and orange prisms. M. CARLTON.

Complex salts obtained by the action of α-picoline on alkali chloroiridites. M. GUILLOT. —See this vol., 737.

cis-trans-Isomerism in platinous salts. H. REIHLEN and K. T. NESTLE (Annalen, 1926, **447**, 211—233).—_cis-_ and _trans-_Dichlorodiammineplatinum do not react with liquid ammonia between −78° and −33°. Determinations in this solvent by an improved tensimetric method similar to that of Stock and Pohland (A., 1925, i, 489) show that the _cis-_ has a normal and the _trans-_ a double mol. wt. Previous determinations with platinous compounds (cf. Fritzmann, A., 1912, i, 71) have probably been vitiated by ionisation and isomeric change. _trans-_Dichlorodiammineplatinum probably has the formula $[Cl_2(NH_3)_2Pt\langle^{NH_3}_{NH_3}\rangle PtCl_2]$ with one tetrahedral and one octahedral platinum atom. This explains the existence of a third isomeride of this formula, and a similar one accounts for the isomerism of tetrammineplatinous salts and of the compound $K_2[Pt(NH_2SO_3)_2Cl_2]$. The bridge consists in each case of basic groups, consequently salts of the types $K_2[PtA_4]$ and $K_2[PtA_2B_2]$, containing acid groups only, do not exhibit isomerism. In many cases of platinous salts with doubly co-ordinated groups (Ramberg, A., 1910, i, 218; 1914, i, 385), the tetrahedral formula shows a strainless configuration for the molecule. H. E. F. NOTTON.

Transformation of mercury into gold. A. PIUTTI and E. BOGGIO-LERA (Giorn. Chim. Ind. Appl., 1926, **8**, 59—61).—No transformation of mercury into gold could be detected under the following conditions. (1) A discharge tube with mercury electrodes was cooled externally with water so that the vapour pressure of the metal was kept low and a high _P.D._ could be maintained between the electrodes. (2) An arc was passed in an atmosphere of hydrogen between two very fine mercury jets; currents of 2—6 amp. were used at 80—220 volts, the current densities at the surface of the electrodes being of the order 100 amp. per sq. mm. (3) An arc was passed between carbon electrodes in an atmosphere of hydrogen, a very fine jet of mercury being directed to the positive crater.

Commercial mercury, and presumably mercury ores also, always contain gold, and it seems possible, therefore, that spontaneous conversion of mercury into gold is continually proceeding in nature. If such is the case, a relation should exist between the geological age of mercury minerals and their gold content. T. H. POPE.

Alleged preparation of "artificial" gold from mercury. F. HABER, J. JAENICKE, and F. MATTHIAS (Z. anorg. Chem., 1926, **153**, 153—183).—Polemical against Miethe and Stammreich (Naturwiss., 1924, **12**, 597, 744) and Nagaoka (A., 1925, ii, 835, 1111). The experiments of the authors have been repeated, and it is shown that no transmutation of mercury into gold takes place even under a much more intensive electronic bombardment or after prolonged treatment with a high-tension current. Minute traces of gold were found in most of the materials used in the work, but the amount present remained constant throughout the experiments. The determination of gold in mercury was carried out by the method of Miethe and Stammreich (this vol., 119, 367, 493) except that the last minute droplet of mercury (obtained either by distillation or by solution of the bulk in nitric acid) was absorbed in a small piece of cadmium which was then taken up in a borax bead and carefully heated in a hydrogen flame until the cadmium and mercury had distilled off, leaving a spherical globule of gold the diameter of which was measured microscopically. A. R. POWELL.

Preparation of pure metals of the titanium group by thermal decomposition of their iodides. I. Zirconium. J. H. DE BOER and J. D. FAST (Z. anorg. Chem., 1926, **153**, 1—8; cf. A., 1925, ii, 1193).—Pure zirconium tetraiodide is prepared by weighing iodine and a slight excess of zirconium into two bulbs connected by a short capillary. After evacuating the apparatus, the iodine is sublimed on to the zirconium, and the tetraiodide thus formed is finally sublimed back into the bulb which originally contained the iodine. Zirconium tetraiodide is very hygroscopic and dissolves in water to a clear solution of zirconium oxyiodide and hydriodic acid. It is oxidised by dry oxygen at 100°, and at higher temperatures burns with the formation of zirconium dioxide and iodine. For the preparation of pure zirconium, the iodide is prepared as above in a vessel of pyrex glass containing two tungsten leads with a fine tungsten wire stretched between them. After the wire has been heated at 1800°, the whole apparatus is heated at 600°, when the iodide sublimes and decomposes on the wire, the temperature of which is maintained constant by increasing the current as its diameter increases to 4 mm. The tungsten then forms only 0·01% by volume of the rod of zirconium, which consists of a series of single crystals 0·5—1·5 cm. long. At lower temperatures, the process is slower and smaller crystals are obtained, whilst at higher temperatures the zirconium melts and attacks the tungsten with the formation of an eutectic. Pure zirconium retains its lustre in the air at the ordinary temperature; at higher temperatures, it is oxidised superficially, and only at very high temperatures does complete combustion take place. Very pure zirconium (m. p. 2200° Abs., _d_ 6·5) is comparable with copper in ductility, but very small amounts of impurities suffice to render it brittle as ordinarily obtained. A. GEAKE.

Preparation of oxygen-free nitrogen. H. KAUTSKY and H. THIELE (Z. anorg. Chem., 1926, **152**, 342—346).—Oxygen is removed by forcing the gas through a porous membrane immersed in a solution of sodium hyposulphite, intimate contact between all parts of the gas and the solution being thus ensured. The product contains less than 0·0007% of oxygen. R. CUTHILL.

Antimony sulphides. L. M. CURRIE.—See B., 1926, 449.

Oxidations with fluorine. II. Preparation of ammonium persulphate. III. Action of fluorine on dry hydrogen sulphates and sulphates. F. FICHTER and K. HUMPERT (Helv. Chim. Acta, 1926, **9**, 467—469, 521—525; cf. A., 1923, ii, 562).—II. When fluorine, prepared by use of Simons' modification of the Argo generator (A., 1924, ii, 847) is passed into a cold, saturated, aqueous solu-

tion of ammonium hydrogen sulphate, slow separation of ammonium persulphate crystals takes place. Ozonised oxygen is given off during the oxidation. The solution gives, besides the ordinary persulphate reactions, a violet coloration with a very dilute solution of manganous sulphate in the cold. When ammonium persulphate is boiled with sodium hydroxide solution, the liberation of ammonia is incomplete owing to partial oxidation of the latter by the persulphate ion. Determination of the ammonia must therefore be carried out in the presence of a reducing agent. The use of Devarda's alloy is recommended.

III. The product obtained by reaction of gaseous fluorine with dry potassium hydrogen sulphate gives, in addition to the ordinary reactions for persulphates, a weak violet coloration with dilute manganous sulphate solution. The persulphate content, determined by the amount of "active" oxygen, varies from 20 to 80%, the higher yields being obtained when smaller amounts of potassium hydrogen sulphate are used. The reaction product also contains potassium fluorosulphonate (A., 1919, ii, 364), since "nitron" acetate gives a precipitate of "nitron" fluorosulphonate after decomposition of the persulphate with Devarda's alloy. Pure fluorine does not react with dry potassium sulphate, but in the presence of hydrofluoric acid a similar reaction to that described above takes place. The reaction probably proceeds thus: $3K_2SO_4+F_2+2HF \rightarrow K_2S_2O_8+3KF+KFSO_3+H_2O$. Ammonium sulphate behaves similarly, the fluorosulphonate being formed with greater ease.

M. Clark.

Ammonium selenide. E. Wendehorst (Z. anorg., 1926, **153**, 263—268).—Ammonia and hydrogen selenide interact at the ordinary temperature to form a white, crystalline mass of ammonium selenide (cf. Bineau, Ann. Chim. Phys., 1838, **67**, 230). Similar crystals are obtained by passing hydrogen selenide into concentrated aqueous ammonia cooled in ice if the air in the apparatus is first displaced with nitrogen. Ammonium selenide is rapidly oxidised in the air with the separation of selenium, otherwise its chemical properties are analogous to those of ammonium sulphide. If the ammonia solution is not cooled during the preparation, crystals of $(NH_4)_2Se,2NH_3$ are deposited, and it appears to be possible, under certain conditions, to obtain solid compounds containing even more ammonia.

A. R. Powell.

Bleaching powder. S. Ochi.—See B., 1926, 438.

High-test bleaching powder—calcium hypochlorite and basic calcium hypochlorite. S. Urano.—See B., 1926, 485.

Apparatus for analysis of small amounts of vapour in permanent gases. I. R. McHaffie (J. Amer. Chem. Soc., 1926, **48**, 1143—1145).—A simple apparatus for determining accurately small amounts of water vapour in air or other gases is described.

S. K. Tweedy.

Gas analysis apparatus. E. Ott.—See B., 1926, 474.

Use of paper pulp in vacuum filtration. J. Mathevet (Ann. Chim. Analyt., 1926, [ii], **8**, 162—164).—A suspension in water of trimmings of ashless Durieux filter-papers or Durieux pulp No. 111 is made by violently stirring and boiling the finely-divided material with a large excess of water. The filtering medium is then prepared in the same way as asbestos, and one filtration is usually absolutely retentive of the precipitate. The shorter the fibres used the longer is the time of filtration. This filtration medium may conveniently be used for the separation of ammonium phosphomolybdate, for silica from steels, for barium sulphate, for lead sulphate, for tin oxide, etc.

D. G. Hewer.

Apparatus for wet ashing. W. A. Turner (Ind. Eng. Chem., 1926, **18**, 630).—The ashings are conducted in Kjeldahl flasks which are placed on a burner rack with their necks fitting into openings in a long, acid-resisting "duriron" tube, with small openings above each for the introduction of nitric acid from dropping funnels supported on heavy glass rods above the "duriron" tube. D. G. Hewer.

Visual conductometric titrations. G. Jander and O. Pfundt (Z. anorg. Chem., 1926, **153**, 219—234).—An apparatus for carrying out conductometric titrations is described in which the usual telephone as zero instrument is replaced by a crystal detector or thermo-junction coupled to a mirror galvanometer and connected to the movable bridge contact through a small transformer. The current in the primary circuit passes through a hammer interrupter with tungsten contacts having a condenser in parallel with them to prevent sparking, through a variable resistance, then through a small transformer to the ends of the bridge wire. The sliding bridge contact is adjusted, before beginning a titration, in the usual way with the telephone, and during the titration this contact is not moved, but the deflexion of the galvanometer mirror is measured after each addition of standard solution. By plotting the c.c. of solution added against the square root of the corresponding galvanometer deflexion, two straight lines are obtained the intersection of which indicates the end-point of the titration. Several examples of the use of the apparatus are given.

A. R. Powell.

New method of conductometric analysis. P. Hirsch (Z. anal. Chem., 1926, **68**, 160—174).—If a solution of a weak acid is added to a large excess of a solution of a strong base, the fall in the specific conductivity of the solution is proportional to the concentration of the weak acid provided that the degree of dissociation of the strong base and of the salt formed remains constant. This may be assured by keeping the volume of the mixture constant by adding the requisite amount of water. By using varying amounts of the weak acid and a definite volume of the strong base, a curve showing the relation between the specific conductivity of the solution and the amount of weak acid added is prepared, and from a determination of the specific conductivity of a similar alkaline solution to which a definite volume of the unknown weak acid solution has been added the content of the latter solution may be found by reference to the curve. The converse of this method is applicable to the deter-

mination of the strength of a solution of a weak base. The results are influenced by the presence of strong electrolytes; in this case, the specific conductivities of the solutions obtained by adding the unknown solution to the standard acid or alkali and to an equivalent solution of the strong electrolyte present in the unknown solution are determined. Knowing the conductivity of the pure solution of electrolyte, an appropriate correction can then be made in the analysis. A. R. POWELL.

Analytical quartz lamp. Luminescence analysis. R. ROBL (Z. angew. Chem., 1926, **39**, 608—611).—Most inorganic substances exhibit no fluorescence or phosphorescence when examined in the ultra-violet light from a quartz-mercury lamp, from which, by the use of a special glass, only light of wave-lengths 440—280$\mu\mu$ is obtained. Fluorescence is shown by lead chloride, bromide, and sulphate, cuprous iodide, mercurous chloride, and bromide, calcium, strontium, and barium pyrovanadates, thallium carbonate, zinc oxide, and barium sulphide. The fluorescence spectra were determined approximately. Phosphorescence is an indication of impurity, and examination for phosphorescence is frequently of value for this reason. A. GEAKE.

Electrometric measurement of the hydrogen-ion concentration with the aid of the quinhydrone electrode and a new apparatus therefor. A. HOCK (Z. angew. Chem., 1926, **39**, 647—651).—The theory and construction of the quinhydrone electrode are discussed at length (cf. Veibel, J.C.S., 1923, **125**, 2203), together with its advantages over the older platinum–hydrogen electrode for the determination of the p_H values of solution. A compact and portable apparatus for carrying out p_H determinations with the aid of the quinhydrone electrode is described with reference to illustrations and wiring diagrams for details of which the original must be consulted. A. R. POWELL.

Methyl-orange error in the colorimetric determination of p_H by comparison with the Clark [hydrogen phthalate] buffer mixtures. I. M. KOLTHOFF (Rec. trav. chim., 1926, **45**, 433—435).—Actual measurements with the quinhydrone electrode show that the use of methyl-orange or dimethyl-yellow as indicator with the Clark hydrogen phthalate series of comparison solutions in the colorimetric determination of p_H, leads to values which are about 0·2 unit too high. Using bromophenol-blue or methyl-red as indicator, the electrometrically and colorimetrically determined values are in good agreement. The Sörensen series of citrate solutions are recommended for use with methyl-orange. J. S. CARTER.

Detection and determination of free chlorine in drinking water. I. M. KOLTHOFF.—See B., 1926, 517.

[Determination of perchloric acid.] F. ARNDT and P. NACHTWEY (Ber., 1926, **59**, [*B*], 1072; cf. this vol., 489).—The author's method has been used previously by Weinland (A., 1922, ii, 767) and by Hofmann (*ibid.*, 1910, **i**, 370). H. WREN.

Potentiometric titration of bromide and chloride. E. LANGE and E. SCHWARTZ (Z. Elektrochem., 1926, **32**, 240—248).—The potentiometric method of titration of chlorides and bromides has been improved so that the variation does not exceed $\pm 0{\cdot}03\%$, as against $\pm 0{\cdot}07\%$ for the nephelometric method. This has been effected by: (i) improvements in the connecting syphon and in the form of the silver electrode; (ii) exclusion of light, especially from the bromide solution; (iii) reduction of adsorption, especially in the case of the bromide, by heating the solution at about 90°, when the titration is almost complete. M. S. BURR.

Preparation of starch solution for use in iodometric titrations. C. L. ALSBERG, E. P. GRIFFING, and J. FIELD (jun.) (J. Amer. Chem. Soc., 1926, **48**, 1299—1300).—Starch (preferably wheat starch) which has been ground in a pebble mill forms colloidal solutions in cold water from which clear starch solutions may be obtained by centrifuging. Such clear solutions may be kept under toluene for months. S. K. TWEEDY.

Determination of the fluorine ion. II. W. D. TREADWELL and A. KÖHL (Helv. Chim. Acta, 1926, **9**, 470—485).—Gravimetric determination of fluoride by precipitation with calcium, strontium, or barium chlorides is inadmissible, since (*a*) the salts, particularly calcium fluoride, tend to form colloidal solutions; for calcium fluoride the ratio of solubilities of hydrosol and hydrogel is 2·2. (*b*) The salting-out effect is rapidly compensated by decrease in ionic activity due to diminishing dissociation; optimum precipitation takes place in presence of an excess of alkaline-earth ion of 0·027 mol./litre.

The electrometric titration method (A., 1925, ii, 1107) is modified for use of aluminium chloride, instead of ferric chloride, as titrating agent. Aluminium chloride quantitatively decomposes the complex Na_3FcF_6, giving Na_3AlF_6 and $Fe^{\cdots}$. Hence, on addition to the fluoride solution to be titrated of a little very dilute ferric chloride solution with some ferrous salt, a satisfactory end-point on the electrometric potential curve is obtained when sufficient aluminium chloride has been run in. Silicic acid gel does not interfere with the titration, but a well-defined end-point is not obtained in the presence of fluosilicate ions. Hydrofluosilicic acid should therefore be removed as far as possible by addition of potassium chloride. M. CLARK.

Colloid adsorption in quantitative analysis, especially in the micro-determination of sulphur in organic substances by Pregl's method. E. EIGENBERGER (Z. anal. Chem., 1926, **68**, 220—231).—When small amounts of sulphuric acid are precipitated by the slow addition of barium chloride solution to a feebly acid solution, a fine, crystalline precipitate of barium sulphate is produced which cannot be filtered readily. Addition of 2 c.c. of a very dilute colloidal solution of celluloid and gentle warming to 30—40° causes rapid flocculation of the barium sulphate due to adsorption of the precipitated celluloid gel. After cooling, the precipitate is collected on a crucible with a porous bottom, washed with 50% alcohol, ignited for 10 min. at a dull red heat, cooled,

and weighed. The adsorption of barium chloride by the precipitate rarely exceeds 0·5%, which is negligible with the small amounts used in micro-analysis. The celluloid solution is made by dissolving 5 g. of the purest celluloid in 250 c.c. of acetone under a reflux condenser, adding 250 c.c. of alcohol, and distilling off 250 c.c. of the solvent (up to 67°); a further 250 c.c. of alcohol is added to the remaining liquid, which is filtered and stored. For use in the determination of sulphur, 10 c.c. of this solution are diluted with 10 c.c. of alcohol and treated with 2 c.c. of ethyl acetate and then with water, drop by drop, until an opalescent liquid is obtained. This is miscible with water in all proportions without flocculation and 2 c.c. are sufficient for each analysis. A. R. POWELL.

Is Kjeldahl's method for the determination of nitrogen in organic substances generally applicable? K. KÜRSCHNER (Z. anal. Chem., 1926, **68**, 209—216).—The original Kjeldahl method is known to give low results for nitrogen in some organic compounds such as phenylhydrazine, alkaloids, and derivatives having a pyrazolone ring, but good results may be obtained with the following modified procedure. The substance is mixed with 5 c.c. of water, 8 g. of an intimate mixture of 1 part of cupric oxide with 7 parts of steel filings, and 20 c.c. of 1 : 1 sulphuric acid. The flask is well shaken and set aside for 1 hr., during which a slow stream of hydrogen is evolved from the copper–iron couple. After addition of 30 c.c. of concentrated sulphuric acid, the flask is heated gently for 15 min., then strongly for 2—3 hrs., and the determination finished as usual (cf. Kürschner and Scharrer, B., 1926, 155, and this vol., 490). A. R. POWELL.

Determination of phosphorus in steels containing tungsten. T. E. ROONEY and L. M. CLARK.—See B., 1926, 493.

Use of liquid amalgams in volumetric analysis. V. Determination of phosphoric acid by uranyl acetate. K. SOMEYA (Z. anorg. Chem., 1926, **152**, 382—385; cf. this vol. 705)—Uranylammonium phosphate in hydrochloric acid solution is reduced with zinc amalgam or bismuth amalgam and titrated with potassium dichromate, using diphenylamine as indicator. CR. CUTHILL.

Volumetric determination of hypophosphorous acid and hypophosphites. D. KÖSZEGI (Z. anal. Chem., 1926, **68**, 216—220).—In neutral solution, permanganate is reduced by hypophosphites to manganese dioxide, which is precipitated in a colloidal form unless a calcium salt is present, when the calcium phosphate formed in the reaction flocculates the manganese dioxide. The analysis is conducted as follows: The hypophosphite solution is neutralised with sodium carbonate, 20—25 c.c. of saturated calcium sulphate solution, and 40 c.c. of 0·1*N*-permanganate are added, and the mixture is boiled for 5 min., cooled, and diluted to 100 c.c. in a graduated flask. 50 C.c. are filtered off, treated with 1·5 g. of potassium iodide, and acidified with hydrochloric acid. The liberated iodine is then titrated with thiosulphate. A. R. POWELL.

Separation of arsenic from selenium and its gravimetric determination. R. FRIDLI (Pharm. Zentr., 1926, **67**, 369—371).—The solution containing arsenic and selenium compounds is mixed with hot Bettendorff's solution and boiled for 10 min. After 1 day, the liquid is diluted and the precipitated arsenic and selenium are collected and treated with bromine water. From the resultant solution the arsenic is precipitated by means of magnesia mixture as ammonium magnesium arsenate hexahydrate. To free the latter from stannic hydroxide, it is dissolved in hydrochloric acid and the above treatment with Bettendorff's reagent etc. repeated, the ammonium magnesium arsenate hexahydrate finally obtained being weighed. B. FULLMAN.

Iodometric determination of arsenic acid. L. ROSENTHALER (Z. anal. Chem., 1926, **68**, 232).—Contrary to the statement of Ormont (this vol., 375), the reaction between arsenic acid and potassium iodide proceeds to completion in acid solution as the iodine is removed during the titration. Ormont's method has no advantage over that previously described by the author (A., 1922, ii, 584) or over that of Fleury (A., 1920, ii, 448). A. R. POWELL.

Determination of carbon monoxide. S. H. KATZ.—See B., 1926, 430.

Determination of carbon in pig-iron, steel, and ferro-alloys. E. SCHIFFER.—See B., 1926, 492.

Application of the Gaspar reagent to the recognition and separation of the alkali metals. F. DIAZ DE RADA and T. GASPAR Y ARNAL (Anal. Fís. Quím., 1926, **24**, 150—152; cf. Gaspar y Arnal, this vol., 591).—The reagent sodium ferrocyanide and calcium chloride may be applied to the separation and recognition of the alkali metals. Rubidium and cæsium give a precipitate in aqueous solution, potassium and ammonium give a precipitate in 50% ethyl alcoholic solution, whilst sodium and lithium are not precipitated. G. W. ROBINSON.

Volumetric determination of potassium as hydrogen tartrate. R. MEURICE (Ann. Chim. Anal., 1926, [ii], **8**, 129—130).—Excess of sodium hydrogen tartrate is added to the potassium solution (containing about 1 g. of potassium chloride) until the acidity is 0·045—0·05*N*. An equal volume of 97% methyl alcohol is then added and the flask kept for 1 hr. at 12°, and then at 20°. The precipitate is washed with 50% aqueous methyl alcohol, dissolved in an excess of standard sodium hydroxide, and the excess titrated. The error is less than 1% of the potassium determined. D. G. HEWER.

Determination of rubidium by means of silicotungstic acid; detection of rubidium in the ashes of *Laminaria flexicaulis*. P. FREUNDLER and (MLLE.) Y. MÉNAGER (Compt. rend., 1926, **182**, 1158—1160; cf. Bulletin de l'Office des Pêches, 1925, **41**, 47).—Rubidium can be precipitated quantitatively as silicotungstate, $Rb_8SiW_{12}O_{42}$, when in 0·4% solution, by the addition of twice the theoretical quantity of silicotungstic acid, but in the presence of more than 1% of potassium chloride, the potassium salt is also precipitated. The mixed precipitate, after

evaporation on the water-bath, is treated with cold 1·25% sodium chloride solution, which dissolves the potassium salt and leaves with the rubidium salt, silica, silicotungstic acid, and its anhydride. This residue is dissolved in ammonia, mercuric nitrate added to remove the free acid, and the rubidium converted to chloride. In this way, 1 part of rubidium chloride in 100 parts of sodium and potassium chlorides can be detected and 1 part in 40 parts can be determined. The amount of rubidium in *Laminaria flexicaulis* is too small to be isolated, but its presence may be shown spectroscopically. *Lithium silicotungstate*, $Li_4H_4SiW_{12}O_{42},25H_2O$, has been isolated.

F. G. SOPER.

Supersaturated solutions. II. Magnesium oxalate and the oxalate separation of calcium and magnesium. W. M. FISCHER [with A. STEIKMAN and A. DOMBROWSKI] (Z. anorg. Chem., 1926, **153**, 62—76; cf. A., 1925, ii, 853).—The analytical separation of calcium and magnesium as oxalates depends on the stability of supersaturated solutions of the magnesium salt. Solutions of magnesium oxalate prepared by mixing magnesium chloride and ammonium oxalate are stable for an indefinite period if the supersaturation is not more than four-fold. Such solutions are not precipitated by the addition of neutral salts or by mechanical means, but are unstable when boiled. When the supersaturation is ten-fold, precipitation begins after 40 hrs., and more rapidly with increasing supersaturation. Precipitation from such solutions may be accelerated mechanically or by the addition of salts, but is retarded by alizarin-Bordeaux, diamond-fuchsin, and agar-agar. Calcium oxalate also precipitates slowly, and it is therefore desirable to heat at 70—90° and not to filter until several hrs. after the addition of the ammonium oxalate. For the exact separation of calcium and magnesium, the supersaturation of the magnesium must not exceed four-fold and the solution must not be boiled. The concentration of magnesium chloride should not exceed 0·1 g. of magnesium per 100 c.c. or the solubility of calcium oxalate becomes significant. It is recommended to use 200 c.c. of solution, and the weights of calcium, magnesium, and ammonium oxalate monohydrate must not exceed 0·085 g., 0·150 g., and 0·3324 g., respectively. Under these conditions, the separation is quantitative.

A. GEAKE.

Spectrographic detection and determination of strontium using a hydrogen flame. J. MEUNIER (Compt. rend., 1926, **182**, 1160—1162; cf. A., 1919, ii, 132; 1921, ii, 351).—Mixtures of strontium acetate with ferric oxide have been examined spectroscopically and the intensity of the strontium line 4600 Å. has been compared with the intensities of the iron lines. For mixtures in which the ratio strontium : iron is 0·04, 0·06, 0·1, 0·2, 0·3, 0·4, 1, 2, 3, and 5%, the strontium line equals in intensity the lines 4494, 4416, 4063, 4271, 4462, 4383, 3720, 3886, >3886<3860, and 3860 Å. of the iron spectrum, respectively. When present as phosphate, no indication as to its presence is obtained, as this salt is not dissociated in the hydrogen flame. This fact allows of the detection of strontium phosphate by further examination after treatment with sulphuric acid. Strontium is very widely distributed.

F. G. SOPER.

Detection of cadmium in the presence of copper. R. MEURICE (Ann. Chim. Anal., 1926, [ii], **8**, 130—131).—One c.c. of 1% brucine sulphate solution with potassium bromide and a trace of a cadmium salt result in the formation of a copious white precipitate of the double bromide of cadmium and brucine, whilst with copper salts no precipitate occurs. Chlorides (giving no precipitates) may thus be distinguished from bromides. None of the metals of the iron group forms precipitates with brucine and an alkali bromide. D. G. HEWER.

Sensitive reagent for thallium. T. GASPAR Y ARNAL (Anal. Fis. Quím., 1926, **24**, 153—155; cf. this vol. 702).—An aqueous solution of sodium ferrocyanide and calcium acetate yields a white precipitate with thallium nitrate. The precipitate probably corresponds with the formula $CaTl_2Fe(CN)_6$. Conversely, ferrocyanides yield precipitates with calcium acetate and thallium nitrate. By means of this reaction, 0·000025 g. of thallium per c.c. may be detected. G. W. ROBINSON.

Volumetric determination of thallium. E. ZINTL and G. RIENÄCKER (Z. anorg. Chem., 1926, **153**, 276—280).—Thallous chloride is quantitatively converted into thallic chloride by titration of its solution in 5% hydrochloric acid at 50° with potassium bromate. The end-point may be ascertained by the use of methyl-orange as indicator or potentiometrically; in the latter case, a very sharp potential change towards the normal calomel electrode takes place. Thallic salts may be titrated potentiometrically with titanous chloride in the presence of ammonium acetate; if the solution contains thallous salt, 10 g. of ammonium acetate, 1 g. of ammonium fluoride, and 10 g. of potassium chloride are added, followed by sufficient 0·1*N*-titanous chloride solution to precipitate metallic thallium. The metal is dissolved by the addition of bromine water and the solution is heated at 80° and titrated potentiometrically with titanous chloride, which first destroys the excess of bromine, giving a sharp potential change; titration is continued to the next sharp change of potential, which indicates complete reduction of thallic to thallous salt.

A. R. POWELL.

Detection and determination of mercury by means of aluminium. P. DENIS (Ann. méd. légale, 1921, **1**, 348—349).—Aluminium filings (0·01 mg.) in a cold aqueous solution of a mercury salt evolve hydrogen, which adheres to the metal and carries it to the surface, where the gas is liberated. The test is extremely delicate. The mercury content may be calculated from a determination of the acid radical in the solution. CHEMICAL ABSTRACTS.

Determination of small quantities of mercury. A. STOCK and R. HELLER (Z. angew. Chem., 1926, **39**, 466—468).—Minute quantities of metallic mercury may be determined with great accuracy by dissolving the metal in chlorine water, expelling the excess of chlorine by means of a current of carbon dioxide, adding 0·1 g. of ammonium oxalate and 1 c.c. of a

saturated solution of oxalic acid diluted to 8 c.c., and depositing the mercury on a gold wire (0·1 g.) by electrolysis at 4 volts for 24 hrs., using a platinum wire anode. The gold wire is washed with water, dried over phosphorus pentoxide, and weighed. For the detection and determination of mercury vapour in air, about 100 litres are passed through U-tubes cooled in liquid air, whereby all the mercury is condensed together with water vapour and carbon dioxide. The latter is allowed to evaporate at the ordinary temperature and the mercury is dissolved in chlorine water. Traces of mercury in urine (700—1200 c.c.) and saliva (150—400 c.c.) are determined by treating the liquid with chlorine for 30 min. at 20°, then for 60 min. at 70—80°. Excess of chlorine is expelled with carbon dioxide, the solution filtered, a small amount of copper sulphate and hydrochloric acid to give 5% of free acid are added, and the metals precipitated with hydrogen sulphide. The precipitate is centrifuged, dispersed in 5 c.c. of water, and treated with chlorine. The solution is filtered and treated with hydrogen sulphide. This precipitate is dissolved as before and the solution is treated with sufficient ammonium oxalate to dissolve the copper oxalate first precipitated. A piece of copper wire 4 cm. long is allowed to remain in the liquid for 2 days, when all the mercury will have been deposited on it providing less than 0·2 mg. is present. The wire is dried over phosphorus pentoxide and heated to redness in a long, narrow tube to obtain a sublimate of metallic mercury, which is visible under the microscope if more than 0·001 mg. of metal is present. As a confirmatory test, the tube containing the sublimate is placed in a test-tube containing a small crystal of iodine; after several hrs., the sublimate will be completely converted into red mercuric iodide. This test will detect as little as 0·0002 mg. of mercury (using a microscope) or 0·001 mg. (by the unassisted eye). For a quantitative test, the mercury sublimate is dissolved in chlorine water and the analysis conducted as described above. A. R. Powell.

Accurate method for the determination of mercury in solutions. B. S. Evans and S. G. Clarke (Analyst, 1926, **51**, 224—229).—The filter tube is packed to 1 in. with copper filings that have passed a 60-mesh sieve, and have been washed with dilute nitric acid and water. The mercury solution should be acidified with either sulphuric or nitric acids (hydrochloric acid if present in any considerable quantity must be eliminated), neutralised with ammonia, and treated with about 2 c.c. of nitric acid per 100 c.c. of liquid. It is introduced into the apparatus by means of the tap funnel, which is then closed and the return tap opened, and percolation allowed to continue for 1·5—2 hrs., when the pump is detached from the top exit tube and attached to the lower one and the solution collected in the flask. The filter is washed twice with water and the tube detached, placed in a hole in the stopper of the filter flask, and the water removed by acetone, after which the filter with the copper carrying the mercury is transferred to a porcelain crucible, very slightly warmed to remove the acetone, and the mercury sublimed by fitting the crucible into a hole in an asbestos board and placing over it a platinum dish containing water which is renewed by siphon as it gets warm. Heating at a dull red heat for 20 min. should be sufficient to sublime 0·1 g. of mercury. D. G. Hewer.

Precipitation of aluminium as hydroxide by means of ammonia. G. Jander and O. Ruperti (Z. anorg. Chem., 1926, **153**, 253—259).—The solubility of aluminium hydroxide in water and in ammonia solutions has been determined by boiling amalgamated aluminium with the solution until a permanent precipitate of hydroxide formed, filtering the liquid through a membrane filter, and evaporating the filtrate to dryness. The figures so found for the solubility of the hydroxide, expressed as mg. of alumina per litre, are as follows: cold water, 0·6; hot water, 1·2; 3·73% ammonia solution, 865; 4·64% ammonia solution, 1174. A solution of 15 g. of ammonium chloride in 1 litre of water dissolves 5 mg. of alumina at 20° and 8 mg. at 100°. In analytical practice it is desirable, therefore, to keep the ammonium chloride used to a minimum and to add only sufficient ammonia to render the solution just alkaline to litmus. Further, prolonged boiling should be avoided, filtration should be made on a membrane filter, and the liquid kept over-night before filtering. A. R. Powell.

Bismuthate method for manganese. B. Park (Ind. Eng. Chem., 1926, **18**, 597—598).—Sulphuric acid may advantageously be substituted for nitric acid as the oxidising medium in the determination of manganese by the bismuthate method. The solution should be cooled below 50°, and oxidation is practically constant for concentrations of manganese between 0·1 and 0·2 mg. per c.c., but is incomplete for concentrations above 0·2 mg. per c.c. D. G. Hewer.

Oxidation of manganese to permanganic acid and its consequences when applied to the determination of manganese. A. Travers (Compt. rend., 1926, **182**, 1088—1090).—Oxidation of manganese to permanganic acid is hindered by secondary reactions. When the concentration of manganese is less than 0·1 g. per litre, manganous salts reduce permanganic acid to manganese dioxide if the solution contains less than 10% of nitric or sulphuric acid. In presence of hydrofluoric acid, the reduction yields Mn_2O_5 in the cold; metaphosphoric acid gives a similar result, but at 100°. For greater concentrations of manganese, a sulphuric or nitric acid solution yields manganese dioxide, but hydrofluoric or metaphosphoric acid induces simultaneous formation of a manganic salt which is stable in presence of excess of acid and manganese dioxide. Complete oxidation of manganese in solutions containing more than 2·5 g. per litre may be effected by boiling with 3% of sulphuric acid and 2% of metaphosphoric acid, the oxidising agent being solid ammonium persulphate with 5 c.c. of 0·1*N*-silver nitrate per 125 mg. of manganese added as catalyst. The reaction varies in its course according to the concentration of manganese in the solution, but may be successfully used in determinations of manganese in minerals and in ferromanganese. H. J. Evans.

Standardisation of thiosulphate solutions with potassium permanganate. K. SCHRÖDER (Z. anal. Chem., 1926, **68**, 233—234).—Polemical against Popov and Whitman (A., 1925, ii, 1093), pointing out that the author in his previous communication (Z. anal. Chem., 1924, **64**, 393) specifies a well-cooled solution for standardising thiosulphate with permanganate, and not a temperature of 50°, as stated by the above authors. A. R. POWELL.

Volumetric determination of chromium and manganese with permanganate in acetic acid solution. II. Manganese. B. REINITZER and P. CONRATH (Z. anal. Chem., 1926, **68**, 129—155; cf. this vol., 492).—Manganese salts may be titrated with permanganate in a similar way to the Volhard method if a large excess of sodium acetate is added to the solution instead of zinc oxide. In this case, however, the whole of the manganese is quantitatively converted into the hydrated dioxide according to the equation $3MnO+Mn_2O_7=5MnO_2$. Addition of potassium fluoride to the solution before titration assists in the flocculation and settling of the precipitate and also prevents the interference of iron owing to the formation of a sandy white precipitate of potassium ferrifluoride which settles readily, but the amount of iron present should not exceed 100 times the weight of manganese. A. R. POWELL.

Organic derivatives of phosphoric acid. III. Determination of iron. I. F. ZETZSCHE and M. NACHMANN (Helv. Chim. Acta, 1926, **9**, 420—428).—Iron is quantitatively precipitated from 2*N*-acid solution, in the presence of 2% of ammonium salt, by slow addition of slight excess of the sodium or ammonium salt of bis-*p*-chlorophenylphosphoric acid in 0·1*N*-solution. After heating on the water-bath with further addition of the reagent, the mixture is cooled and filtered. The precipitate is washed with *N*-hydrochloric acid and water and is then decomposed with warm ammonium hydroxide and chloride solution, yielding ferric hydroxide, which is weighed as oxide. The following acids are described: bis-*p*-chlorophenylphosphoric acid, m. p. 133—135° (*sodium* and *ferric* salts); *bis-o-chlorophenylphosphoric acid*, m. p. 105—106° (*ferric* and *ammonium* salts) from phosphorus oxychloride and *o*-chlorophenol; p-*bromophenylphosphoric acid*, m. p. 161° (*ferric* salt), from bromine and phenylphosphoric acid in chloroform solution; decomp. by hydrochloric acid, giving *p*-bromophenol; *bis*-p-*bromophenylphosphoric acid*, m. p. 199—201° (*ferric* salt), from bromine and diphenylphosphoric acid in chloroform solution.

M. CLARK.

Use of liquid amalgams in volumetric analysis. VI. Determination of chromic acid, ferric iron, and ferricyanide by means of titanous sulphate. K. SOMEYA (Z. anorg. Chem., 1926, **152**, 386—390; cf. this vol., 702).—The chromic acid or ferricyanide is titrated with titanous sulphate, prepared by reduction of titanic sulphate with zinc amalgam, using diphenylamine as indicator. Chromic acid and ferric iron in a mixture of the two are determined by titrating with titanous sulphate, using diphenylamine as indicator, until all the chromic acid is reduced, then adding potassium thiocyanate as indicator, and titrating further until the iron is reduced. Using diphenylamine as indicator, ferricyanide can be titrated with stannous chloride. R. CUTHILL.

Use of liquid amalgams in volumetric analysis. IV. Reducing action of bismuth amalgam, reduction of uranium, and application of dichromate titration. K. SOMEYA (Z. anorg. Chem., 1926, **152**, 368—381; cf. A., 1925, ii, 1201).—Ferric acetate in hydrochloric acid solution, or titanic chloride or sulphate, can be reduced with bismuth amalgam and then titrated with potassium dichromate, the indicator being diphenylamine. Chlorates and chromic acid can be determined by treatment with excess of titanous chloride and titration of the excess. The reduction by bismuth amalgam of molybdenum in hydrochloric acid solution, or of vanadium in sulphuric acid solution, can be accurately controlled by regulating the acidity, and therefore bismuth amalgam can be used instead of lead amalgam in the method previously described for the determination of phosphoric acid (*loc. cit.*). In hydrochloric or sulphuric acid solution, uranyl salts are readily reduced to the quadrivalent state by bismuth amalgam, and can be titrated with dichromate as described above. Zinc amalgam reduces uranyl salts to the tervalent state, titanic chloride to titanous chloride.

R. CUTHILL.

Detection of tin in minerals, using the blowpipe. A. BRALY (Bull. Soc. franç. Min., 1925, **48**, 94—98; from Chem. Zentr., 1926, I, 988).—Sulphur, arsenic, and antimony are first driven off and the residue is mixed with 3 parts of sodium carbonate and 1 part of borax and heated in the reducing flame on carbon. In presence of sufficient lead, a dull, warty bead of metal is obtained. In the absence of lead, the bead is lustrous when the content of tin is small, but dull when much tin is present. In such cases, lead is added and the resulting warty bead scorified in the oxidising flame, when, according to the tin content, a fine crust or a film of stannic oxide results, which is examined in the usual manner.

J. S. CARTER.

Separation of zirconium from titanium. K. SCHRÖDER (Z. anal. Chem., 1926, **68**, 233).—A correction of an error in the paper of Moser and Lessnig (A., 1925, ii, 718); zirconium cannot be separated from titanium by cupferron.

A. R. POWELL.

Determination of vanadium in presence of iron. K. SOMEYA (Z. anorg. Chem., 1926, **152**, 391—392).—The titration of vanadium with ferrous sulphate in hot solution, using diphenylamine as indicator as previously described (A., 1925, ii, 161), is impracticable, owing to decomposition of the indicator under the experimental conditions. R. CUTHILL.

Small mercury-vapour lamp for laboratory use. W. CLARK.—See B., 1926, 445.

Laboratory mercury lamp. E. O. HULBURT (J. Opt. Soc. Amer., 1926, **12**, 519—520).—A simple mercury lamp, made of pyrex glass or quartz, is described. It is so designed that the seals for the electrodes and for the stopcock through which the lamp is exhausted can be made of wax. It will run

normally for 20 hrs. or more before it requires re-exhausting. A. B. MANNING.

Barium sulphate as a protective material against Röntgen radiation. F. L. HUNT (Amer. J. Roentgenology, 1925, **14**, 524—528).—"Protective coefficients" are obtained by comparison of barium sulphate plasters with lead.
CHEMICAL ABSTRACTS.

New multiple X-ray spectrograph combining the powder diffraction and monochromatic pinhole methods. G. L. CLARK, E. W. BRUGMANN, and R. H. ABORN (J. Opt. Soc. Amer., 1926, **12**, 379—385).—A description is given of an apparatus designed primarily for examining technical materials, in which eighteen exposures can be made simultaneously through apertures arranged radially around a water-cooled self-rectifying molybdenum Coolidge tube of which the axis is vertical. Details of the apertures, tube mounting, pinhole and powder cassettes, preparation and mounting of samples, exposures, protection, and ventilation are given. Examples are shown of photographs of drawn and annealed steels. W. CLARK.

Sensitivity of selenium cells. T. T. BAKER (Nature, 1926, **117**, 858—859).

Ultra-violet photometry. G. M. B. DOBSON and D. N. HARRISON (Nature, 1926, **117**, 724).—Neutral gelatin wedges can be conveniently used for wave-lengths of 2380 Å. or less. A. A. ELDRIDGE.

Electric high-temperature furnaces to 3300°. E. LÖWENSTEIN (Z. anorg. Chem., 1926, **154**, 173—177).—A short-circuit oven with heating tube of carbon or graphite well insulated to prevent loss of heat by radiation is best worked with an alternating current at 10—15 volts. The oven can be rotated and fixed in any desired position; there is an induction regulating contrivance by means of which the temperature can be kept constant. M. CARLTON.

Modification of the deflexion balance. J. W. TREVAN (Biochem. J., 1926, **20**, 419—422).—The balance depends on the bending of a steel wire. By using steel wires of varying thicknesses, weights from 1 mg. to 1 g. can be determined with an accuracy of ±1 in 10,000. The time taken to carry out a weighing is 30 sec. S. S. ZILVA.

Copper covers for calorimeter jackets. W. P. WHITE (J. Amer. Chem. Soc., 1926, **48**, 1149—1154).—Blanketed sheet-copper calorimeter covers, dipping in the jacket water, are more efficient than insulating covers. Except that they are inferior for preventing flow of heat along thermometers, rods, wires, etc., they may replace the water-cap or submarine covers, even in work of the highest precision.
S. K. TWEEDY.

Production of polarising surfaces by the deposition of "herapathite" on vertical plates. A. ZIMMERN and M. COUTIN (Compt. rend., 1926, **182**, 1214—1215; cf. this vol., 774).—The method previously described is improved by the use of a vertical glass plate placed in the mother-liquor. Iodine vapour is allowed to fall on to the meniscus, the liquid being kept at 30° and allowed to flow slowly from the vessel. The crystals are formed at the point of the meniscus. J. GRANT.

Scale for direct reading of p_H values [from millivoltmeter readings]. A. HOCK (Z. angew. Chem., 1926, **39**, 646—647).—The scale consists of a circular piece of metal with an outer scale of millivoltmeter readings (quinhydrone electrode on one side and platinum-hydrogen electrode on the other) taken at a standard temperature of 20°, and an inner scale of the corresponding p_H values. A movable arm rotating about the centre of the disc assists in reading the scale and provides a vernier arrangement for correcting for change of temperature, reading in 0·01 p_H units against temperature spirals about the central part of the disc. A. R. POWELL.

Micro-volumetric apparatus. E. SCHILOW (Z. angew. Chem., 1926, **39**, 582—583).—A tapless burette (cf. *ibid.*, 232) has an internal diameter at its capillary tip of 0·2—0·4 mm., with scale readings about 1 mm. apart; as little as 0·0005 c.c. of liquid can be run out at a time, and a 0·1% accuracy in calibration is attainable. It is necessary that the discharge should take place at a standard rate. The micro-pipette has a curved capillary tip, above which is etched a mark; the liquid is run out to this level. A volume is discharged with an accuracy of 0·01—0·02%. Absolute cleanliness of the apparatus is essential to prevent gross errors due to adherence of liquid. Variations in temperature require the same considerations as for macro-volumetric apparatus. The degree of accuracy is similar to that obtaining for ordinary volumetric analysis.
L. M. CLARK.

Micro-wash-out pipette. K. SCHUHECKER (Biochem. Z., 1926, **171**, 287—295).—The micro-pipette consists of two parts, that which contains the wash-out liquid being ground into the other, which contains the substance to be measured.
P. W. CLUTTERBUCK.

Preparation of nickel membranes for ultrafiltration. J. MANNING (J.C.S., 1926, 1127—1132).—Membranes suitable for the ultrafiltration of most organic and inorganic colloids from solutions have been prepared by nickel-plating 200-mesh nickel or phosphor-bronze gauze under such conditions that the deposit is slightly porous owing to a slow evolution of hydrogen at the cathode. The most satisfactory plating bath consisted of a solution of 100 g. of nickel sulphate, 80 g. of nickel chloride, and 20 g. of sodium acetate trihydrate in 1500 g. of water. With a backing of a perforated nickel sheet, the nickel membranes could be used for ultrafiltration under a pressure up to 16 atm. Any unduly large holes in the membrane usually became closed after a few c.c. of liquid had passed through. Examples are given of the use of the membranes for the ultrafiltration of colloidal silver, sodium stearate, cellulose acetate, and gelatin. A. R. POWELL.

Effect of air in the Jones reducer. W. L. BURDICK (J. Amer. Chem. Soc., 1926, **48**, 1179—1181).—The introduction of air into the Jones reducer has no effect on the subsequent permanganate titra-

tions, since, under ordinary conditions of analysis, no hydrogen peroxide is formed. S. K. TWEEDY.

Oberhoffer's etching mixture. F. HEINRICH and W. VOIGT (Z. anorg. Chem., 1926, **154**, 209—212).—Of the various etching mixtures for examining the primary distribution of phosphorus in iron and steel, Oberhoffer's etches zones rich in phosphorus less than those poor in phosphorus, whereas Heyn's mixture acts conversely. This behaviour was previously explained by the different copper chloride content of the two solutions. The authors etched a steel of known structure. Three series of experiments were performed, starting with aqueous solutions of copper chloride, hydrochloric acid, and ferric chloride, and to each in turn the usual remaining reagents were added singly. Results are tabulated and show that the action of Oberhoffer's etching mixture does not depend on the copper chloride content, but on the ferric chloride. The presence of alcohol may reduce the vigour of the ferric chloride reaction; copper chloride and zinc chloride possibly act catalytically. M. CARLTON.

Apparatus for continuous percolation and for filtration in neutral atmospheres. B. S. EVANS (Analyst, 1926, **51**, 229—235).—A flask carries a rubber stopper through which pass the stem of a cylindrical funnel; the return tube, drawn to a point and reaching practically to the bottom of the flask and connecting to the upper end of the funnel by a bend on itself passing through a stopper in the funnel, and a lower exit tube. The rubber stopper closing the upper end of the cylindrical funnel is also pierced by three holes and carries a small tap funnel, the upper exit tube, and the bent-over end of the return tube. The material to be percolated is placed in a short open glass tube with one end constricted and is held in place by, *e.g.*, glass wool. The tube is attached by rubber tubing to the stem of the main funnel, so that it hangs down into the flask. The upper exit tube is attached to a filter-pump and the percolating liquid introduced through the tap funnel. As soon as sufficient liquid collects in the bottom of the flask to cover the end of the return tube, pressure conditions are changed and the liquid goes up the tube followed by air bubbles which drive it right back to the main funnel. A tap between the body and stem of the main funnel provides means of adjusting the resistance in the downward branch of the circuit. A tap inserted in the return tube is an advantage. If suction applied to the upper exit tube be replaced by pressure to the lower exit tube, percolation may be conducted in an inert atmosphere. D. G. HEWER.

Modified gas volume-meter for the determination of densities of solids. G. M. KARNS (J. Amer. Chem. Soc., 1926, **48**, 1176—1178).—A simple modification of the Washburn and Bunting volume-meter is described, by means of which the density of 0·1—0·5 g. of solid may be determined with an accuracy of 0·5% (cf. A., 1922, ii, 401; Zender, Ann. Physik, 1924, **15**, 328). S. K. TWEEDY.

Capillary valves for gases. J. J. HOPFIELD (J. Opt. Soc. Amer., 1926, **12**, 391—392).—Two capillary valves designed to allow of a variable flow of gas in spectroscopic discharge tubes are described. One is a glass needle valve operated electromagnetically which permits a flow from atmospheric pressure into a vacuum of 0·1 c.c./hr., up to 250 times this rate. In the other valve, gas flow is controlled by a crack in a glass tube which is opened to varying degrees by slightly twisting the tube. W. CLARK.

[Acidified] sodium chloride solution as a confining liquid for gas analysis. H. TROPSCH. —See B., 1926, 427.

Danger of mercury vapour. A. STOCK (Z. angew Chem., 1926, **39**, 461—466).—Prolonged exposure to the vapours given off at the ordinary temperature by metallic mercury slowly results in very serious mercury poisoning. The symptoms described slowly develop in workers using apparatus containing mercury, *e.g.*, mercury pumps, gas analysis apparatus, etc., unless there is an extremely good system of ventilation The condition once developed can be cured only by abstention from all work involving the use of mercury, and even then the cure takes several years. All the usual dental amalgams slowly but regularly lose mercury at the temperature of the month (30—35°), some losing as much as 5—6 mg. per week. Continual use of mercurial ointments may also give rise to symptoms of mercury poisoning. A. R. POWELL.

Spiral gas-washing bottle. L. H. MILLIGAN (J. Opt. Soc. Amer., 1926, **12**, 518; cf. A., 1924, ii, 776).—The gas-washing bottle previously described has been modified by the introduction of a cylindrical shield fitting loosely into the outer cylinder and closely to the spirally corrugated tube, which it serves to support. The liquid circulates upward with the bubbles and then down through the centre of the spiral and round the outside of the shield. A. B. MANNING.

Non-inflammable liquids for cryostats. C. W. KANOLT (Sci. Papers U.S. Bur. Standards, No. 520, 1926, **20**, 619—633).—Determinations have been made of the f. p. of chloroform, carbon tetrachloride, dichloromethane, ethyl chloride, ethyl bromide, *s*-dichloroethylene, and trichloroethylene, and of mixtures of two, three, four, and five of these substances. As the utility of these liquids in cryostats is sometimes limited by their inflammability, viscosity, or corrosiveness, these properties were also studied. The f. p. were determined by cooling in a vessel jacketed with liquid air and the addition of small drops of liquid air to the liquid from time to time was found very effective in preventing over-cooling.

The f. p. for pure liquids are in satisfactory agreement with the accepted values and, in general, the compositions and f. p. of eutectic mixtures were determined, in order to obtain as low f. p. as possible. None of the mixtures studied shows any evidence of the formation of compounds; mixtures of ethyl chloride and bromide form solid solutions and no eutectic was obtained. Some of the mixtures become very viscous when the f. p. is approached and are thus unsuitable as cryostat liquids at these temperatures. Viscosities were also determined in a tube surrounded

with liquid air, and a means was provided for filtering the liquids after cooling and for excluding moisture. When pure, all the liquids have little corrosive action on metals, but corrosive impurities are formed by the atmospheric oxidation of dichloromethane, ethyl bromide, dichloroethylene, and especially trichloroethylene. Such impurities are removed by aqueous sodium carbonate. Iron, copper, and brass are more subject to corrosion than are German silver, lead, tin, and lead–tin solder. The following liquids, none of which is inflammable, are recommended for use down to the temperatures stated: carbon tetrachloride, −23°; chloroform, −63°; 49·4% carbon tetrachloride and 50·6% chloroform, −81°; ethyl bromide, −119°; 19·7% chloroform, 44·9% ethyl bromide, 13·8% *s*-dichloroethylene, and 21·6% trichloroethylene, −139°; 14·5% chloroform, 25·3% dichloromethane, 33·4% ethyl bromide, 10·4% dichloroethylene, and 16·4% trichloroethylene, −145° to −150°; 18·1% chloroform, 8·0% ethyl chloride, 41·3% ethyl bromide, 12·7% *s*-dichloroethylene, and 19·9% trichloroethylene, about −150°. Below −150°, inflammable substances, such as technical butane or boiling methane, are unavoidable. Below −180°, boiling liquid oxygen, argon, or nitrogen may be used, and the temperature is controlled by varying the pressure. A. GEAKE.

Improved method of preparation of Weigert's elastin stain. F. HAYNES (J. Roy. Micros. Soc., 1926, II, **46**, 29—30).—Two per cent. of phenol is added to a 1% aqueous solution of basic magenta, the mixture raised to the b. p., and excess of a 50% solution of ferric chloride added. After boiling for 10 min., the precipitate is collected, washed, and dried. For use, 0·75 g. is added to 100 c.c. of 96% alcohol containing a few drops of concentrated hydrochloric acid, boiled for 15 min., cooled, filtered, and 2% of concentrated hydrochloric acid added. The powder keeps indefinitely and the stain for at least 2 months. A. GEAKE.

History of the word "alum." A. M. PATTERSON (Ind. Eng. Chem., 1926, **78**, 634—635).

[Formation of ozone under pressure.] H. VON WARTENBERG (Z. Elektrochem., 1926, **32**, 218; cf. this vol., 260).—The occurrence of high-frequency vibrations in ozone tubes was first mentioned by Moeller ("Das Ozon," 1921), not by Warburg. R. CUTHILL.

Mineralogical Chemistry.

Examination of Dead Sea water for eka-cæsium and eka-iodine. J. N. FRIEND (Nature, 1926, **117**, 789—790).—Dead Sea water, collected in the summer at a depth of 2 ft., had d^{18} 1·2089, and contained small quantities of strontium. From the mother-liquor after removal of non-alkali metals and fractional crystallisation of sodium chloride, potassium chloroplatinate was precipitated, but neither this compound nor potassium chloride prepared from it gave any indication of the presence of eka-cæsium when examined by *X*-ray analysis. Eka-iodine was likewise not found. A. A. ELDRIDGE.

Hot springs at Nasavusavu [Fiji]. C. H. WRIGHT (Analyst, 1926, **51**, 235—236).—Analysis of water from the largest of the three hot springs gave (as ions per 100,000): calcium, 177·5; magnesium, 0·4; sodium, 129·9; potassium, 19·2; chlorine, 496·0; SO_4, 24·2; SiO_3, 19·9; difference 4·8; total solids dried at 120°, 871·9. Thus the general composition of the water has remained unchanged since 1876. D. G. HEWER.

Spectroscopic examination of minerals. III. Topaz. IV. Diamond. V. Spodumene. G. O. WILD and R. KLEMM (Centr. Min., A., 1925, 321—323, 324—326; from Chem. Zentr., 1926, I, 864; cf. this vol., 594).—III. The depth of colour of yellow varieties of topaz increases with the content of chromium. This element is hence the "pigment" and is not present in the colourless mineral. Iron, vanadium, silver, and sodium are usually present, but not manganese, magnesium, lithium, calcium, or gallium. Aquamarine blue types give only strong lines of iron.

IV.—A canary-yellow and white specimens of diamond gave no lines not already present in the electrode-spectrum.

V.—A colourless specimen of spodumeno showed lines of iron, cobalt, tin, and sodium. A comparison of the intensity of the spectral lines with the depth of colour of the green variety, hiddenite, shows that chromium is the "pigment." Sodium, tin, vanadium, manganese, cobalt, silver, titanium, and lithium are also present. Yellow varieties show strong lines of iron, manganese, and cobalt. Rose or lilac kunzite contains most of the above foreign elements, calcium, cobalt, and vanadium, however, being absent. J. S. CARTER.

[Schallerite.] J. ORCEL (Bull. Soc. franç. Min., 1925, **48**, 238; from Chem. Zentr., 1926, I, 866).—The brown, volatile mineral *schallerite*, $12MnO,9SiO_2,As_2O_5,7H_2O$, occurs in zinc ore veins in New Jersey. The crystals are optically uniaxial and negative, n_α 1·704; n_β 1·679. The mineral is slowly attacked by hydrochloric acid. Hardness, 4·5—5; *d*, 3·368. J. S. CARTER.

"Eisenbrucite." P. GAUBERT (Bull. Soc. franç. Min., 1925, **48**, 216—219; from Chem. Zentr., 1926, I, 865).—"Eisenbrucite" (Sandberger, N. Jahrb. Min., 1880, II, 289) is not a pure, hydrated iron-magnesium hydroxide. Silica is not present as quartz, but as chrysotil. The composition is $7(Mg,Fe)O,CO_2,10H_2O$. J. S. CARTER.

Chemical characters of okaite. J. STANSFIELD (Amer. J. Sci., 1926, [v], **11**, 396—398).—Full analyses are given of okaite and nepheline-okaite. Pyrrhotite being absent, sulphide-sulphur is ascribed to sodium sulphide (1·25% and 0·12%, respectively) forming

part of the hauyne constituent. By comparison with the associated monticellite-aluoite, a progressive increase in alumina, lime, soda, and a decrease in magnesia and potash are noted. The author regards calcium carbonate as being the chief agent in the development of these rocks. W. A. CASPARI.

Pollucite. A. KASTLER (Compt. rend., 1926, **182**, 1285—1286).—Pollucite is a non-radioactive cæsium-bearing felspar represented by $R_2Al_2H_2(SiO_3)_5$, in which R is the entire content of alkali metals. The composition of American pollucite is SiO_2 46·3; $Al_2O_3+Fe_2O_3$ 18·0, Cs_2O 30·5, Na_2O 3, H_2O 2·3%. This material is identical with pollucite from Elba. R. A. MORTON.

Chemical composition of orthite from Ambatofotsikely (Madagascar). G. CAROBBI (Atti R. Accad. Lincei, 1926, [vi], **3**, 206—209).—A carefully selected sample of orthite from Ambatofotsikely, *d* 3·38, identical with that examined by Pisani (cf. Lacroix, Minéralogie de Madagascar, 1922, 452), gave the composition:

SiO_2.	ThO_2.	Al_2O_3.	Ce_2O_3.	La(etc.)$_2O_3$.	Y_2O_3.
30·42	2·37	17·00	8·09	8·31	1·42

Fe_2O_3.	FeO.	MnO.	CaO.	H_2O.	Total.
5·45	11·96	0·80	13·38	0·73	99·93

These results give the molecular ratios $R^{II}O : R_2^{III}O_3 : SiO_2 = 1·58 : 1 : 1·93$, which correspond approximately with those of typical orthite, but differ considerably from those given by Pisani. T. H. POPE.

Antimonite from Wolfsberg (Harz). P. GRAVINO (Atti R. Accad. Lincei, 1926, [vi], **3**, 210—215).—Crystallographic measurements of an especially pure sample of antimonite, free from arsenic, bismuth, lead, and copper, found at Wolfsberg give results in good agreement with those obtained by Dana on Japanese specimens of this mineral (Amer. J. Sci., 1883, **26**, 219). T. H. POPE.

Minerals of the Keweenawan copper deposits: pumpellyite, sericite, saponite. C. PALACHE and H. VASSAR (Amer. Mineral., 1925, **10**, 412—418).—Pumpellyite is orthorhombic, positive, 2V large, $\rho < \nu$ strong, n_α 1·698, n_β 1·700, n_γ 1·708, α and γ colourless, β green, *H* 5·5, *d* 3·2. It contains SiO_2 36·85, Al_2O_3 23·81, Fe_2O_3 4·38, FeO 3·62, MgO 3·94, CaO 21·62, MnO 0·14, K_2O and Na_2O 0·80, H_2O 5·00%. Analyses of sericite and saponite are given; the latter is monoclinic or orthorhombic, negative, 2V moderate to small, α 1·479—1·490; β 1·510—1·525; γ 1·511—1·527. CHEMICAL ABSTRACTS.

Germanium in a British mineral. W. SCUTT (Phil. Mag., 1926, [vii], **1**, 1007—1009).—Spectrographic examination of some specimens of zinc blende from Aberystwyth, Wales, showed that it contained an appreciable quantity of germanium. From a comparison of the intensity of its spectrum with that obtained from a sample of germanite, it is estimated that the blende contains 2—4% of germanium. A. E. MITCHELL.

Zirconium in Colorado pitchblende. O. FREE (Phil. Mag., 1926, [vii], **1**, 950—960).—A pitchblende from Colorado containing 78·9% U_3O_8 and 5·25% ZrO_2, with silica, pyrites, and moisture as important constituents, and traces of lead, titanium, and vanadium, was found to have so small a lead : uranium ratio as to indicate a maximum age of 2×10^6 years. It is thus of recent formation in comparison with the other uraninites of the U.S.A. examined by Hillebrand and others. A comparison of the density of the zirconia extracted from this source, with that from other localities indicates that it contains very little hafnium. In the spectra of zirconia obtained from the pitchblende the scandium lines were clearly evident. A. E. MITCHELL.

Penroseite and trudellite, two new minerals. S. G. GORDON (Proc. Acad. Nat. Sci. Philadelphia, 1926, **77** (for 1925), 317—324).—Penroseite from Bolivia is a lead-grey mineral with metallic lustre and radiating columnar structure. It is orthorhombic with perfect pinakoidal cleavages, *d* 6·93, *H* 3. Microscopical examination of polished surfaces shows the presence of some limonite and silver selenide (?). The mineral dissolves readily in nitric acid. It is easily fusible, colouring the flame azure-blue and emitting reddish-brown fumes: in a bulb-tube selenium is deposited. Analysis by J. E. WHITFIELD gave: Se 59·80, Ag 2·04, Pb 17·13, Cu 7·84, Ni 11·14, Co 1·34, Fe_2O_3 1·08, total 100·37. Approximate alternative formulæ are written as $2PbSe_2,3CuSe,5(Ni,Co)Se_2$ and $PbSe,Cu_2Se(Ni,Co)Se_3$.

Trudellite occurs with pickeringite, anhydrite, and gypsum in a breccia near Pintados, Tarapacá, Chile. It forms amber-yellow, compact masses with *d* 1·93, H 2½. It is optically uniaxial and negative, ω 1·560, ε 1·495, with indistinct rhombohedral cleavage. Analysis by E. V. SHANNON gave SO_3 13·60, Cl 24·42, Al_2O_3 25·67, Fe_2O_3 1·00, CaO 1·56, MgO 0·66, Na_2O 1·58, SiO_2 0·57, H_2O 36·69, total (less O for Cl) 100·17, agreeing with the formula $Al_2(SO_4)_3,4AlCl_3,4Al(OH)_3,30H_2O$. The mineral is very deliquescent, and when dissolved in water some of the alumina is precipitated. L. J. SPENCER.

Identity of carrollite with linnaeite. E. V. SHANNON (Amer. J. Sci., 1926, [v], **11**, 489—493).—Five new analyses of "carrollite" from Carroll Co., Maryland, show S 41·34—44·89, Co 36·08—48·70, Ni trace—7·65, Cu 2·40—15·43, Fe 0·28—4·57%. The mineral has a reddish colour and a good cubic cleavage. Microscopical examination of polished surfaces shows the material to be optically isotropic and to be intergrown with chalcopyrite and chalcosine. It is therefore a mixture of linnaeite and copper ores. L. J. SPENCER.

Identity of ectropite and bementite. E. S. LARSEN (Amer. Mineral., 1925, **10**, 418—421).—The identity is established; the latter name is retained. CHEMICAL ABSTRACTS.

Identity of "lehnerite" and ludlamite. H. BERMAN (Amer. Mineral., 1925, **10**, 428—429).—"Lehnerite" is regarded as a manganese-magnesium variety of ludlamite. CHEMICAL ABSTRACTS.

Identity of newtonite with alunite. W. F. FOSHAG (Amer. Mineral., 1926, **11**, 33—35).—Alunite,

with which newtonite is identical, has n 1·58; ω 1·572; ε 1·592. A. A. ELDRIDGE.

Identity of gilpinite and johannite. E. S. LARSEN and H. BERMAN (Amer. Mineral., 1926, **11**, 1—5).—The identity is established. Instead, however, of the formula $CuO,3UO_3,3SO_3,4H_2O$, the formula $(CuFeNa_2)O,UO_3,SO_3,4H_2O$ better expresses the composition of johannite, which is greenish- to canary-yellow, and strongly pleochroic; triclinic, negative, n_α 1·572, n_β 1·595, n_γ 1·614; $2V_{Na}$ about 90°; $\rho<\nu$ strong. A. A. ELDRIDGE.

Rocks from eastern China. H. S. WASHINGTON and M. G. KEYES (J. Washington Acad. Sci., 1926, **16**, 291—301).—Petrographical descriptions with ten detailed chemical analyses are given of igneous rocks, including a nepheline-syenite. L. J. SPENCER.

Detection of tin in minerals using the blowpipe. A. BRALY.—See this vol., 705.

Organic Chemistry.

Chemical effects in ionised gases. S. C. LIND and D. C. BARDWELL.—See this vol., 654.

Carbon tetrafluoride. P. LEBEAU and A. DAMIENS (Compt. rend., 1926, **182**, 1340—1342).—During the preparation of beryllium by the electrolysis of fused beryllium fluoride and an alkali fluoride, a gas liberated at the anode yields two fractions, one liquid at −80° and *carbon tetrafluoride*, b. p. −150°, d^0 3·034, M 87·4 (theory 88). Sodium decomposes the gas at 500°, yielding carbon and sodium fluoride, whilst calcium reacts at 600—700°, giving calcium carbide, carbon, and calcium fluoride. When heated at 1100°, carbon tetrafluoride undergoes partial decomposition. The compounds described by Moissan and Chabrié as carbon tetrafluoride were mixtures. L. F. HEWITT.

Preparation of ethyl chloride. CHEM. FABR. VORM. WEILER-TER MEER.—See B., 1926, 463.

Preparation of propargyl bromide. A. KIRRMANN (Bull. Soc. chim., 1926, [iv], **39**, 698—699).—By the addition of about 15% of pyridine, the yield of propargyl bromide, b. p. 82°, 35°/130 mm., d^{19} 1·579, n_D^{19} 1·4942, from phosphorus tribromide and propargyl alcohol is raised to 80%, the action of the hydrogen bromide formed on the triple linking being thereby eliminated. The method is general for unsaturated alcohols. R. BRIGHTMAN.

Liberation of hydrogen from carbon compounds. II. Interaction of ethyl alcohol, acetaldehyde, and acetone with fused alkali hydroxides. H. S. FRY and E. L. SCHULZE (J. Amer. Chem. Soc., 1926, **48**, 958—968; cf. A., 1924, i, 1277).—Ethyl alcohol reacts very slowly with fused alkali hydroxides at 250—300°. The proportions of products formed do not conform to any single equation, but the data obtained indicate the occurrence of the following reactions: $EtOH + NaOH \longrightarrow NaOAc + 2H_2$; $NaOAc + NaOH \longrightarrow Na_2CO_3 + CH_4$; $EtOH + 6NaOH \longrightarrow Na_2CO_3 + Na_4CO_4 + 6H_2$, and $EtOH \longrightarrow C_2H_4 + H_2O$. Reaction between acetaldehyde and fused alkali hydroxides is practically complete at 250°, the products conforming, to the extent of 90%, to the scheme $C_2H_4O + NaOH \longrightarrow NaOAc + H_2$; whilst at 300° and 350° the reaction is represented by the scheme $C_2H_4O + 2NaOH \longrightarrow H_2 + CH_4 + Na_2CO_3$. Acetone behaves analogously, reactions at 250° and 350° being represented by the respective schemes $C_3H_6O + NaOH \longrightarrow NaOAc + CH_4$ and $C_3H_6O + 2NaOH \longrightarrow Na_2CO_3 + 2CH_4$. F. G. WILLSON.

Catalytic dehydration of alkylvinylcarbinols. J. M. DUMOULIN (Compt. rend., 1926, **182**, 974—976; cf. Prévost, this vol., 496).—Alkylvinylcarbinols are dehydrated by potassium hydrogen sulphate in a yield of 25%, by aluminium sulphate with a yield of 35%, and by freshly precipitated aluminium hydroxide with a yield of 50—65%. Ethylvinylcarbinol on dehydration gives $\Delta^{\alpha\gamma}$-pentadiene with a small amount of the $\Delta^{\alpha\beta}$-isomeride, which on oxidation give acetic acid and a trace of propionic acid. By the direct action of bromine on the pentadienes, a *tetrabromide*, m. p. 114°, by the action of bromine in chloroform or carbon disulphide solution a *dibromide*, b. p. 75—80°/20 mm., are formed. Propylvinylcarbinol is dehydrated, giving a mixture of $\Delta^{\alpha\gamma}$- and $\Delta^{\beta\delta}$-hexadienes, which, when oxidised, yields a mixture of formic, acetic, and propionic acids. Bromine in chloroform solution gives a *dibromide*, b. p. 111—112°/25 mm., whilst bromine alone yields the same dibromide, possibly $\alpha\beta\gamma\delta$-tetrabromohexane, and a *tetrabromide*, m. p. 179·5°. Butylvinylcarbinol is dehydrated, giving a mixture of $\Delta^{\alpha\gamma}$- and $\Delta^{\beta\delta}$-heptadienes, which, when oxidised, gives a mixture of acetic, propionic, and butyric acids. $\Delta^{\beta\delta}$-Heptadiene, m. p. 103—106°, d_0^0 0·7436, n_D^{19} 1·4524, predominates. L. F. HEWITT.

Molecular transpositions in the ααα-alkyldiarylethanol series. RAMART and AMAGAT (Compt. rend., 1926, **182**, 1342—1344).—$\beta\beta\gamma$-*Triphenylpropan-α-ol*, b. p. 240°/16 mm., m. p. 80° (*phenylurethane*, m. p. 169°, *benzoate*, m. p. 95°), is obtained together with a small amount of triphenylethane when benzyl-ααβ-triphenylpropionate is reduced by sodium and ethyl alcohol. When dehydrated with phosphoric oxide, $\alpha\beta\gamma$-triphenyl-Δ^α-propene and a smaller quantity of $\alpha\alpha\gamma$-triphenyl-Δ^α-propene are formed, the phenyl group thus showing a greater migratory tendency than the benzyl radical. L. F. HEWITT.

Properties of glycol diacetate. C. A. TAYLOR and W. H. RINKENBACH (J. Amer. Chem. Soc., 1926, **48**, 1305—1309).—The following physical properties of glycol diacetate are recorded: m. p. $-31\pm1°$; vapour pressure at 100°, 26 mm., increasing linearly to the b. p. 190·2°/760 mm.; d_{15}^0 1·1266, decreasing linearly to d_{15}^{20} 1·1040; n_D^{20} 1·4150. F. G. WILLSON.

Pinacones. L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 651—655; cf. this vol., 596).—Dehydration of βγ-dimethylheptane-βγ-diol with phosphoric acid (*d* 1·13) at 150—160° yields *γγ-dimethylheptane-β-one*, b. p. 169·5°/735 mm., d_4^{11} 0·834 (*semicarbazone*, m. p. 130·5°), oxidised by sodium hypobromite to αα-dimethylhexoic acid, b. p. 117—119°/12 mm. (cf. Meerwein, A., 1920, i, 2) (*chloride*, b. p. 55°/10 mm., *amide*, m. p. 92°), together with a little brominated product which on boiling with concentrated sodium hydroxide is converted into (?) *α-hydroxy-ββ-dimethylheptoic acid*, $C_9H_{18}O_3$, m. p. 92—93°. The isomeric ββ-*dimethylheptan-γ-one*, obtained by the action of pivaloyl chloride on zinc butyl iodide, has b. p. 164°/735 mm., d_4^{11} 0·823 (*semicarbazone*, m. p. 142—143°). Similarly, βγε-trimethylhexane-βγ-diol with cold concentrated sulphuric acid gives βδδ-*trimethylhexan-ε-one*, b. p. 164—165°/750 mm., d_4^0 0·845 (*semicarbazone*, m. p. 133°, *oxime*, m. p. 61°, b. p. 110—111°/14 mm.), the constitution of which is established by its oxidation with 52% nitric acid to a saturated *monocarboxylic acid*, b. p. 114°/14 mm. (*chloride*, b. p. 67°/14 mm., and an *amide*, $C_8H_{17}ON$, m. p. 71°). The isomeric ββε-trimethylhexan-γ-one, obtained by the action of zinc *iso*butyl iodide on pivaloyl chloride (cf. Haller and Bauer, A., 1910, i, 219), gives a *semicarbazone*, m. p. 145°. Dehydration of βγ-dimethyloctane-βγ-diol with cold concentrated sulphuric acid gives *γγ-dimethyloctan-β-one*, b. p. 75°/10 mm., d_4^0 0·843 (*semicarbazone*, m. p. 106°), oxidised by 58% nitric acid to *αα-dimethylheptoic acid*, b. p. 130°/12 mm. (*chloride*, b. p. 74—76°/10 mm., *amide*, m. p. 101—102°). With 20% phosphoric acid at 150—160° this pinacone is largely unchanged. The isomeric ββ-*dimethyloctan-γ-one*, obtained in the usual way from pivaloyl chloride, has b. p. 72°/10 mm., d_4^0 0·834 (*semicarbazone*, m. p. 139—140°).

R. BRIGHTMAN.

Dehydration of pinacones. R. LOCQUIN and L. LEERS (Bull. Soc. chim., 1926, [iv], **39**, 655—657; cf. this vol., 599, and preceding abstract).—In the dehydration of eight pinacones, $CRMe(OH)\cdot CMe_2OH$, where *R* is a saturated alkyl group, the pinacoline $CRMe_2\cdot CO\cdot Me$ is formed exclusively except when *R* is *iso*propyl or *tert.*-butyl. In these cases, small amounts of the isomeric ketone, $R\cdot CO\cdot CMe_3$, are also formed. No sound conclusions as to the mechanism of the migration are possible.

R. BRIGHTMAN.

Compounds of bivalent carbon. I. Carbon monoxide diethylacetal [diethoxymethylene], its preparation from ethyl diethoxyacetate or ethyl formate. H. SCHEIBLER (Ber., 1926, **59**, [*B*], 1022—1032).—The addition of successive portions of ethyl diethoxyacetate to an ethereal suspension of sodium ethoxide with intermittent removal and replacement of the ether gives the ester-enolate which is decomposed by ice, yielding diethoxymethylene (in place of the expected diethoxyketendiethylacetal) in small yield. Better results are obtained by converting ethyl formate similarly into *sodiumoxyethoxymethylene*, C(ONa)·OEt (which does not behave as a true ester-enolate since, on hydrolysis, it yields carbon monoxide, sodium hydroxide, and alcohol instead of regenerating the ester), and converting the latter substance by phosphoryl chloride into chloroethoxymethylene, which, with sodium ethoxide, affords diethoxymethylene. The preparation from ethyl formate and sodamide is described. *Diethoxymethylene* has b. p. 56—57°/365 mm., d_4^{20} 0·7879, n_D^{14} 1·38023. It is slowly hydrolysed by water and dilute alkalis, rapidly by dilute acids, yielding carbon monoxide. It is stable towards bromine even in sunlight, but readily oxidised by permanganate.

H. WREN.

Ethyl hydrogen sulphate. II. M. A. HAMID, K. SINGH, and H. B. DUNNICLIFF (J.C.S., 1926, 1098—1102; cf. *ibid.*, 1921, **119**, 1384).—Attempts to prepare the pure ester from the anhydrous lead and barium salts and by passing ethylene into sulphuric acid under various conditions, failed. The solubility of ethyl hydrogen sulphate in ether containing varying small concentrations of sulphuric acid has been determined. The reaction between ethyl alcohol and 60—75% sulphuric acid is of the first order.

A. DAVIDSON.

Preparation of pure α-monochlorohydrin. I. RIBAS and E. FOURNEAU (Anal. Fís. Quím., 1926, **24**, 165—167).—Pure α-monochlorohydrin may be prepared by heating epichlorohydrin (1 mol.) with water (3 mols.) on a water-bath, using sulphuric acid as catalyst.

G. W. ROBINSON.

Preparation of glycerol α-monochlorohydrin. E. FOURNEAU and T. R. Y. MARQUÈS (Bull. Soc. chim., 1926, [iv], **39**, 699—700).—Glycerol dichlorohydrin, by treatment with 1 mol. of concentrated sodium hydroxide, is converted (yield 90%) into glycerol epichlorohydrin, which on boiling with 3 mols. of water containing 5 c.c. of 10% sulphuric acid per mol. of epichlorohydrin as catalyst gives an 85—90% yield of glycerol α-monochlorohydrin.

R. BRIGHTMAN.

Production of alkyl esters [formates]. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 462.

Compounds containing ferric acetato- or propionato-complexes. R. WEINLAND and A. HÖRN (Z. anorg. Chem., 1926, **152**, 1—15; cf. A., 1924, ii, 265).—The three complex compounds, obtained by Weinland, Kessler, and Bayerl by the action of acetic acid on ferric chloride, are probably all tetrachloroferriates of the hexa-acetatotriferric cation. The supposed dinitrate of a penta-acetatodihydroxytriferric cation, obtained from ferric nitrate hexahydrate and sodium acetate, is a mixture of sodium nitrate and the ordinary nitrate of the hexa-acetatotriferric base, $[Fe_3,(OAc)_6,(OH)_2]NO_3,4H_2O$. The four compounds obtained from ferric sesquiacetate and ferric nitrate also have this composition, the analytical data previously obtained being due to the presence of impurities. The compound obtained by Scheurer-Kestner (Ann. Chim. Phys., 1861, [iii], **63**, 422) and by Weinland, Kessler, and Bayerl by dissolving ferric hydroxide in nitric and acetic acids has the composition $[Fe_3,(OAc)_6OH]OAc,NO_3,3H_2O$. When ferric hydroxide is dissolved in the calculated amount of hydrobromic acid, the bromide, $Fe_3Br_8,6H_2O$, is

obtained; this is formulated as $[Fe^{II}(H_2O)_6][Fe^{III}Br_4]_2$. From this by the action of glacial acetic acid the *tetrabromoferriate*, $[Fe_3(OAc)_6](OAc)_2,FeBr_4,3H_2O$, is obtained, and by the action of sodium acetate the *bromide*, $[Fe_3(OAc)_6(OH)_2]Br,5H_2O$. Ferric perchlorate and sodium acetate combine to form the complex *perchlorate*, $[Fe_3(OAc)_6(OH)_2]ClO_4,4H_2O$. By the action of oxalic acid or potassium oxalate on ferric sesquiacetate, a *compound*, $Fe_4(OAc)_8(C_2O_4)(OH)_2,2H_2O$, of uncertain constitution is obtained. Alkali thiocyanates and ferric sesquiacetate yield the complex *compound*, $[Fe_3(OAc)_6(OH)]CNS,OAc,[Fe_3(OAc)_6(OH)_2]CNS,2H_2O$, which by treatment with pyridine is converted into the *compound* $[Fe_3(OAc)_6(OH)_2(C_5H_5N)_3]CNS,H_2O$. Propionic acid behaves like acetic acid in forming complex ferric compounds; thus from ferric chloride and sodium propionate the complex *chloride*, $[Fe_3(C_3H_5O_2)_6(OH)_2]Cl,2H_2O$, is obtained. By analogy with the compound obtained from glacial acetic acid, the compound obtained by Benrath (A., 1905, i, 734) from ferric chloride and propionic acid, and having the stoicheiometric composition $Fe(C_3H_5O_2)_2Cl$, probably has the constitution $[Fe(C_3H_5O_2)_6](C_3H_5O_2)_2(FeCl_4)$. A. GEAKE.

Preparation of butyric acid. C. W. HANCOCK.—See B., 1926, 463.

Crystalline-liquid thallous salts of organic acids. R. WALTER (Ber., 1926, **59**, [*B*], 962—972; cf. Holde and Selim, A., 1925, i, 504; Holde and Takehara, *ibid.*, 1233).—The majority of thallous salts of organic acids are enantiotropic, crystalline liquids. The following data are recorded, the m. p. I and II being given successively: formate, m. p. 104°; acetate, m. p. 130°; propionate, m. p. 188° (all not liquid crystalline); *n-butyrate*, m. p. 182° (latent liquid crystalline); *n-valerate* solid II, $\overset{76°}{\rightleftharpoons}$ solid I $\overset{175°}{\rightleftharpoons}$ crystalline liquid $\overset{212°}{\rightleftharpoons}$ amorphous liquid; *hexoate*, m. p. 223—224°, 152°; *heptoate*, m. p. 227°, 143°; *octoate*, m. p. 220°, 135—136°; *nonoate*, m. p. 215°, 130°; *decoate*, m. p. 207°, 127°; *undecoate*, m. p. 200—201°, 126°; laurate, m. p. 197°, 123°; myristate, m. p. 181·5°, 119·5°; palmitate, m. p. 172°, 114—116°; stearate, m. p. 163°, 118°; *cerolate*, m. p. 125°, 113—114°; iso*butyrate*, m. p. 124°; *α-ethylbutyrate*, m. p. 112°; *α-propylvalerate*, m. p. 122—123°; *β-methylbutyrate*, m. p. 174°, 156·5°; *γ-methylhexoate*, m. p. 218°, 118·5°; *hexahydrobenzoate*, m. p. 238°, 218°; *crotonate*, m. p. 122° after softening at 119°; iso*crotonate*, m. p. 107°; oleate, m. p. 131—132°, 81°; *elaidate*, m. p. 144°, 90°; *erucate*, m. p. 125°, 78·5°; *brassidate*, m. p. 122°, 96°; *benzoate*, m. p. 340—345°; o-*toluate*, m. p. 115—118°; m-*toluate*, m. p. 193—195°, 180°; p-*toluate*, m. p. 317°; *phenylacetate*, m. p. 157—158°; *β-phenylpropionate*, m. p. 193—195°. The determination of the m. p. of monotropic or latent liquid crystalline phases by mixture with salts of known m. p. does not appear possible. H. WREN.

***X*-Ray identification of the higher fatty acids.** G. T. MORGAN and E. HOLMES (Nature, 1926, **117**, 624).—Isolation from arachis oil of an acid, m. p. 77°, which has been shown by *X*-ray examination to be a C_{26} acid almost certainly possessing an unbranched carbon chain, confirms the observation of Holde and Godbole (this vol., 268) of the presence of hexacosoic acid. A. A. ELDRIDGE.

Stereoisomerism of ethylenic acids. Hydrogenation of stearolic and behenolic acids. A. GONZÁLEZ (Anal. Fís. Quim., 1926, **24**, 156—164).—By the catalytic partial hydrogenation of acetylenic acids, ethylenic acids of higher m. p. are obtained. From thermochemical considerations, it is concluded that there are no secondary reactions and that the products have the *cis*-configuration. Partial hydrogenation of stearolic acid with reduced nickel as catalyst yields oleic acid. Similarly, behenolic acid by partial hydrogenation yields erucic acid. The corresponding products of total reduction with zinc and acetic acid are elaidic and brassidic acids, respectively. It is concluded that oleic and erucic acids have the *cis*-configuration, whilst elaidic and brassidic acids have the *trans*-configuration. G. W. ROBINSON.

Drying of fatty oils. L. AUER.—See B., 1926, 450.

Drying process of the "drying" oils. H. WOLFF.—See B., 1926, 450.

Preparation and use of aldehyde esters formed by ozonisation of the methyl esters of unsaturated acids. C. R. NOLLER and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 1074—1080).—*Methyl η-aldehydo-octoate*, b. p. 111—112°/3 mm., n_D^{20} 1·4384, d_4^{20} 0·9704; *methyl* ω-*aldehydononoate*, b. p. 120—121°/3 mm., n_D^{20} 1·4410, d_4^{20} 0·9663, and *methyl* λ-*aldehydododecoate*, m. p. 19—20°, b. p. 152—153°/3 mm., n_D^{20} 1·4469, d_D^{20} 0·9399 (*semicarbazones*, m. p. 104—105°, 98—100°, and 116·5—117·5°, respectively), are obtained in 55—60% yields by passing ozonised air into an acetic acid solution of the appropriate unsaturated ester (methyl oleate, undecenoate, or erucate) until it no longer decolorises bromine. The solution is diluted with ether and boiled with zinc dust and water under reflux until it no longer gives a blue coloration with starch-iodide. After removal of the zinc sludge, water is added and the ethereal layer fractionated under reduced pressure. When kept, methyl η-aldehydo-octoate is partly converted into a *trimeride*, m. p. 34—36°, which is depolymerised when heated at 200°/3 mm., and yields, on hydrolysis with alcoholic sodium hydroxide, a *trimeride* of *η-aldehydo-octoic acid*, m. p. 112—113°. Oxidation of the above aldehyde esters by atmospheric oxygen affords *monomethyl azelate*, m. p. 22—24°, b. p. 158—159°/3 mm., n_D^{25} 1·4451, d_4^{25} 1·0348, *monomethyl sebacate*, m. p. 40—41°, and *monomethyl brassylate*, m. p. 57—57·5°, respectively. Condensation of methyl η-aldehydo-octoate with ethereal magnesium *n*-butyl bromide affords the *methyl* ester, b. p. 154—155°/3 mm., n_D^{20} 1·4490, d_4^{20} 0·9316, of θ-*hydroxytridecoic acid*, m. p. 49—51°. Treatment of the former with phosphorus tribromide, followed by conversion of the bromo-ester into the mixed unsaturated acids by hydrolysis with alcoholic potassium hydroxide, and reduction of these with hydrogen in presence of

platinum oxide in alcohol, affords *tridecoic acid*, m. p. 42—42·5°. F. G. WILLSON.

Derivatives of acetylpyruvic acid and ethoxalylacetmethylanilide. W. KÜSTER and E. ERFLE (Ber., 1926, **59**, [*B*], 1015—1017).—Acetylpyruvic acid and methylaniline in ethereal or aqueous solution afford *α-hydroxy-β-acetylacrylmethylanilide*, m. p. 85°, whereas in benzene–alcohol they yield *α-phenylmethylamino-β-acetylacrylic acid*, $CHAc{:}C(NPhMe)\cdot CO_2H$, softening at 57°, converted into the corresponding *ethyl* ester, m. p. indef. (obtained also from ethoxalylacetone and methylaniline in alcohol). The nitroso-derivative of acetylpyruvanilide (Küster and Schlack, A., 1924, i, 542) contains the nitroso-group attached to nitrogen. Ethoxalylacetmethylanilide gives a *nitroso*-derivative, m. p. 143°, from which the complex *ferrous* salt, $C_{26}H_{26}O_{10}N_4Fe$, is derived. H. WREN.

Decomposition of complex cyclic esters on heating. Decomposition of ethylene succinate. M. D. TILITSCHEEV (J. Russ. Phys. Chem. Soc., 1925, **57**, 143—150).—At the ordinary pressure, decomposition of ethylene succinate begins at 310° and proceeds mainly at 350—355°, the products consisting principally of succinic anhydride and acetaldehyde; a small proportion of the ester decomposes, however, into ethylene and carbon dioxide. When the decomposition is carried out at the pressure 5—6 mm., the products consist mainly of the isomeric form of ethylene succinate, m. p. 129—130° (cf. Vorländer, A., 1895, i, 18), and succinic anhydride (cf. A., 1923, i, 1173). T. H. POPE.

Iodination of acetylene derivatives. I. Preparation of di-iodofumaric acid. L. EICHELBERGER (J. Amer. Chem. Soc., 1926, **48**, 1320—1322).—Di-iodofumaric acid is obtained in 81% yield by heating an aqueous solution of potassium acetylenedicarboxylate with potassium iodide and iodine at 37° for 5—7 days. F. G. WILLSON.

Derivatives of ethyl β-acetyl-α-methylsuccinate; constitution of hæmatoporphyrin. W. KÜSTER, H. MAURER, and A. PALM (Ber., 1926, **59**, [*B*], 1018—1021).—The main product of the hydrolysis of the imide, $C_8H_{11}O_3N$ (obtained by oxidation of hæmatoporphyrin dimethyl ether), is not identical with the lactonic acid (*methyl* ester, b. p. 210°; *ammonium* salt) prepared by Sprankling (J.C.S., 1897, **71**, 1162) from ethyl β-acetyl-α-methylsuccinate and must therefore have the constitution $\begin{matrix}CMe\text{———}CO\\ \|\\ C(CO_2H)\cdot CHMe\end{matrix}\!>\!O$. Cautious hydrolysis of ethyl β-acetyl-α-methylsuccinate gives successively the *hydrogen* ester, m. p. 66—67°, and *β-acetyl-α-methylsuccinic acid*, m. p. 105—108°. The ester is converted by successive action of phosphorus pentachloride and water into (?) *γ-chloro-α-methyl-Δ$^{\beta}$-pentenoic acid*, m. p. 154°, and *γ-chloro-αγ-dimethylitaconic acid*, m. p. 128° (*ammonium* salt, m. p. 157°; *ethyl* ester, b. p. 216°). The latter acid yields its *anhydride*, m. p. 145°, when distilled under 15 mm. pressure, whereas at atmospheric pressure it forms a chlorinated maleic acid derivative converted by barium hydroxide into a substance, $C_7H_8O_4$, probably identical with the hydrolytic product from the imide, $C_8H_{11}O_3N$. H. WREN.

Electrolytic processes in organic chemistry. Electrolytic decomposition of alkali ethyl tartrate. B. L. VANZETTI and E. MANCA (Gazzetta, 1926, **56**, 112—121; cf. Sihvonen, Ann. Acad. Sci. Fenn., 1921, **16**, 1—188).—Electrolysis of solutions of barium or potassium ethyl *d*-tartrate follows a course similar to that of tartaric acid, the products including also the esters of the acids formed. Saccharic acid could not be detected. T. H. POPE.

Relative ease of αδ- and αζ-addition. E. P. KOHLER and F. R. BUTLER (J. Amer. Chem. Soc., 1926, **48**, 1036—1048).—The action of methyl sodiomalonate on methyl Δ$^{\beta\delta}$-pentadienoate in boiling ethereal solution affords, by αζ-addition, *trimethyl Δ$^{\gamma}$-pentene-ααε-tricarboxylate*, b. p. 147—150°/11 mm., no evidence of αδ-addition being obtained. Methyl sorbate yields similarly *trimethyl β-methyl-Δ$^{\gamma}$-pentene-ααε-tricarboxylate*, b. p. 185°/23 mm., b. p. 155°/10 mm., by αζ-addition, as the chief product. On ozonising the crude additive product, followed by esterification, *trimethyl propane-ααβ-tricarboxylate*, b. p. 127—131°/7 mm., is obtained, together with a small proportion of a *liquid*, b. p. 164—167°, possibly the *aldehyde* ester, $CO_2Me\cdot CH_2\cdot CH(CHO)\cdot CH(CO_2Me)_2$, which would be derived from an αδ-additive product. Hydrolysis of the above methyl propanetricarboxylate affords methylsuccinic anhydride. The *trihydrazide* of propane-ααβ-tricarboxylic acid, m. p. 208° (decomp.), and that of carballylic acid, m. p. 183—186°, were prepared for comparison.

Treatment of ethyl Δ$^{\beta\delta}$-pentadienoate with excess of ethereal magnesium phenyl bromide affords *β-phenyl-β-vinylpropiophenone*, b. p. 190°/8—10 mm. (identified by oxidation with permanganate in acetone to formic and β-benzoyl-α-phenylpropionic acids), together with a red product which decomposed on distillation at 8—10 mm. On oxidation with chromic acid, the latter affords benzophenone, and is probably a *polymeride* of the αβ-additive product, $CH_2{:}CH\cdot CH{:}CH\cdot CPh_2\cdot OH$. *Methyl β-phenylcinnamylideneacetate*, m. p. 49°, is obtained from methyl γβ-hydroxybenzylidene-β-phenylbutyrate (cf. Kohler and Heritage, A., 1910, i, 484) by boiling with methyl-alcoholic hydrochloric acid. It does not form additive products with methyl malonate, but condenses with ethereal magnesium phenyl bromide with formation of *ααγε-tetraphenyl-Δ$^{\beta\delta}$-pentadien-α-ol*, m. p. 121°. The latter, on treatment with methyl-alcoholic hydrogen chloride, affords a *chloride*, m. p. 64°, which readily loses hydrogen chloride with formation of *ααγε-tetraphenyl-Δ$^{\alpha\beta\delta}$-pentatriene*, m. p. 158°. It is concluded that αζ-addition does not take place as readily as αδ-addition. F. G. WILLSON.

Preparation of formaldehyde from methyl alcohol. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 463.

Production of butaldehyde. C. E. PIGG.—See B., 1926, 463.

Electrolytic reduction of acraldehyde. R. R. READ and R. M. FREER (J. Amer. Chem. Soc., 1926, 48, 1401—1405; cf. A., 1924, i, 613).—Electrolytic reduction of acraldehyde in dilute sulphuric acid, using lead electrodes, affords propaldehyde (6%), allyl and propyl alcohols (9%), Δ^1-*cyclo*pentenaldehyde (20%), and probably Δ^1-*cyclo*pentenylcarbinol. Divinyl glycol does not isomerise, under conditions similar to those obtaining in the above electrolysis, to form any product resembling the *cyclo*pentenaldehyde.
F. G. WILLSON.

Preparation and specific gravity of mesityl oxide. C. A. YLLNER (Svensk Kem. Tidskr., 1925, 37, 227—229; from Chem. Zentr., 1926, I, 51).—A mixture of acetone and concentrated sulphuric acid is stirred until homogeneous, and is poured into ice-water as soon as it becomes dark brown. The mesityl oxide is extracted with ether and is obtained in 25% yield, b. p. 128—131°, $d_4^{11.5}$ 0·8634.
F. H. HAMER.

Theory of catalysis. II. Kinetics of mutarotation. II. H. VON EULER and A. ÖLANDER.—See this vol., 580.

Reaction velocity and equilibrium between mutameric forms. H. VON EULER and I. HEDSTRÖM (Arkiv Kemi, Min., Geol., 1926, 9, No. 17, 1—6).—Neutral salts affect largely the speed of mutarotation of α- and β-dextrose, which show minimum stability at about the same p_H; it does not follow, however, that the dissociation constants of the sugars correspond. There is no evidence in favour of the existence of a third, undissociated, intermediate form.
C. RIMINGTON.

Relations between rotatory power and structure in the sugar group. XIII. Classification of various substances of the mannose and rhamnose series according to ring types. XIV. Determination of ring structures in the dextrose, mannose, and rhamnose series. C. S. HUDSON (J. Amer. Chem. Soc., 1926, 48, 1424—1434, 1434—1443; cf. this vol., 501).—XIII. Whilst many pairs of substances in the mannose, rhamnose, and lyxose series exhibit comparative rotation differences which are abnormal with respect to similar differences in the dextrose series, regarded as the normal values, other pairs in these series show normal comparative rotations. The abnormal differences are ascribed to the existence, in these series, of substances of varying ring type, whilst normal comparative rotations exist between substances of the same ring type.

XIV. A proof is given, based on rotatory relationships and on the amylene oxide ring structure of methyl-xyloside (Hirst and Purves, J.C.S., 1923, 123, 1352), -arabinoside (Hirst and Robinson, J.C.S., 1925, 127, 358), and -galactoside (Pryde, J.C.S., 1923, 123, 1808), that α- and β-methylglucosides and β-methyl-*iso*rhamnoside possess a butylene oxide ring, a conclusion corroborated by Hirst and Macbeth's (this vol., 273) chemical proof of the amylene oxide ring structure of methylrhamnoside, but at variance with Charlton, Haworth, and Peat's formulation (this vol., 273) of methylglucosides as possessing amylene oxide rings.
F. G. WILLSON.

Reactions between sugars and amines. I. Reaction between dextrose and glycine. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, 153, 1—9).—A mixture of equal quantities of 40% solution of dextrose and a 2*M*-solution of glycine shows at p_H 5·9 a change in optical rotation after 30 hrs. equal to 2·1% of the original rotation. If, however, the p_H is increased by the addition of sodium hydroxide solution, the change in rotation is much greater, and at p_H 9·6, after 24 hrs., it amounts to 32% of the original rotation. It is considered that, in presence of alkali, the equilibrium between the cyclic and aldehydic forms of dextrose is so altered as to increase the percentage of aldehyde, which then reacts with the amino-group of glycine. In presence of aniline a similar change in rotation is observed.
W. O. KERMACK.

Constitution of diacetonegalactose [galactose di*iso*propylidene ether]. O. SVANBERG (Arkiv Kemi, Min., Geol., 1926, 9, No. 16, 7—9).—Oxidation by alkaline permanganate yielded oxalic acid (30%) and a lævorotatory, non-reducing substance which gave the phloroglucinol, orcinol, and furfuraldehyde reactions. In acid solution, acetone was eliminated and galacturonic acid (60%) remained. The ζ-hydroxyl group of diacetonegalactose was unsubstituted.
C. RIMINGTON.

Behaviour of mannosediacetone [mannose di*iso*propylidene ether] on methylation. J. C. IRVINE and A. F. SKINNER (J.C.S., 1926, 1089—1097).—Mannose di*iso*propylidene ether displays normal mutarotation in *s*-tetrachloroethane or in faintly alkaline acetone; in water, mutarotation is abnormal. Like other reducing sugars, mannose di*iso*propylidene ether condenses with phenylhydrazine and aniline; it is converted by cold methyl-alcoholic acid into methylmannose di*iso*propylidene ether. It therefore contains one unsubstituted hydroxyl group in the reducing position and its behaviour towards alkylation is not abnormal.
A. DAVIDSON.

Variation of the hydrolysis constant of sucrose with the concentration. H. COLIN and (MLLE.) A. CHAUDUN.—See this vol., 580.

***iso*Maltose.** J. V. ISAJEV (Chem. Listy, 1926, 20, 251—254).—In addition to maltose and revertose, gentiobiose (isolated as the β-octa-acetate) is formed by the action of a yeast of low activity on dextrose in concentrated aqueous solution. The "*iso*maltose" of Emmerling (J.C.S., 1898, 73, 634) and probably those of Lintner and Ling and Nanji (*ibid.*, 1923, 123, 2666) are considered to be gentiobiose (cf. Berlin, this vol., 602).
L. M. CLARK.

An associated hexosan. M. BERGMANN and E. KNEHE (Annalen, 1926, 448, 76—89).—Lichosan prepared by Pringsheim's method (A., 1925, i, 1385) is never free from traces of solvents. When, however, these are removed by drying over phosphoric oxide at 78° in a vacuum, well-defined *lichohexosan* $(C_6H_{10}O_5)_4$ (monomeric *triacetate*, m. p. 180—182° after sintering at 145°, $[\alpha]_D^{20}$ −18·9° or −19·5° in chloroform), is obtained. Pure lichohexosan behaves as a typical non-reducing polysaccharide and affords cellobiose

octa-acetate on acetolysis. It is the first known complex carbohydrate which is readily soluble in water without depolymerisation. In solutions containing small quantities of electrolytes, however, the mol. wt. is much lower; this may explain the low values obtained by Pringsheim. It is unlikely that lichohexosan is the unit substance of lichenin.

H. E. F. NOTTON.

Violutoside, a new methyl salicylate glucoside extracted from *Viola cornuta*, L. P. PICARD (Compt. rend., 1926, **182**, 1167—1169).—By extraction of *Viola cornuta*, L., with alcohol, 0·001% of a glucoside, *violutoside*, m. p. 168·5°, $[\alpha]_D$ −36·2°, is obtained. It yields 31·14% of salicylic acid; when treated with sulphuric acid, 75·74% of reducing sugars are obtained, and when fermented by enzymes, the solution becomes dextrorotatory, probably owing to the formation of vicianose. It is suggested therefore that violutoside contains methyl salicylate combined with dextrose and *l*-arabinose. L. F. HEWITT.

Starch. XVII. Amylobiose. H. PRINGSHEIM and A. STEINGROEVER (Ber., 1926, **59**, [*B*], 1001—1006; cf. A., 1924, i, 714, 1171).—Amylobiose is converted by treatment with sodium hydroxide and methyl sulphate followed by silver oxide and methyl iodide into *hexamethylamylobiose*; further methylation appears impossible. The substance when acetylated in pyridine affords *monoacetylhexamethylamylobiose*, which, when methylated according to Heuser and Hiemer (this vol., 502), regenerates hexamethylamylobiose. Hydrolysis of the latter substance by 5% sulphuric acid or 1% methyl-alcoholic hydrogen chloride gives normal tetramethylglucose (identified as anilide or methylglucoside), thus establishing the normal structure of the glucoside portion of the molecule (cf. A., 1924, i, 1171). The glucose part of the disaccharide affords a monomethyl-methylglucoside closely resembling the 3-methyl-methylglucoside of Irvine and Scott (J.C.S., 1913, **103**, 572), from which it can only be deduced that the 3-hydroxy-group is not concerned with the union of the sugar residues or formation of the lactol ring. The γ-structure of the glucose portion is shown by the instability of the monomethyl-methylglucoside towards permanganate. Limited ability of becoming methylated appears common to the γ-sugars.

Trihexosan is readily dimethylated in one operation, but further methylation is very slow.

β-Hexa-amylose is obtained by the action of concentrated hydrochloric acid on α-tetra-amylose if the period of reaction is restricted. H. WREN.

Starch. XV. Specific action of amylases. H. PRINGSHEIM and J. LEIBOWITZ [with R. PEREWOSKY and W. KUSENACK] (Ber., 1926, **59**, [*B*], 991—995; cf. Pringsheim, Leibowitz and Silmann, A., 1925, i, 1244).—Quantitative conversion of starch, amylose, or amylopectin into dextrose is effected by a suitable combination of pancreatic and malt amylase (cf. Pringsheim and Leibowitz, A., 1925, i, 1043). Mixtures of salivary and pancreatic amylase have a similar action, but it is not possible to consider the former substance as a β-amylase, since it is inactive towards the characteristic substrate, amylobiose. The classification of the enzyme into two types is no longer adequate to explain the mechanism of the hydrolysis of starch. H. WREN.

Starch. XVI. Fermentative degradation of starch by "biolase." H. PRINGSHEIM and E. SCHAPIRO (Ber., 1926, **59**, [*B*], 996—1000).—"Biolase," a technical ferment of undisclosed origin, converts starch, but not amylobiose, at 37° into dextrose with small proportions of a reducing trisaccharide. The latter substance, $[\alpha]_D$ +160° or 165° to +128° or 129° in water (period 24 hrs.), is obtained by fermenting starch at 70°, removing dextrose by *Saccharomyces Marxianus*, concentration of the solution, and precipitation by alcohol; the phenylosazone, m. p. 120—122°, and *undeca-acetyl* derivative, $[\alpha]_D^{20}$ +120·8° in chloroform, are described. The trisaccharide appears identical with β-glucosidomaltose (Ling and Nanji, A., 1925, i, 516), but its behaviour towards enzymes does not afford certain evidence of the presence of a maltose or an *iso*maltose linking.

H. WREN.

Cellulose. XIX. Cryoscopic behaviour of crystalline cellulose acetates. K. HESS and G. SCHULTZE (Annalen, 1926, **448**, 99—120).—The anomalous results (cf. A., 1924, i, 143) obtained by the cryoscopic method for the mol. wt. of cellulose acetates in glacial acetic acid are due to dissolved air. The solubility of oxygen in acetic acid is considerably exalted by adding cellulose acetate. When the determination is carried out in an evacuated apparatus, correct results are obtained. Under these conditions, the mol. wt. of crystalline cellulose diacetate (A., 1925, i, 1245) in 0·05—0·6% solutions falls rapidly after dissolution to a mean value closely approximating to that required for a glucose anhydride diacetate. After remaining constant at this value for some days, it gradually increases to infinity. No indication is observed of the intermediate formation of molecules $(C_6H_{10}O_5)_2$, and the mol. wt. is not altered by heating the solution at 60°. The substance isolated from a solution which shows no further depression is identical in composition and crystalline form with the starting-material and undergoes the same changes when redissolved in acetic acid. Crystalline cellulose triacetate and *lichenin triacetate*, $[\alpha]_D$ −35·5°, behave in an exactly similar way. In presence of air, the mol. wt. decreases from a high initial value to one lower than that required for a C_6 molecule. When the solution is heated at 60°, the mol. wt. is temporarily exalted, but the complete reassociation observed in a vacuum does not take place. Since the cellulose acetates and cellulose are mutually interconvertible without change in structure, these observations afford strong evidence for the view that cellulose consists of glucose anhydride units bound together by cohesive forces only.

H. E. F. NOTTON.

Metallic complexes with aliphatic polyamines. F. G. MANN and (Sir) W. J. POPE (Proc. Camb. Phil. Soc., 1926, **23**, 183—186).—See this vol., 387.

Complex compounds of chromium with amino-acids. G. FLORENCE and E. COUTURE (Bull. Soc. chim., 1926, [iv], **39**, 643—646).—The violet and red compounds of chromium and glycine described by

Hugounenq and Morel (A., 1912, i, 168) are regarded as belonging to Werner's purpureo- and rhodoso-series, respectively, and are assigned the structures (I) and (II).

(I.) $\left[Cr\begin{matrix}(H_2O)_2\\(C_2H_5O_2N)_4\end{matrix}\right]$ $\left[\begin{matrix}&Cr&&\\OH&OH&OH&(C_2H_5O_2N)_3\\&Cr&&(C_2H_5O_2N)_3\end{matrix}\right]$ (II.)

The analogous asparagine rhodoso-*compound* (microscopic red needles) has been obtained by dissolving chromium hydroxide in a boiling solution of asparagine and by the action of an ammoniacal solution of asparagine on Pfeiffer's double compound of pyridine with chromium sesquichloride (A., 1900, i, 559). This compound does not lose water at 180°, but when boiled with water yields the hydrate $[Cr_2(OH)_3\cdot(C_4H_8O_3N_2)_6],2H_2O$, which loses 2 mols. of water again at 110°. Confirmation of these views is afforded by the preparation of a glycine derivative of the roseo-purpureo series (III), when ammonia is replaced by glycine in Jorgensen's chromous chloride method.

$\left[\begin{matrix}Cl\\Cr\ H_2O\\(C_2H_5O_2N_4)\end{matrix}\right],2H_2O$ (III.)

R. BRIGHTMAN.

Glycerol esters of the amino-acids. A. FODOR and M. WEIZMANN (Z. physiol. Chem., 1926, **154**, 290—292).—dl-*Leucine glyceryl ester*, m. p. 196—198°, is obtained in 10% yield by treatment of the dry sodium salt of *dl*-leucine with glycerol monochlorohydrin. C. R. HARINGTON.

Reaction product from glycylglycine. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1926, **153**, 147—149).—Glycylglycine heated with 10 parts of diphenylamine at 185—190° for 1½ hrs. yields, besides the enolic form of glycylglycine anhydride, a *substance*, $C_4H_8O_3N_2$, which on treatment with alcoholic hydrogen chloride, gives the hydrochloride of ethyl glycollate. No similar substance is obtained when glycyl-leucine is heated with diphenylamine.

W. O. KERMACK.

Preparation of peptides. R. SCHÖNHEIMER (Z. physiol. Chem., 1926, **154**, 203—224).—The toluenesulphonyl group can be eliminated from the toluenesulphonyl derivatives of dipeptides by warming at 50—60° with hydriodic acid (*d* 1·96) and phosphonium iodide, without appreciable hydrolysis of the peptide linking; it therefore becomes possible to synthesise peptides by coupling one amino-acid with the azide of the toluenesulphonyl derivative of another and subsequent treatment as above. From the ethyl ester of toluenesulphonylglycine were obtained the *hydrazide*, m. p. 155·5°, and the *azide*, which gave *toluenesulphonylglycylglycine*, m. p. 178·5°, *toluenesulphonylglycyl*-dl-*alanine*, m. p. 167°, and *toluenesulphonylglycyl*-dl-*leucine*, m. p. 87°. The ethyl ester of toluenesulphonyl-*dl*-alanine, m. p. 68°, yielded the *hydrazide*, m. p. 171°, *azide*, and *toluenesulphonyl*-dl-*alanylglycine*, m. p. 147°. The ethyl ester of toluenesulphonyl-*dl*-leucine, m. p. 83·5°, gave the *hydrazide*, m. p. 146°, *azide*, and *toluenesulphonyl*-dl-*leucylglycine*, m. p. 121·5°. The toluenesulphonyl derivatives of glycine, *dl*-leucine, *d*-alanine, and sarcosine were converted into the corresponding acid chlorides and these were used for the preparation, by Fischer's method, of *toluenesulphonylglycyl*-dl-*phenylalanine*, *toluenesulphonyl*-d-*alanyl*-l-*leucine*, m. p. 186°, $[\alpha]_D^{20}$ −30·52° in alcohol, and *toluenesulphonylsarcosyl*-d-*alanine*, m. p. 157°, $[\alpha]_D^{18}$ −6·09° in alcohol, from which the corresponding dipeptides were obtained in yields of 84—94%. C. R. HARINGTON.

Derivatives of carbamide. E. FROMM [with R. KAPELLER, L. PIRK, P. FANTL, L. CHAJKIN, A. HAHN, T. LIEPERT, M. ADLER, M. FENIGER, P. KRAUSS, M. SCHWANENFELD, and L. WETTERNIK] (Annalen, 1926, **447**, 259—313).—With the object of elucidating the tautomerism of derivatives of hydantoic acid (A., 1925, i, 595), the following reactions have been carried out. *Diethyl allophanylacetate*, $CO_2Et\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 120—121°, prepared by a modification of Saitzew's method (Annalen, 1865, **135**, 229), yields, on hydrolysis, the *monoethyl* ester, $CO_2Et\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, identical with the substance to which he attributed the formula $CO_2H\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$. *Ethyl allophanylacetamide*, $CO_2Et\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, m. p. 195°, and *biuretacetamide*, $NH_2\cdot CO\cdot NH\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, m. p. 225° (decomp.), are successively obtained from the diethyl ester and ammonia, whilst the monoethyl ester yields *biuretacetic acid*, m. p. 184—186°. *Ethyl biuretacetate* has m. p. 168°. The compound of this name described by Eppinger is ethyl hydantoate, and his biuretacetamide and glycollyldicarbamide are impure hydantoamide. 2-*Amino-oxazoline acetate* has m. p. 135°.

Methyl iodide acts on the amino-group, giving 2-*methylamino-oxazoline hydriodide*, m. p. 179°, from which 2-*benzamidomethyloxazoline*, m. p. 166°, is obtained. When 2-amino-oxazoline reacts with a thiocarbimide, two different thiocarbamides,

$\begin{matrix}CHX\cdot CH_2\\O\text{–}C(:NH)\end{matrix}\!\!>\!N\cdot CS\cdot NHR$ (I.) and $\begin{matrix}CH_2\text{–}N\\CHX\cdot O\end{matrix}\!\!>\!C\cdot NH\cdot CS\cdot NHR$ (II.)

are obtained, according to the temperature at which the reaction is carried out. The first, low-melting form is readily hydrolysed to the ketone,

$\begin{matrix}CHX\cdot CH_2\\O\text{——}CO\end{matrix}\!\!>\!N\cdot CS\cdot NH_2$ (III); when heated in solvents above its m. p., it is converted into the second, high-melting form. This is due to redissociation into base and thiocarbimide, followed by tautomeric change in the amino-oxazoline and recombination to the stable isomeride. The following compounds are described: 2-*imino-oxazolinyl*-3-*phenylthiocarbamide* [(I), R=Ph, X=H], m. p. 76°, resolidifying with m. p. 161°; *oxazolidonyl*-3-*phenylthiocarbamide* (III), m. p. 105°; *oxazolinyl*-2-*phenylthiocarbamide* (II), m. p. 161° (*sulphate*, m. p. 171°); 2-*imino-oxazolinyl*-3-*allylthiocarbamide*, m. p. 101° [*dibromide*, m. p. 200° (decomp.)]; *oxazolidonyl*-3-*allylthiocarbamide*, m. p. 65° (*dibromide*, m. p. 159°); *oxazolinyl*-2-*allylthiocarbamide*, m. p. 121°; 2-*amino*-5-*iodomethyloxazoline*, m. p. 129°; *monoacetyl*-5-*chloromethyloxazoline acetate*, m. p. 180°; the corresponding *bromomethyl* compound, m. p. 167·5°; 2-*imino*-5-*chloromethyloxazolinyl*-3-*phenylthiocarbamide* [(I), R=Ph, X=CH_2Cl], m. p. 78°; 5-*chloromethyloxazolidonyl*-3-*phenylthiocarbamide* (III), m. p. 124°; 5-*chloromethyloxazolinyl*-2-*phenylthiocarbamide*, m. p. 159°; 2-*imino*-5-*chloromethyl*-

oxazolinyl-3-*allylthiocarbamide*, m. p. 84° (*dibromide*, m. p. 130°), which condenses in presence of hydrochloric acid to 3-*methylthiazolinyl*-5-*chloromethyloxazolidone*, $\begin{matrix}CH_2—N\\ CHMe\cdot S\end{matrix}\!\!>\!C\cdot N<\!\!\begin{matrix}CO—O\\ CH_2\cdot CH\cdot CH_2Cl\end{matrix}$, m. p. 100°; 5-*chloromethyloxazolinyl*-2-*allylthiocarbamide*, m. p. 125°, and 5-*chloromethyloxazolidonyl*-3-*allylthiocarbamide*, m. p. 50°.

Hydroxylamine acts on organic disulphides with adjacent double linkings (cf. A., 1906, i, 656) in various ways. Thiobenzoylthioacetic acid disulphide (A., 1897, i, 191) is unattacked. Perthiocyanic acid undergoes alkaline hydrolysis. Phenylthiourethane sulphide is reduced to phenylthiourethane. Formamidine disulphide nitrate forms, possibly, oxyguanidine. The above nitrate gives with aniline phenylguanidine and with diethylamine *as*.-diethylguanidine (*picrate*, m. p. 220°). With hydroxylamine, benzoyl disulphide gives *dibenzhydroxamic acid*, Ph·CO·NH·O·CO·Ph, m. p. 160°, and some benzhydroxamic acid. Phenylthiuret affords a compound, m. p. 130°, 3(?5)-*amino*-5(?3)-*anilino*-2 : 4-*furodiazole*. The *nitrate*, m. p. 210—215° (decomp.), *hydrochloride* (+$1H_2O$), m. p. 137°, *picrate*, m. p. 236°, *dibenzoyl* derivative, m. p. 168°, and the *nitro-nitrate*, $C_8H_7ON_4(NO_2)$,HNO_3, m. p. 205° (decomp.), of the base are described. Hydroxylamine reacts incompletely with hydrogen sulphide, forming sulphur and ammonia in stoicheiometrical proportions.

Hydrazodithiodicarbonamide yields on acetylation and benzoylation 3 : 5-diacetamido- and 3 : 5-dibenzamido-4 : 1 : 2-thiodiazole (A., 1923, i, 1239), whilst with hydroxylamine, 3 : 5-diamino-4 : 1 : 2-thiodiazole (*thiocyanate*, m. p. 208°) is formed. 5-*Thiol*-4-*benzoyl*-3-*phenyl*-1 : 2 : 4-*triazole*, $\begin{matrix}N=CPh\\ N:C(SH)\end{matrix}\!\!>\!NBz$, m. p. 235° (*benzyl* derivative, m. p. 174°), is obtained on benzoylating both thiosemicarbazide and the so-called phenylaminothiodiazoline of Young and Eyre (J.C.S., 1901, **79**, 54), which must therefore be 5-*thiol*-3-*phenyl*-1 : 2 : 4-*triazole* (*benzyl* derivative, m. p. 160°). 5-Amino-3-methyl-4 : 1 : 2-thiodiazole (A., 1897, i, 122) (*benzoyl* derivative, m. p. 250°) gives with phenylthiocarbimide 5-*amino*-3-*methyl*-4 : 1 : 2-*thiodiazolylphenylthiocarbamide*, m. p. 230—255°. 4-p-*Tolylthiosemicarbazide*, m. p. 142°, yields *semicarbazones* with benzaldehyde and acetone of m. p. 171° and 142°, respectively. On benzoylation, it behaves normally (cf. A., 1924, i, 93), yielding unstable yellow benzoyl derivatives, from which, when heated with sodium hydroxide, 4-p-*tolylsemicarbazide tetrabenzoate*, m. p. 157—158°, and *dibenzoate*, m. p. 239°, are produced. The latter is converted by phosphoryl chloride into 2-*benzoyl*-5-*phenyl*-4-p-*tolyl*-1 : 2 : 4-*triazol*-3-*one*, m. p. 139°. When 4-*p*-tolylthiosemicarbazide is heated with benzoyl chloride, 3-*tolylimino*-5-*phenyl*-4 : 1 : 2-*thiodiazoline*, m. p. 201°, its 2-*benzoyl* derivative, m. p. 214°, and 3-*thio*-2-*benzoyl*-5-*phenyl*-4-*tolyl*-1 : 2 : 4-*triazole*, m. p. 175—180°, are formed. This last is hydrolysed by alcoholic sodium hydroxide to 3-*thio*-5-*phenyl*-4-*tolyl*-1 : 2 : 4-*triazole*, m. p. 224—225° (*benzyl* derivatives, m. p. 166°). *Di*-p-*tolylhydrazodithiodicarbonamide*, m. p. 205°, is converted by sodium hydroxide into the *compound*, $C_{16}H_{16}N_4S$, m. p. 198° (*benzyl* derivative, m. p. 127°), and by iodine into 3 : 5-*ditoluidino*-4 : 1 : 2-*thiodiazole*, m. p. 251° (*dibenzoate*, m. p. 217°). Diphenylhydrazodithiodicarbonamide affords with excess of acetyl chloride 3 : 5-dianilino-4 : 1 : 2-thiodiazole (*diacetate*, m. p. 227°; *dibenzoate*, m. p. 243°), and, on benzoylation, 2-*benzoyl*-3-*anilino*-5-*thiol*-4-*phenyl*-1 : 2 : 4-*triazole*, m. p. 279° (*benzyl* derivative, m. p. 162°), and the 1 : 2-*dibenzoyl* derivative, m. p. 179°. The corresponding *acetyl* derivative has m. p. 281° (*benzyl* derivative, m. p. 157°). The benzylbenzylidene derivative (N-*benzoyl* derivative, m. p. 235°) of 3 : 4-diamino-5-thiol-1 : 2 : 4-triazole (*benzyldibenzylidene* derivative, m. p. 170°) has a unimolecular formula (cf. Arndt and Bielich, A., 1923, i, 612). The *lead* salt and *benzyl* derivative, m. p. 234°, of 3-thiol-1 : 2 : 4-triazolyl-5-benzylidenehydrazone, 1 : 2 : 4-*triazolyl*-5-*benzylidenehydrazone* 3-*disulphide*, m. p. 252°, and 3-*thiol*-1 : 2 : 4-*triazolyl*-4-*phenylthiosemicarbazide*, m. p. 238°, are described. H. E. F. NOTTON.

Ethylguanidine and *NN*-dimethyl-*N'*-ethylguanidine. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1926, **154**, 293—301).—*Ethylguanidine* [*chloroaurate*, m. p. 100—103°, *chloroplatinate*, m. p. 188—190° (decomp.), *picrate*, m. p. 178—180°, *picrolonate*, m. p. 285° (efferv.)] was prepared (1) from methyl-ψ-thiocarbamide hydroiodide and ethylamine, (2) from methyl-*N*-ethyl-ψ-thiocarbamide hydriodide and ammonia. NN-*Dimethyl*-N'-*ethylguanidine*, from triethyl-ψ-thiocarbamide hydriodide and ethylamine, has *chloroaurate*, m. p. 82—84°, *chloroplatinate*, m. p. 165—167°, *picrate*, m. p. 148—152°, *picrolonate*, m. p. 174°. C. R. HARINGTON.

***N'N'S*-Trimethyl-ψ-thiocarbamide. Formation of methylated guanidines.** M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1926, **153**, 150—165).—*N'N'S*-Trimethyl-ψ-thiocarbamide, obtained as the methosulphate by the action of methyl sulphate on *NN'*-dimethylthiocarbamide, reacts with ammonia to yield *NN'*-dimethylguanidine [*chloroaurate*, m. p. 246—247° (decomp.); *picrate*, m. p. 228°; *picrolonate*, decomp. 276—277°]. Methylamine yields similarly trimethylguanidine, NH:C(NHMe)·NMe_2 [*chloroaurate*, m. p. 155—156°; *chloroplatinate*, m. p. 175—177° (decomp.); *picrate*, m. p. 151—152°; *picrolonate*, m. p. 210°]. When, however, the reaction takes place at 130°, there is formed *s*-trimethylguanidine, $NMe:C(NHMe)_2$ [*chloroaurate*, m. p. 156°; *chloroplatinate*, m. p. 226—227° (decomp.); *picrate*, m. p. 216°; *picrolonate*, decomp. 232°], whilst at 100° the product consists of a mixture of *s*-trimethylguanidine and *s*-dimethylguanidine, $NH:C(NHMe)_2$ (*chloroaurate*, m. p. 122°; *picrolonate*, m. p. 260—262°). W. O. KERMACK.

Guanidine studies. I. Synthesis of *N*-methyl-*N*-(β-guanidinoethyl)guanidine (Kutscher's vitiatine?). H. SCHOTTE and H. PRIEWE (Z. physiol. Chem., 1926, **153**, 67—73; cf. *ibid.*, 1907, **51**, 457).—Methyl-(β-aminoethyl)amine prepared by the action of hydrochloric acid on *N*-methyl-*N*-(β-hydroxyethyl)guanidine reacts with the hydrobromide of *S*-ethyl*iso*thiocarbamide to yield *N*-methyl-*N*-(β-guanidinoethyl)guanidine (*picrate*, m. p. 241°;

picrolonate, decomp. 283—284°; *hydrochloride*; *chloroaurate*, softening at 240—242°).

W. O. KERMACK.

Synthesis of alkylthiocarbimides and thiocarbamide derivatives by means of thiocarbonyl chloride. G. M. DYSON and R. F. HUNTER (Rec. trav. chim., 1926, **45**, 421—423).—Alkylthiocarbimides are readily obtained in good yield by the action of a primary amine on thiocarbonyl chloride in presence of water. G. M. BENNETT.

Alkylation of aliphatic nitriles. Preparation of di- and tri-alkylacetonitriles. P. RAMART (Compt. rend., 1926, **182**, 1226—1227).—Hydrocarbon radicals may be introduced into aliphatic nitriles by the action of halides on the nitriles, using sodamide as condensing agent. Benzyl chloride reacts with *n*-valeronitrile, yielding *α-benzylvaleronitrile*, b. p. 157—159°/20 mm. (*α-benzylvaleramide*, m. p. 100—101°). Benzyl chloride reacts with octonitrile, giving *α-benzyloctonitrile*, b. p. 170—172°/15 mm. (*α-benzyloctamide*, m. p. 90°). *α-Benzyl-α-ethylbutyronitrile*, b. p. 175°/35 mm., is obtained by the action of benzyl chloride on ethylbutyronitrile. L. F. HEWITT.

Regularities in m. p. and b. p. of methyl mercuri-salts and the corresponding acids. Structure of hydrocyanic acid and the cyanides. C. J. ENKLAAR (Rec. trav. chim., 1926, **45**, 414—416; cf. A., 1925, i, 1394).—From analogies in m. p. and b. p. between cyanogen and halogen compounds such as α-trichloroethane, acetonitrile, chloroform, hydrogen cyanide, and the mercuric methyl halides and the isomeric mercuric methyl cyanides, the conclusion is reached that hydrocyanic acid should have b. p. 69° and *iso*hydrocyanic acid b. p. 129·7°. The formula H·NC is deduced for ordinary hydrocyanic acid from which the sodium and potassium salts are structurally derived, whilst for the labile *iso*hydrocyanic acid the formula $H_2(CN)_2$ is advocated (cf. Nef, A., 1896, i, 76), and the mercury, silver, and palladium salts are regarded as derived from this form. (Cf. Pauling and Hendricks, this vol., 458.)

G. M. BENNETT.

Direct preparation of mixed organoberyllium compounds. J. F. DURAND (Compt. rend., 1926, **182**, 1162—1164).—Beryllium does not react with organic halides like magnesium, probably owing to the formation of a coating of insoluble beryllium organic halide on the surface of the metal; in the presence of a small amount of mercuric chloride, beryllium reacts with warm methyl iodide in anhydrous ethereal solution, giving *beryllium methyl iodide*. *Beryllium ethyl iodide*, prepared in a similar manner, reacts with hydrochloric acid, yielding ethane, but does not appear to be decomposed by water. L. F. HEWITT.

Preparation of a Grignard reagent in a test-tube in the presence of moisture. H. SCHMALFUSS (J. pr. Chem., 1926, [ii], **113**, 46—47).—Magnesium ethyl bromide is easily prepared with ordinary instead of anhydrous ether, a crystal of iodine being used to induce reaction. C. HOLLINS.

Reaction between organomagnesium halides and the aryl esters of boric, carbonic, silicic, and phosphoric acids. H. GILMAN and C. C. VERNON (J. Amer. Chem. Soc., 1926, **48**, 1063—1066).—The formation of toluene in the reaction between trimethyl borate and magnesium phenyl bromide, as reported by Khotinsky and Melamed (A., 1909, i, 864), is not confirmed. Similarly, no arylating action takes place in the reactions between triphenyl borate and magnesium *n*-butyl bromide, diphenyl carbonate and magnesium phenyl bromide, tetra-*p*-tolyl silicate and magnesium phenyl bromide, triphenyl and tri-*p*-tolyl phosphates, and magnesium phenyl bromide and magnesium benzyl chloride, respectively, and between triphenyl phosphite and magnesium phenyl bromide, the aryloxy-group being replaced in each case. F. G. WILLSON.

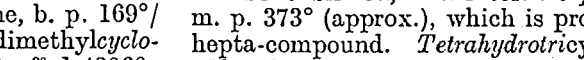
Atomic refraction of zinc in its dialkyl compounds and preparation of homogeneous, mixed zinc dialkyls. E. KRAUSE and W. FROMM (Ber., 1926, **59**, [*B*], 931—934).—The atomic refraction of zinc increases in the zinc dialkyls with increasing weight of the hydrocarbon residues. Mixed zinc dialkyls are prepared by the interaction of zinc alkyl iodides with magnesium alkyl halides, all operations being conducted at the lowest possible temperature. *Zinc ethyl*-n-*propyl*, b. p. 27°/10 mm., $d_4^{18\cdot5}$ 1·1558, $n_D^{17\cdot0}$ 1·48913; *zinc ethyl*isobutyl, b. p. 48°/11 mm., $d_4^{16\cdot6}$ 1·0861, $n_D^{16\cdot6}$ 1·47507; *zinc* n-*propyl*isobutyl, b. p. 52°/9 mm., $d_4^{17\cdot0}$ 1·0465, $n_D^{15\cdot9}$ 1·46966, and *zinc* isobutylisoamyl, b. p. 84°/11 mm., $d_4^{18\cdot1}$ 1·0058, $n_D^{16\cdot0}$ 1·46937, are described. The unsymmetrical derivatives become rearranged more or less readily to symmetrical compounds. H. WREN.

Atomic refraction and atomic dispersion of mercury in mercury dimethyl and mercury diethyl. E. KRAUSE (Ber., 1926, **59**, [*B*], 935—936; cf. preceding abstract).—Mercury dimethyl, prepared by the action of magnesium methyl bromide on mercuric bromide, has b. p. 92°/761 mm., $d_4^{19\cdot2}$ 3·0836, $n_D^{16\cdot8}$ 1·54735, whereas mercury diethyl has b. p. 57°/16 mm., d_4^{20} 2·4660, $n_D^{16\cdot9}$ 1·54765. The atomic refraction and dispersion of mercury are greater in the diethyl than in the dimethyl compound. The increment caused by the replacement of methyl by ethyl is approximately a constant quantity for mercury, cadmium, tin, and lead in analogous compounds. H. WREN.

Molecular coefficients of refraction of polymethylene compounds. F. EISENLOHR with G. GORR (Fortschr. Chem., 1925, **B**, **18**, 1—48; from Chem. Zentr., 1926, I, 73—76; cf. A., 1921, ii, 229).—The optical constants of polymethylene compounds have been determined and the values of the molecular refractivities in the case of *cis*- and *trans*-forms are compared. Various regularities are discussed.

The following data are recorded: *cyclo*pentane, b. p. 50·0°/756 mm., d_4^{20} 0·7510, n_{He}^{20} 1·40609; methyl*cyclo*pentane, b. p. 70·0—70·5°/755 mm., d_4^{20} 0·7459, n_{He}^{20} 1·40947; ethyl*cyclo*pentane, b. p. 100·5—101·0°/756 mm., d_4^{20} 0·7610, n_{He}^{20} 1·41840; propyl*cyclo*pentane, b. p. 129·5°/754 mm., d_4^{20} 0·7718, n_{He}^{20} 1·42470; *iso*propyl*cyclo*pentane, b. p. 128—129°/754 mm., d_4^{20} 0·7717, n_{He}^{20} 1·42470; *iso*butyl*cyclo*pentane, b. p. 148—

149°/756 mm., d_4^{20} 0·7795, n_{He}^{20} 1·42950; *cyclo*hexane, b. p. 80·3°/750 mm., d_4^{20} 0·7783, n_{He}^{20} 1·42680; methyl*cyclo*hexane, b. p. 100·0°/758 mm., d_4^{20} 0·7748, n_{He}^{20} 1·42630 and also b. p. 100·0°/770 mm., d_4^{20} 0·7725, n_{He}^{20} 1·42500; ethyl*cyclo*hexane, b. p. 129·5°/756 mm., d_4^{20} 0·7840, n_{He}^{20} 1·43251; propyl*cyclo*hexane, b. p. 154·5—155·5°/756 mm., d_4^{20} 0·7898, n_{He}^{20} 1·43592; *iso*propyl*cyclo*hexane, b. p. 152—153°/756 mm., d_4^{20} 0·7902, n_{He}^{20} 1·43642; *iso*butyl*cyclo*hexane, b. p. 169°/754 mm., d_4^{20} 0·7950, n_{He}^{20} 1·43904; *cis-o*-dimethyl*cyclo*hexane, b. p. 126·5°/750 mm., d_4^{20} 0·7822, n_{He}^{20} 1·43060; *trans-o*-dimethyl*cyclo*hexane, b. p. 124·5°/755 mm., d_4^{20} 0·7798, n_{He}^{20} 1·42990; *cis-m*-dimethyl*cyclo*hexane, b. p. 121·0°/760 mm., d_4^{20} 0·7735, n_{He}^{20} 1·42600; *trans-m*-dimethyl*cyclo*hexane, b. p. 119°/756 mm., n_{He}^{20} 1·42480; *cis-p*-dimethyl*cyclo*hexane, b. p. 120·5°/755 mm., d_4^{20} 0·7671, n_{He}^{20} 1·42270; *trans-p*-dimethyl*cyclo*hexane, b. p. 119·0—119·5°/760 mm., d_4^{20} 0·7638, n_{He}^{20} 1·42120; *cis*-1 : 2 : 3-trimethyl*cyclo*hexane, b. p. 144—146°/755 mm., d_4^{20} 0·7930, n_{He}^{20} 1·43682; *trans*-1 : 2 : 3-trimethyl*cyclo*hexane, b. p. 142—146·5°/762 mm., d_4^{20} 0·7914, n_{He}^{20} 1·43582; *cis*-1 : 2 : 4-trimethyl*cyclo*hexane, b. p. 141·5°/760 mm., d_4^{20} 0·7850, n_{He}^{20} 1·43341; *trans*-1 : 2 : 4-trimethyl*cyclo*hexane, b. p. 138·5—139·5°/755 mm., d_4^{20} 0·7813, n_{He}^{20} 1·43121; *cis*-1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 140·0—140·5°/752 mm., d_4^{20} 0·7773, n_{He}^{20} 1·43010; *trans*-1 : 3 : 5-trimethyl*cyclo*hexane, b. p. 138—139°/761 mm., d_4^{20} 0·7720, n_{He}^{20} 1·42710; *cis*-1 : 2 : 3 : 5-tetramethyl*cyclo*hexane, b. p. 168—170°/762 mm., d_4^{20} 0·8166, n_{He}^{20} 1·44847; *trans*-1 : 2 : 3 : 5-tetramethyl*cyclo*hexane, b. p. 162—164°/765 mm., d_4^{20} 0·8140, n_{He}^{20} 1·44657; *cis*-1 : 2 : 4 : 5-tetramethyl*cyclo*hexane, b. p. 171°/755 mm., d_4^{20} 0·8122, n_{He}^{20} 1·44647; *trans*-1 : 2 : 4 : 5-tetramethyl*cyclo*hexane, b. p. 166—168°/760 mm., 169—170°/765 mm., d_4^{20} 0·8100, n_{He}^{20} 1·44446, 1·44527; *cis-o*-methyl*cyclo*hexanol, b. p. 170·0°/755 mm., d_4^{20} 0·9280, n_{He}^{20} 1·46225; *trans-o*-methyl*cyclo*hexanol, b. p. 168·5°/750 mm., d_4^{20} 0·9254, n_{He}^{20} 1·46165; *cis-m*-methyl*cyclo*hexanol, b. p. 175·5°/760 mm., d_4^{20} 0·9250, n_{He}^{20} 1·46086; *trans-m*-methyl*cyclo*hexanol, b. p. 174·5—174·7°/762 mm., d_4^{20} 0·9234, n_{He}^{20} 1·45931; *cis-p*-methyl*cyclo*hexanol, b. p. 175·5°/760 mm., d_4^{20} 0·9223, n_{He}^{20} 1·45926; *trans-p*-methyl*cyclo*hexanol, b. p. 174·5°/760 mm., d_4^{20} 0·9172, n_{He}^{20} 1·45727; *o*-methyl*cyclo*hexanone, b. p. 165·0°/757 mm., d_4^{20} 0·9240, n_{He}^{20} 1·44747; *m*-methyl*cyclo*hexanone, b. p. 170·5°/755 mm., d_4^{20} 0·9182, n_{He}^{20} 1·44526; *p*-methyl*cyclo*hexanone, b. p. 171·0°/748 mm., d_4^{20} 0·9130, n_{He}^{20} 1·44336; propyl*cyclo*pentene, b. p. 131—133°/760 mm., d_4^{20} 0·8062, n_{He}^{20} 1·45047; *iso*butyl*cyclo*pentene, b. p. 152—154°/758 mm., d_4^{20} 0·8203, n_{He}^{20} 1·46046; *methyl*cyclo*hexene*, b. p. 108·0—108·5°/769 mm., d_4^{20} 0·8106, n_{He}^{20} 1·45017; ethyl*cyclo*hexene, b. p. 134·0—134·5°/760 mm., d_4^{20} 0·8217, n_{He}^{20} 1·46020; propyl*cyclo*hexene, b. p. 157·5—158·5°/756 mm., d_4^{20} 0·8210, n_{He}^{20} 1·46251; *iso*butyl*cyclo*hexene, b. p. 172—174·5°/755 mm., d_4^{20} 0·8401, n_{He}^{20} 1·47166. F. M. HAMER.

Highly polymerised compounds. VII. Di*cyclo*pentadiene and other polymeric *cyclo*pentadienes. VIII. Polymerisation (catalysed) of *cyclo*pentadiene. H. STAUDINGER and H. A. BRUSON (Annalen, 1926, **447**, 97—110, 110—122).—VII. For the most part, a detailed account of work already described (A., 1924, i, 274; this vol., 56). The general formula,  best accounts for the progressive formation of the poly*cyclo*pentadienes and their ready depolymerisation to *cyclo*pentadiene. Poly*cyclo*pentadiene has been resolved into *penta*cyclo*pentadiene*, m. p. 270°, which can be sublimed, and insoluble *poly*cyclo*pentadiene*, m. p. 373° (approx.), which is probably the hexa- or hepta-compound. *Tetrahydrotri*cyclo*pentadiene*, m. p. 43°, closely resembles the other tetrahydropolymerides. *X*-Ray analysis shows that all the polymerides are crystalline, tetra-, penta-, and poly-*cyclo*pentadienes giving an identical spectrum.

VIII. *cyclo*Pentadiene is converted by catalysts into a white amorphous powder, closely resembling caoutchouc in appearance, and in its power of forming colloidal, thinly viscous solutions in organic solvents. Stannic chloride, titanium tetrachloride, antimony pentachloride, and other compounds which exhibit "auxiliary valency" are the best catalysts. The polymeride is conveniently identified by the blue colour which it gives with hydrogen chloride in benzene solution. Various specimens show mol. wts. from 20 to 100 times that of *cyclo*pentadiene. It unites with 1 mol. of bromine or one atom of oxygen per mol. of *cyclo*pentadiene. The yellow, amorphous *oxide*, *ozonide*, *nitrosite*, and sulphur monochloride additive *product* decompose on heating. Dry distillation of the polymeride yields *cyclo*pentadiene with some products of higher b. p. H. E. F. NOTTON.

Methylation of xylene. Preparation of durene, pentamethylbenzene, and hexamethylbenzene. L. I. SMITH and F. J. DOBROVOLNY (J. Amer. Chem. Soc., 1926, **48**, 1413—1419).—Xylene and aluminium chloride are heated to 95° and methyl chloride is passed rapidly through the mixture. The main fraction, b. p. 180—205°, of the product, when cooled, yields durene. The yield of the latter can be increased to 25—35% by heating the filtrate from the first crop of durene with aluminium chloride, and by methylation of the trimethylbenzene fraction, b. p. 150—180°. Pentamethylbenzene can be obtained in about 33% yield by continuing the methylation, whilst hexamethylbenzene is best prepared by a similar methylation of pentamethylbenzene in presence of a large proportion of aluminium chloride, and fractionating the crude product under reduced pressure. F. G. WILLSON.

Hydrogenation of naphthalene. "PRAX" CHEM. VERSUCHS- U. VERWERTUNGS-G.M.B.H.—See B., 1926, 433.

Diacene (diacenaphthylene) and its ketonic derivatives. K. DZIEWOŃSKI and T. LITYŃSKI (Rocz. Chem., 1926, **6**, 15—22).—See this vol., 160.

Derivatives of *p*-bromoallylbenzene. R. QUELET (Compt. rend., 1926, **182**, 1283—1285).—*p-Bromoallylbenzene*, b. p. 99°/15 mm., is obtained in 70% yield by condensation of allyl bromide and the magnesium derivative of *p*-dibromobenzene. Bromine addition occurs readily to give a liquid, b. p. 185°/41 mm. (decomp.). *p*-Bromoallylbenzene forms *p*-bromopropenylbenzene, m. p. 35°, when heated with

amyl-alcoholic potassium hydroxide. Magnesium *p*-propenylphenyl bromide with oxygen yields *p*-propenylphenol, and with ethyl orthoformate *p*-propenylbenzaldehyde, b. p. 132°/17 mm., d_4^{11} 1·044, n_D^{11} 1·606 (*semicarbazone*, m. p. 230°). Magnesium *p*-allylphenyl bromide gives, similarly, p-*allylbenzaldehyde*, b. p. 112°/15 mm., and *p*-allylphenol.

R. A. MORTON.

Action of alcoholic alkali hydroxide on *m*-nitrobenzylidene halides. A. KLIEGL and W. HÖLLE (Ber., 1926, **59**, [*B*], 901—909).—Nitrobenzylidene chloride is converted by ethyl-alcoholic sodium ethoxide below 30° into *m*-nitrobenzaldehydediethylacetal with small proportions of 5-*nitro*-2-*ethoxybenzyl ethyl ether*, m. p. 93°, and 3-*nitro*-4-*ethoxybenzyl ethyl ether*, b. p. 183—184°/11 mm. The constitution of the former compound is established by its conversion successively into 5-*nitro*-2-*ethoxybenzyl bromide*, m. p. 85·5°, 5-*nitro*-2-*ethoxybenzyl acetate*, m. p. 54°, 5-*nitro*-2-*ethoxybenzyl alcohol*, m. p. 103°, and 5-nitro-2-ethoxybenzoic acid, m. p. 161—161·2°. Similarly, 3-nitro-4-ethoxybenzyl ethyl ether affords 3-*nitro*-4-*ethoxybenzyl bromide*, m. p. 97—98°, 3-*nitro*-4-*ethoxybenzyl acetate*, m. p. 46—46·5°, 3-nitro-4-ethoxybenzyl alcohol, m. p. 66°, and 3-*nitro*-4-*ethoxybenzoic acid*, m. p. 197°, which is dealkylated to 3-nitro-4-hydroxybenzoic acid.

[With B. VON KLITZING.]—*m*-Nitrobenzylidene bromide reacts similarly to the chloride with sodium ethoxide, except that it affords more than twice the proportion of ethers at the expense of the acetal.

m-Nitrobenzylidene chloride and sodium methoxide yield 5-*nitro*-2(?)-*methoxybenzyl methyl ether*, m. p. 71°, and 3-nitro-4-methoxybenzyl methyl ether identified by conversion into 3-nitro-4-methoxybenzyl bromide, m. p. 108° (cf. Shoesmith and Hetherington, A., 1924, i, 842).

[With G. BALZ.]—The action between *m*-nitrobenzylidene chloride and sodium propoxide proceeds similarly to those just described; 5-*nitro*-2-*propoxybenzyl propyl ether*, m. p. 65°, and 3-*nitro*-4-*propoxybenzyl bromide*, m. p. 59·5—60°, have been isolated.

H. WREN.

Separation of *o*- and *p*-chloronitrobenzene. VEREIN FÜR CHEM. U. METALLURGISCHE PRODUKTION.—See B., 1926, 433.

Crystal forms of some position-isomeric dinitrotoluenes. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 54—58).—Detailed crystallographic data are given for 2 : 3-, 2 : 4-, 2 : 6-, 3 : 4-, and 3 : 5-dinitrotoluene. The first and third are rhombic-bipyramidal and the remainder monoclinic-prismatic. Measurements have also been made of crystals of 2 : 4 : 6- and 3 : 4 : 6-trinitrotoluene, which are both rhombic-pyramidal. The results show that there does not exist a close form analogy between the mono-, di-, and tri-nitrotoluenes.

M. S. BURR.

Reduction of nitro- to azoxy-compounds by magnesium and ammonium chloride solution. L. ZECHMEISTER and P. ROM (Ber., 1926, **59**, [*B*], 867—874).—Azoxy-compounds are obtained by the addition of magnesium turnings (twice the theoretical quantity) to dilute solutions of substituted nitrobenzenes in methyl alcohol to which 0·3—0·5 vol. of saturated aqueous ammonium chloride solution has been added. The yields with *o*-, *m*-, and *p*-nitrotoluene are 61%, 69%, and 71%, with the chloronitrobenzenes, 57%, 90%, and 81%, and with the corresponding bromo-derivatives, 30% 59%, and 57%. Nitrobenzene does not give more than 40% of azoxybenzene or 37% in the absence of organic solvent. The stability of the azoxy-compounds under the experimental conditions is remarkable, since azoxybenzene (and also azobenzene) is quantitatively converted by magnesium and ammonium chloride into hydrazobenzene. Under certain conditions, arylhydroxylamines are obtained in small amount. Azoxy-compounds may also be prepared in good yield by treatment of nitro-derivatives with magnesium and slightly aqueous methyl alcohol.

Benzophenone is reduced to benzhydrol by the ammonium chloride method. H. WREN.

Oxidation of sulphides to sulphoxides. R. KNOLL (J. pr. Chem., 1926, [ii], **113**, 40—45).—Sulphides are dissolved in 70—80% acetic acid and 10—20% excess of chromic acid in a little water is added at 60—80°, whereby sulphoxides are produced. *Phenyl diphenylmethyl sulphide*, m. p. 82°, from ω-bromodiphenylmethane and thiophenol at 60—70°, yields with chromic–acetic acid (even in 100% excess) the *sulphoxide*, m. p. 139°, whereas with hydrogen peroxide or potassium permanganate the product is the *sulphone*, m. p. 188°. *α-Naphthyl diphenylmethyl sulphide*, m. p. 77°, similarly prepared from α-thionaphthol, gives with chromic–acetic acid or hydrogen peroxide the *sulphoxide*, m. p. 128°. Phenyl triphenylmethyl sulphide, m. p. 105—106°, is unattacked by hydrogen peroxide, but the *sulphoxide*, m. p. 163°, is readily obtained by the chromic–acetic acid method, which is also applied to the preparation of diphenyl, dibenzyl, diamyl, and di-α-naphthyl sulphoxides.

C. HOLLINS.

Preparation of di-iodoacetanilides. I. L. VECCHIOTTI (Gazzetta, 1926, **56**, 152—154).—Treatment of acetanilide-2 : 4-dimercuriacetate (A., 1914, i, 1063) with iodine in aqueous potassium iodide solution yields 2 : 4-*di-iodoacetanilide*, m. p. 169°.

T. H. POPE.

Colour reaction for cyclic primary amines. J. A. SANCHEZ (Anal. Asoc. Quím. Argentina, 1925, **13**, 431—439).—A cold saturated aqueous solution of furfuraldehyde acidified with acetic acid gives with cyclic primary amines such as aniline a red coloration which is intensified by the addition of one or two drops of hydrochloric acid and a few c.c. of ethyl alcohol. Colorations are also given by acetanilide, aminophenols, aminophenols substituted in the amino- or the phenolic group, amino-acids, aminohydroxy-acids, phenylurethane, atoxyl, salvarsan, neosalvarsan, and diamines. Secondary amines do not give colorations. G. W. ROBINSON.

Preparation of cyclic thiocarbamides. L. GUGLIALMELLI and A. NOVELLI (Anal. Asoc. Quím. Argentina, 1925, **13**, 255—265).—Di-α-naphthylthiocarbamide may be obtained in 90% yield in 1½ hrs.

by the reaction of carbon disulphide with α-naphthylamine in ethyl-alcoholic solution at boiling temperature, using potassium xanthate as catalyst. The same yield is obtained in 3 hrs. using sodium sulphide as catalyst. Low yields are obtained when potassium hydroxide or sulphur is used as catalyst.

G. W. ROBINSON.

Manufacture of ω-aminoalkylaminonaphthalene compounds.—F. BAYER UND CO.—See B., 1926, 433.

Azo dyes. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 432.

Azo dye. F. BAYER UND CO.—See B., 1926, 432.

Substantive green azo dyes. A.-G. FÜR ANILIN-FABR.—See B., 1926, 432.

New azo dyes and intermediate products [from 2 : 3-hydroxynaphthoic acid].—CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1926, 432.

Reactions of hydroaromatic amines. A. KÖTZ and P. MERKEL (J. pr. Chem., 1926, [ii], **113**, 49—76).—Hot ammonia under pressure converts 4-chloro-1-methyl*cyclo*hexan-3-ol (A., 1924, i, 635) or the corresponding 1-methyl-Δ^3-*cyclo*hexene oxide into 3-amino-1-methyl*cyclo*hexan-4-ol, previously prepared in another way (Takens, Diss., Göttingen, 1910; cf. A., 1915, i, 263). Formation of the oxide therefore precedes the conversion of the chlorohydrin to the amino-alcohol.

Esters of 2-dialkylamino*cyclo*hexanols were prepared by esterification of the tertiary base or of the chloro-*cyclo*hexanol followed by the action of secondary amines. Esterification took place most satisfactorily with the acid chloride in benzene solution in presence of potassium carbonate. The following compounds are described: 2-*diethylamino*cyclo*hexyl benzoate*, m. p. 36° ($1H_2O$, not lost in a vacuum over sulphuric acid); 2-*dimethylamino*cyclo*hexanol*, b. p. 198°/760 mm. (*hydrochloride*, m. p. 183—184°); 2-*chloro*cyclo*hexyl acetate*, b. p. 99—101°/13 mm., *benzoate*, m. p. 120—121°, p-*nitrobenzoate*, m. p. 240°; 2-*dimethylamino*cyclo*hexyl benzoate hydrochloride*, m. p. 190°; p-*nitrobenzoate*, m. p. 80—81°, *hydrochloride*, m. p. 226°. Reduction of the last with aluminium amalgam or catalytically yielded the *mono-* or *di-hydrochloride* of 2-*dimethylamino*cyclo*hexyl* p-*aminobenzoate*, m. p. 210—211° and 220°, respectively (*benzoyl* derivative, m. p. 150—153°).

2 : 2′-Dihydroxydi*cyclo*hexylamine (A., 1905, i, 869) (*triacetate*, m. p. 134°) is dehydrated by hot 60% sulphuric acid to *di*cyclo*hexanemorpholine* (*dodeca-hydrophenoxazine*) (*hydrochloride*, m. p. 208°; *nitroso*-compound, m. p. 119°), which gave characteristic precipitates with alkaloid reagents.

Interaction of *cyclo*hexanonecyanohydrin with *cyclo*hexylamine or 2-amino*cyclo*hexanol led to the following compounds: 1-*cyano*-1-cyclo*hexylamino*-cyclo*hexane*, m. p. 63—64°, *hydrochloride*, m. p. 104°; 1-*cyano*-1-2′-*hydroxy*cyclo*hexylamino*cyclo*hexane*, m. p. 80—81°, *dihydrochloride*, m. p. 147°; a poor yield of the corresponding *carboxylic acid*, m. p. 224°, was obtained by heating under pressure with hydrochloric acid.

Condensation of *cyclo*hexanone, piperidine hydrochloride, and potassium cyanide gave a theoretical yield of 1-*cyano*-1-*piperidyl*cyclo*hexane*, m. p. 59° (*hydrochloride*, m. p. 217°), which is decomposed into its constituents by boiling alkali. The corresponding *amide*, m. p. 91°, is not hydrolysed by nitrous acid.

J. M. GULLAND.

Preparation of phenols [from higher homologues]. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 433.

New compounds of cobalt with nitrophenols. A. BERNARDI and G. PIACENTINI (Gazzetta, 1926, **56**, 126—130).—The action of freshly-prepared cobaltous hydroxide on *o*-nitrophenol in alcoholic solution yields the garnet-red, crystalline *compound* $Co(NO_2{\cdot}C_6H_4{\cdot}O)_2$, which deflagrates when heated. Similarly, picric acid yields the deep red, crystalline *compound*, $Co[C_6H_2(NO_2)_3{\cdot}O]_2$, which explodes violently when heated on platinum foil. 2 : 4-Dinitrophenol gives, however, the orange-brown basic *compound*, $[Co_2\{O{\cdot}C_6H_3(NO_2)_2\}_2(EtOH)_3OH][O{\cdot}C_6H_3(NO_2)_2]$, which deflagrates violently when heated and loses its alcohol with formation of the compound $[Co_2\{O{\cdot}C_6H_3(NO_2)_2\}_2OH][O{\cdot}C_6H_3(NO_2)_2]$ when dried for some hours at about 100°.

T. H. POPE.

Mechanism of the Wurtz–Fischer synthesis. S. GOLDSCHMIDT and W. SCHÖN (Ber., 1926, **59**, [*B*], 948—955).—The action of sodium on 3-*iodo*-2-*ethoxy-toluene*, b. p. 127—128°, yields *o*-tolyl ethyl ether, 2 : 4′-*diethoxydi*-m-*tolyl*, m. p. 53° (hydrolysed to 2 : 4′-*dihydroxydi*-m-*tolyl*, m. p. 110°), 2 : 2′-*diethoxydi*-m-*tolyl*, m. p. 85° (characterised by very difficult hydrolysis to 2 : 2′-*dihydroxydi*-m-*tolyl*, m. p. 113°, which resembles 2 : 2′-dihydroxydiphenyl in giving a transitory violet colour when treated in ether with lead dioxide at −78°), and a non-homogeneous liquid containing mainly *o*-tolyl β-2-ethoxy-*m*-tolylethyl ether, which affords *o*-cresol when hydrolysed; the fractions of highest b. p. contain trinuclear compounds. In ethereal solution, *o*-tolyl ethyl ether (yield 65%), 2 : 2′-diethoxydi-*m*-tolyl, and a non-homogeneous liquid containing iodinated products with two or three benzene nuclei are formed.

The course of the Wurtz–Fittig synthesis is adequately expressed by the schemes: $RI+2Na \rightarrow RNa+NaI$, $RNa+IR' \rightarrow NaI+RR'$, $RNa+R'H \rightleftharpoons R'Na+RH$; the assumption of intermediate free radicals is unnecessary (cf. Schorigin, A., 1910, i, 547; Schlubach, *ibid.*, 1920, i, 19).

H. WREN.

Dye intermediates [2 : 4-diaminodiaryl ethers]. M. T. BOGERT.—See B., 1926, 433.

2 : 4-Dinitro-α-naphthyl azide. E. MÜLLER and K. WEISBROD (J. pr. Chem., 1926, [ii], **113**, 30—39).—1-Chloro-2 : 4-dinitronaphthalene reacts with sodium azide in hot absolute alcohol to form 2 : 4-dinitro-α-naphthyl azide, m. p. 105°, in 75% yield. This is converted by concentrated sulphuric acid at 110—115°, or by boiling with xylene, into 4-nitro-1 : 2-naphthaquinonedioxime peroxide, $NO_2{\cdot}C_{10}H_5<^{N{\cdot}O}_{N{\cdot}O}{>}O$, m. p. 136°. The azide reacts with ethyl sodiomalonate, giving dinitronaphthalene and a small amount of a *substance*, m. p. 172°, or with sodium

ethoxide alone, even in the cold, to form 2 : 4-*dinitro-α-naphthyl ethyl ether*, m. p. 94°, and dinitro-α-naphthol. C. HOLLINS.

Oxidation of acenaphthene. R. MARQUIS (Compt. rend., 1926, **182**, 1227—1229; cf. von Braun and Bayer, this vol., 729).—When treated with lead peroxide in acetic acid solution, acenaphthene yields acenaphthenol in rather poor yield; the *phenylurethane* has m. p. 137°. Acenaphthylene is obtained when the alcohol is treated with thionyl chloride. The oxidation of acenaphthenol provides a convenient method for the preparation of acenaphthenone. L. F. HEWITT.

Synthesis of adrenaline. [Preparation of pyrocatechol chloroacetates.] E. OTT (Ber., 1926, **59**, [*B*], 1068—1072).—Pyrocatechol in benzene or toluene is converted by chloroacetyl chloride (prepared from thionyl chloride and excess of chloroacetic acid) into the *monochloroacetate*, b. p. 174°/15 mm., m. p. 81°, and dichloroacetate. With chloroacetyl chloride prepared by means of phosphorus trichloride, chloroacetylpyrocatechol is obtained in 37% yield. Pure phosphoryl chloride is very suitable for the isomerisation of the monochloroacetate to the chloroacetyl derivative. H. WREN.

Rate of oxidation of unsaturated compounds by perbenzoic acid. H. MEERWEIN (with A. OGAIT, W. PRANG, and A. SERINI) (J. pr. Chem., 1926, [ii], **113**, 9—29).—In the oxidation of unsaturated compounds by perbenzoic acid, one atom of oxygen is usually taken up for each double linking present, exceptions being disubstituted ethylenes of the type $CR_2{:}CH_2$, which may absorb twice this amount. The rate of oxidation varies so widely in different substances that it is possible in some instances to determine isomerides quantitatively in the presence of each other, *e.g.*, eugenol and *iso*eugenol, safrole and *iso*safrole. Amongst terpenes, pinene is very rapidly oxidised, camphene and α-fenchene less rapidly, pure bornylene very slowly. The nuclear double linking in limonene is very much more readily attacked by perbenzoic acid than that in the side-chain.

Bornylene may be freed from camphene by partial oxidation with perbenzoic acid; it then has b. p. 146—147°, setting point 112·5°, and contains traces of tricyclene. Limonene is oxidised in chloroform solution to limonene-1 : 2-oxide (Prileschaev, A., 1910, i, 86), b. p. 82—84°/14—15 mm., which by hydration gives the corresponding glycol, m. p. 72·5—73° (anhyd.; cf. Prileschaev, m. p. 66·5—67·5°). The glycol is reduced by hydrogen and platinum-black to *menthane*-1 : 2-*diol* (1 : 2-dihydroxymenthane), m. p. 89—89·5°, from which are obtained *d*-tetrahydrocarvone by the action of boiling 10% sulphuric acid, and ε-keto-β-*iso*propylheptoic acid (semicarbazone, m. p. 162—164°) by oxidation with chromic acid.

Tables and graphs are given showing the rate of oxidation of *as*-diphenylethylene, *as*-phenylanisylethylene, *as*-dianisylethylene, αα-diphenylpropylene, eugenol, *iso*eugenol, safrole, *iso*safrole, pinene, camphene, *l*-α-fenchene, bornylene, *d*-limonene, α-terpineol, and $\Delta^{8,9}$-menthene-1 : 2-diol. C. HOLLINS.

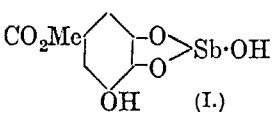
Reactivity of the methylene group. S. SKRAUP and K. BÖHM (Ber., 1926, **59**, [*B*], 1007—1015).—Comparative study of the action of diphenylmethane, 1-benzylnaphthalene, 4-benzyl- and 4-ethyl-resorcinol dimethyl ether, 4-nitro- and 2 : 4-dinitro-toluene, 2 : 4-dinitroethylbenzene, 2-methylquinoline, 9-ethyl- and 9-methyl-acridine, 2-ethyl-, 2-methyl-, and 2-benzyl-benzoxazole, 2-benzylbenzothiazole, 2-benzylbenziminazole, and deoxybenzoin on benzaldehyde, *p*-nitrosodimethylaniline, nitrous esters, and diazonium salts shows that in all cases the methylene group reacts most readily with benzaldehyde, irregularly with the other reactants, and extends the series of "negative" groups to heterocyclic complexes, but indicates also that some factor is involved besides the negative nature of the substituent.

The following new compounds are described: 2 : 4-*dimethoxydiphenylmethane*, b. p. 188—190°/13 mm., which couples with diazotised 2 : 4-dinitroaniline, yielding 2 : 4-*dimethoxybenzophenone*-2' : 4'-*dinitrophenylhydrazone*, m. p. 238·5°, thus showing that enolisation of a methylene group does not necessarily precede its reaction (contrast Lapworth, Proc. C.S., 1900, **16**, 108); 2 : 4-*dimethoxy*-1-*ethylbenzene*, b. p. 113°/13 mm., which couples in the nucleus with diazotised 2 : 4-dinitroaniline, yielding the *compound* $C_{16}H_{16}O_6N_4$, m. p. 232° (decomp.), differing from the 2 : 4-*dinitrophenylhydrazone* of resacetophenone dimethyl ether, m. p. 192°; *benzylidene*-1-*benzylbenzoxazole*, m. p. 140—141°; p-*dimethylaminoanilo*-1-*benzylbenzothiazole*, $C_6H_4\langle{}^{N}_{S}\rangle C{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}NMe_2$, m. p. 253°; 2-*benzylidenebenzylbenziminazole*, m. p. 269° (and a *substance*, m. p. 171°); the *compound* $CHPh\left[N\langle{}^{C(CH_2Ph)}_{C_6H_4}\rangle N\right]_2$ from benzaldehyde (1 mol.) and benzylbenziminazole (2 mols.); p-*dimethylaminoanilodeoxybenzoin*, m. p. 166°; a *substance*, m. p. 231°, from deoxybenzoin, and diazotised 2 : 4-dinitroaniline. H. WREN.

Rapid preparation of the molybdophosphotungstic acid reagent for polyhydric phenols and vitamins. N. BEZSSONOFF (Compt. rend., 1926, **182**, 1223—1224; cf. A., 1924, i, 588, 686, 789).—Dilute sulphuric acid is added to an aqueous solution of potassium permanganate, sodium tungstate, phosphomolybdic acid, and orthophosphoric acid, and the crystals which separate on cooling are recrystallised from dilute sulphuric acid. The reagent should give a yellowish-brown coloration, which is stable for at least 2 hrs., with 0·1% pyrogallol solution. L. F. HEWITT.

Reaction of some polyhydric phenols with sodium antimonyl tartrate. W. G. CHRISTIANSEN (J. Amer. Chem. Soc., 1926, **48**, 1365—1369).—Antimonyl derivatives, to which structures analogous with (I) are ascribed, have been prepared by boiling the following polyhydric phenols with sodium antimonyl tartrate in aqueous solution (cf. Rosing, Compt. rend., 1858, **46**, 1140; Causse, A., 1899, i, 362): *pyrogallol*, *gallic acid*, and its *methyl*, *isopropyl*, and *n-butyl* esters, *gallamide*, 3 : 4 : 5-*trihydroxybenzoylglycollic acid* and its *amide*, 2 : 3-*dihydroxy*-5-*carboxyphenoxyacetic acid*, and 2 : 3 : 4-*trihydroxy*

benzaldehyde and its *phenylhydrazone*. Treatment of the antimonyl derivative of 2 : 3 : 4-trihydroxybenzaldehyde with salvarsan in aqueous hydrochloric acid solution affords the *diantimonyl* derivative of *di*-2 : 3 : 4-*trihydroxybenzylidene*-3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene*, deep orange. Whilst the reaction is not influenced by the introduction of substituted or unsubstituted alkyl groups into the carboxylic group of gallic acid, the reaction is inhibited by the replacement of one of the phenolic hydrogen atoms of pyrogallol or gallic acid. Trihydroxybenzylidene derivatives of sulphanilic and *o*-toluidine-4-sulphonic acids did not react with sodium antimonyl tartrate. The above antimonyl derivatives possess trypanocidal activity.


(I.)

F. G. WILLSON.

Hydrates of γ-methylamino-α-phenyl-*n*-propyl methyl ether (synthetic ephedrine). W. DULIÈRE (Bull. Soc. chim., 1926, [iv], **39**, 658—664).—Continuing earlier work (A., 1924, i, 826), *γ-methylamino-α-phenyl*-n-*propyl methyl ether*, m. p. 7°, b. p. 155°/15 mm., d^{15} 0·993 (*hydrochloride*, m. p. 117°), has been obtained by the action of methylamine on γ-chloro-α-phenyl-*n*-propyl methyl ether in a sealed tube at 70°. In contact with cold water the base is converted into solid hydrates, which yield the anhydrous base when dried under reduced pressure or above 25°. By Muller-Erzbach's method (A., 1896, ii, 295), the existence of four hydrates, containing $\frac{1}{2}H_2O$, $1H_2O$, $1\frac{1}{2}H_2O$, and $2H_2O$, has been established. The vapour pressures of the first three hydrates at 14·5° are 8·13, 9·7, and 12·19 mm., respectively, and for the first two at 17°, 11·76 and 13·44 mm.; the heat of hydration of the first hydrate is 13·9 cal./mol. H_2O and, for the second stage of hydration, 11 cal. *Methyldi-(γ-methoxy-γ-phenyl*-n-*propyl)amine*, b. p. 270°/15 mm., d^{20} 1·0181, is produced at the same time as the above secondary base; it forms a readily crystallisable *hydrochloride*.

R. BRIGHTMAN.

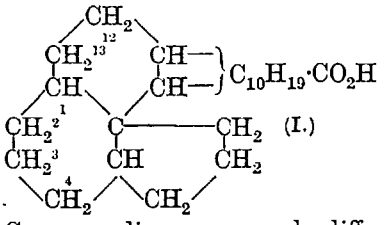
Action of mercuric acetate on cholesterol. W. MERZ (Z. physiol. Chem., 1926, **154**, 225—251).—On heating cholesterol in acetic acid solution with mercuric acetate and pouring the reaction product into potassium chloride solution, there was obtained 13% of a *compound*, $C_{27}H_{45}OHgCl$, m. p. 206—208°, together with a larger amount of an additive compound of the latter with a second molecule of cholesterol, which had m. p. 153—154°. The compound $C_{27}H_{45}OHgCl$, on treatment with a mixture of ether and concentrated hydrochloric acid, gave cholesterol; with iodine in chloroform it gave *iodocholesterol*, $C_{27}H_{45}OI$, m. p. 158°; this substance lost iodine readily in acid solution, but was stable towards alkalis; the iodine was therefore not in the *o*-position to the hydroxyl group; it took up bromine, and yielded an *acetate*, m. p. 116·5°; it therefore retained both the double linking and the hydroxyl group of cholesterol; on reduction with aluminium amalgam it yielded cholesterol. On oxidation with potassium hypobromite, the iodocholesterol gave an amorphous dibasic *acid*, $C_{27}H_{43}O_4I$, together with a small amount of a hydroxydicarboxylic *acid*, $C_{27}H_{46}O_5$, m. p. 267° (decomp.). From the products of oxidation of the substance $C_{27}H_{45}OHgCl$ with potassium permanganate in acetone there were isolated a dicarboxylic *acid*, $C_{27}H_{44}O_8$, m. p. 120°, and a tetrahydroxymonocarboxylic *acid*, $C_{27}H_{46}O_6$ or $C_{26}H_{44}O_6$, m. p. 172—173°. It is thought that the acid $C_{27}H_{44}O_8$ is formed by the addition of two –OH groups at the double linking, the substitution of –HgCl by –OH, and the oxidation of the *iso*propyl group to give a malonic acid derivative; in this case, the second acid is formed from the first by loss of carbon dioxide, and its correct formula is $C_{26}H_{44}O_6$. The position of the –HgCl group remains undetermined.

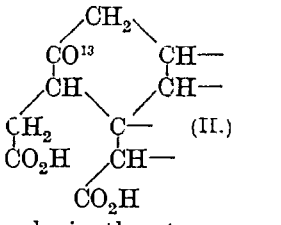
C. R. HARINGTON.

Triphenylmethane group. H. LUND (Diss., Copenhagen, 1926, 7—102).—Introduction of methoxyl into the *para*- and *ortho*-positions in triphenylcarbinol yields compounds that react with increasing readiness with hydrogen ions to form water and substituted triphenylmethyl cations. The change from triphenylcarbinol, which is not ionised in concentrated hydrochloric acid, to its heptamethoxy-derivative, which is highly ionised in aqueous hydrogen cyanide, is gradual. The solid normal carbinyl chlorides are colourless when the number of substituents is three or less; the coloured tetra- (or higher) methoxyl derivatives are salts, almost completely dissociated in acetone and in water. Some may be used as indicators. It is considered that the rearrangement of the triarylmethyl group from the alkyl to the ionic form does not involve a special orientation of the methoxyl groups.

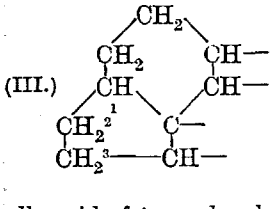
CHEMICAL ABSTRACTS.

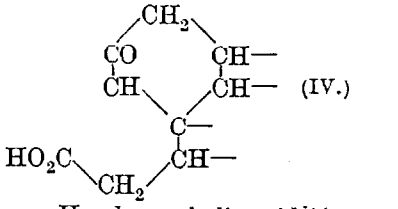
Constitution of hyodeoxycholic acid. A. WINDAUS [with A. BOHNE, O. LINSERT, KNEHE, KOCH, JACOBI, MECKE, and GRABBE] (Annalen, 1926, **447**, 233—258).—The compounds described below fall into two series, derived from cholanic and *allo*cholanic acids (I), respectively.


(I.)


(II.)

Corresponding compounds differ only in the stereochemical arrangement of groups attached to carbon atom 1. Cholanic acid is a derivative of *cis*- and the


(III.)


(IV.)

allo-acid of *trans*-decalene. Hyodeoxycholic acid (A., 1924, i, 47) yields a *diacetyl* derivative, m. p. 106° (*methyl* ester, m. p. 100°). α-Dehydrohyodeoxycholic acid, m. p. 161—162°, is converted by acids or alkalis into an isomeric, optically inactive β-*acid*, m. p. 209° (*methyl* ester, m. p. 148°). Catalytic hydrogenation of either acid yields 3 : 13-*dihydroxy*-allo*cholanic acid*, m. p. 273—274° (*methyl* ester, m. p.

181°); and both form the same *monoanisylidene* derivative, m. p. 203°. On oxidation with permanganate or hypobromite, they afford 13-ketostadenic acid (II) (hyodeoxybilianic acid, cf. A., 1925, i, 553) (*nitro*-derivative, m. p. 217—218°, which gives a *trimethyl* ester, m. p. 176—177°). The latter yields, on catalytic hydrogenation, a *lactonedicarboxylic acid*, $C_{24}H_{36}O_6$, m. p. 226—227° (*dimethyl* ester, m. p. 148°); when reduced with sodium ethoxide, however, an isomeric *lactonedicarboxylic acid*, m. p. 270° (*dimethyl* ester, m. p. 148°), is produced. The *hydrazide*, m. p. 228°, of ketostadenic acid is converted by sodium ethoxide in alcohol at 200° into *iso*lithobilianic acid (A., 1922, i, 1160), together with its stereoisomeride, *stadenic acid*, m. p. 239—240° (*trimethyl* ester, m. p. 88°). On boiling with acetic anhydride and distilling, these acids yield *pyroisolithobilianic acid* [3-*ketodeoxypyrolithobilianic acid* (cf. III)], $C_{23}H_{36}O_3,0{\cdot}5H_2O$, m. p. 168° (*methyl* ester, m. p. 82°), and the stereoisomeric *pyrostadenic acid*, m. p. 156° (*ethyl* ester, m. p. 106°), respectively. 13-*Hydroxylithobilianic acid*, $C_{24}H_{38}O_7$, m. p. 257° (*trimethyl* ester, m. p. 117—118°), is prepared by oxidising hyodeoxycholic acid with sodium hypobromite; it is reduced by hydriodic acid and red phosphorus to lithobilianic acid. When it is heated with sodium ethoxide, *lithobilienic acid*, $C_{24}H_{36}O_6$, m. p. 197° (*trimethyl* ester, m. p. 99°), is formed, which yields, on catalytic hydrogenation, allo*lithobilianic acid*, m. p. 212° (*trimethyl* ester, m. p. 101°). The pyro-acid from the latter is identical with pyrolithobilianic acid [2-ketodeoxypyrolithobilianic acid (cf. III)]. Careful oxidation of trimethyl hydroxyllithobilianate yields *trimethyl* 13-*ketolithobilianate*, $C_{27}H_{42}O_7$, m. p. 78°, which readily isomerises to *trimethyl* allo*ketolithobilianate*, m. p. 127°. Both isomerides are decomposed on hydrolysis, forming a *ketodicarboxylic acid*, $C_{23}H_{36}O_5$, m. p. 233° (*dimethyl* ester, m. p. 99°), which is also obtained by direct oxidation of hydroxylithobilianic acid. Reduction of pyro- or pyro*iso*-lithobilianic acid leads to *deoxypyrolithobilianic acid*, $C_{23}H_{38}O_2$, m. p. 163° (*monomethyl* ester, m. p. 62°). H. E. F. Notton.

Normal hydrazide and azide of phenylpropiolic acid. T. Curtius and E. Kenngott (J. pr. Chem., 1926, [ii], **112**, 314—330; cf. Z. angew. Chem., 1923, **36**, 15).—By the action of hydrazine hydrate at 20° on ethyl phenylpropiolate (b. p. 152—153°/21 mm.) there is obtained, in place of 3-phenyl-5-pyrazolone, m. p. 236°, the true *phenylpropiolhydrazide*, m. p. 110—113° (solidifying and remelting at 235°). The *hydrochloride*, m. p. 138—139°, *benzylidene*, m. p. 150°, iso*propylidene*, m. p. 127—128°, and *anisylidene*, m. p. 151°, derivatives are described. The *picrate* of the hydrazide melts at 105—110°, whilst 3-*phenyl*-5-*pyrazolone picrate* has m. p. 192°. *Phenylpropiolazide*, m. p. 55° (exploding mildly at 65°), obtained from the hydrazide and nitrous acid, is decomposed in boiling ether to form phenylacetonitrile, b. p. 130°/40 mm., and in boiling benzene yields a *substance*, m. p. 140°. The azide is readily converted into the anilide, m. p. 126°, p-*toluidide*, m. p. 142°, *ethylurethane*, m. p. 112°, and *methylurethane*, m. p. 156°, of phenylpropiolic acid. The urethanes are hydrolysed by hydrochloric acid at 110° to give phenylacetic acid, m. p. 75°. C. Hollins.

Action of high temperature and pressure on some benzoic acid derivatives. V. Ipatiev, N. Orlov, and A. Petrov (Bull. Soc. chim., 1926, [iv], **39**, 664—666).—When methyl salicylate is heated in a bomb at 340—350° for 2—3 hrs. it gives a 60—70% yield of anisole, 15% of phenol, and some resin. Ethyl salicylate is similarly converted into phenetole. The gaseous products contained 64% of carbon dioxide and 1% of carbon monoxide. Methyl *o*-methoxybenzoate is unchanged when heated at 400—430° for 4 hrs., whilst in 2 hrs. at 430° methyl *p*-methoxybenzoate is decomposed into carbon dioxide, ethylene, anisole, and some carbon and resin. Salol (phenyl salicylate) yields at 400—420° a little diphenyl ether in addition to the xanthone and phenol. *o*-Nitrobenzoic acid heated with water and alumina at 310° for 2 hrs., and barium *o*-nitrobenzoate, similarly heated with water, yield about 2—3% of nitrobenzene and are mainly decomposed with formation of carbon and resin. *p*-Nitrobenzoic acid, treated similarly, is carbonised. R. Brightman.

Thyroxin. II. Constitution and synthesis of deiodothyroxin. C. R. Harington (Biochem. J., 1926, **20**, 300—313; cf. this vol., 644).—Deiodothyroxin, $C_{15}H_{15}O_4N$, is shown by degradation and by synthesis to be α-amino-β-4-(*p*-hydroxyphenoxy)phenyl propionic acid, $HO{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H$. It is obtained from thyroxin by shaking a 1% solution of the latter in normal potassium hydroxide in an atmosphere of hydrogen with palladium hydroxide–calcium carbonate as catalyst. In this way, all the iodine is removed, and the hydrogen taken up is found to be equivalent to the iodine displaced, thus showing that no secondary reductive change occurs. On fusion with potassium hydroxide at 250°, deiodothyroxin gives *p*-hydroxybenzoic acid, ammonia, oxalic acid, a minute quantity of quinol, and p-*hydroxyphenyl* p-*tolyl ether* (m. p. 72—73° and 56° on reheating; *benzoyl* derivative, m. p. 75—77°), which was synthesised by condensing *p*-bromoanisole with potassium *p*-tolyloxide in the presence of copper-bronze and treating the resulting compound with hydriodic acid. On fusion with potassium hydroxide at 310° in an atmosphere of hydrogen, deiodothyroxin gives *p*-hydroxybenzoic acid and quinol in good yield, ammonia, and oxalic acid. On exhaustive methylation, deiodothyroxin yields a compound which loses trimethylamine on boiling with alkali and gives an unsaturated acid, $C_{16}H_{14}O_4$, found by synthesis to be 4-p-*anisyloxycinnamic acid*, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, m. p. 175·5°. On oxidation with potassium permanganate, the last substance gave oxalic acid and 4-p-*anisyloxybenzaldehyde*, m. p. 60·5° (*semicarbazone*, m. p. 211°, *oxime*, m. p. 75°), which was prepared synthetically from *p*-hydroxydiphenyl ether. This aldehyde on further oxidation yielded 4-p-*anisyloxybenzoic acid*, m. p. 176°.

The final synthesis of deiodothyroxin was carried out in two ways. By Sasaki's method (A., 1921, i, 196), 4-*p*-anisyloxybenzaldehyde was condensed with glycine anhydride in presence of acetic anhydride and

sodium acetate. The condensation product was then boiled with hydriodic acid and red phosphorus, undergoing simultaneous reduction, hydrolysis, and demethylation, yielding *α-amino-β-4-(hydroxyphenoxy)-phenylpropionic acid* (deiodothyroxin), m. p. 253—254° (decomp.), *hydrochloride*, m. p. 238—240°. By Wheeler and Hoffmann's method (A., 1911, i, 498), 4-*p*-anisyloxybenzaldehyde was condensed with hydantoin, giving 4-p-*anisyloxybenzylidenehydantoin*, m. p. 211°. This when reduced with sodium and alcohol gives 4-p-*anisyloxybenzylhydantoin*, m. p. 177·5°. When boiled with hydriodic acid and red phosphorus, the benzylidene compound gave an amino-acid identical with deiodothyroxin.

S. S. ZILVA.

Ring-chain tautomerism. XV. Phenol-succineins and -glutareins. S. DUTT (J.C.S., 1926, 1132—1139).—In continuation of the work of Dutt and Thorpe (A., 1925, i, 140), phenol-succineins (I) and -glutareins (II) (RR′=H_2, Me_2, MeEt, Et_2, and *cyclo*hexane residue) have been prepared, using

$$\begin{matrix} CRR'\cdot CH_2 \\ | \\ CO\text{———}O \end{matrix}\!>\!C(C_6H_4\cdot OH)_2 \qquad \begin{matrix} CRR'\cdot CH_2 \\ | \\ CH_2\cdot CO\cdot O \end{matrix}\!>\!C(C_6H_4\cdot OH)_2$$

(I.) (II.)

stannic chloride as condensing agent. Determinations of their absorption maxima in dilute alkaline solution give results confirming the generalisation arrived at by Dutt and Thorpe (*loc. cit.*). Addition of excess of alkali to the pink solutions of the quinonoid forms decolorises them owing to hydration to the carbinol salts. Of the free carbinol compounds, only that of phenolglutarein, $(HO\cdot C_6H_4)_2\cdot C(OH)\cdot[CH_2]_3\cdot CO_2H$, is stable under ordinary conditions, forming a colourless, crystalline substance, which is converted into the lactone by heating or by dehydrating agents. The rate of hydration of the phenolglutareins in alkaline solution increases with increasing complexity of the substituents in the glutaric acid group. The hydration is a unimolecular reaction. A. DAVIDSON.

Derivatives of gallic acid and pyrogallol. W. G. CHRISTIANSEN (J. Amer. Chem. Soc., 1926, **48**, 1358—1365).—n-*Butyl gallate*, m. p. 133—134°, is obtained in 90% yield by saturating a suspension of gallic acid in *n*-butyl alcohol with hydrogen chloride, but this process affords a much smaller yield of iso-*propyl gallate*, m. p. 123—124·5°. Treatment of gallic acid with chloroacetic acid in presence of aqueous alkali (3 mols.) in an atmosphere of nitrogen yields 2 : 3-*dihydroxy*-5-*carboxyphenoxyacetic acid*, m. p. 262° (heated slowly), or, heated rapidly, m. p. 270° after becoming pasty and resolidifying at 193—195°, or, after drying at 105°, m. p. 266—268° after sintering at 246—250° (*methyl* ester, m. p. 143—145°). The acid is not hydrolysed when boiled with aqueous 2·5*N*-sodium hydroxide. Gallic acid and ethyl chloroacetate afford similarly 3 : 4 : 5-*trihydroxybenzoylglycollic acid*, m. p. 216° (*amide*, m. p. 231—232°, obtained from chloroacetamide). Treatment of gallic acid in alkaline solution with benzoyl chloride affords a mixture of the 3-*benzoyl* and 3 : 5-*dibenzoyl* derivatives, m. p. 224—227° (decomp.) and 218—221°, respectively. Treatment of pyrogallol with chloroacetic acid or chloroacetamide in alkaline solution in an atmosphere of nitrogen affords 2 : 3-*dihydroxyphenoxyacetic acid*, m. p. 153—155·5° (*methyl* ester, m. p. 156—157·5°). 2 : 3 : 4-*Trihydroxybenzylideneo-toluidine*-4′-*sulphonic acid*, yellow, m. p. not below 304°, 2 : 3 : 4-*trihydroxybenzylideneaniline*-4′-*sulphonic acid*, yellow, m. p. not below 300°, 2 : 3 : 4-*trihydroxybenzylideneaniline*-2′-*carboxylic acid*, yellow, m. p. 252° (decomp.) after darkening above 200°, and *di*-2 : 3 : 4-*trihydroxybenzylidene*-3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene*, brick-red, are obtained by condensing trihydroxybenzaldehyde with the appropriate amines in warm aqueous solution.

F. G. WILLSON.

Hydrated ketonic ether. J. BOUGAULT (Compt. rend., 1926, **182**, 1224—1226; cf. this vol., 167, 613).—The compound to which the constitution (I) has been assigned (cf. this vol., 167), has the constitution (II), and similarly the derivatives should be

(I.) $\begin{matrix} CH_2Ph\cdot C\text{—}CO \\ \quad\quad O \quad\quad | \\ CH_2Ph\cdot CH_2\cdot C\text{—}CO \end{matrix}\!\!\begin{matrix} \\ \diagup \\ \diagdown \end{matrix}\!\!\begin{matrix} \\ NH \\ \\ \end{matrix}$ $\qquad$ $\begin{matrix} CH_2Ph\cdot CH\cdot CO \\ \quad\quad\quad | \quad\quad | \\ CH_2Ph\cdot CH_2\cdot CH\cdot CO \end{matrix}\!\!\begin{matrix} \\ O \\ \\ \end{matrix}\!\!\begin{matrix} \\ NH \\ \\ \end{matrix}$ (II.)

represented as possessing two additional hydrogen atoms, thus obviating the necessity of a direct linking between the two carbon atoms already joined through an oxygen atom. L. F. HEWITT.

Constitution and configuration of pulvinic and vulpinic acids. P. KARRER, K. A. GEHRCKENS, and W. HEUSS (Helv. Chim. Acta, 1926, **9**, 446—457; cf. Spiegel, A., 1884, 841; Volhard, *ibid.*, 1895, i, 99; Schenk, *ibid.*, i, 100).—The action of acetyl or benzoyl chloride on a solution of pulvinic acid in pyridine at the ordinary temperature gives *pulvinic lactone*, m. p. 124—125°, reconverted into the acid by treatment with dilute alkali. The ethylene oxide formula (I) for pulvinic acid, which would require an anhydride structure for this compound, is finally excluded by preparation of two isomeric series of dialkyl derivatives. The lactone formula (II) for pulvinic acid is therefore established. Methylation of the carboxyl group gives vulpinic acid.

(I.) $\begin{matrix} CPh{:}C\text{—}C{:}CPh \\ \quad\quad\quad\quad O \\ CO_2H \quad\quad CO_2H \end{matrix}$ $\qquad$ $\begin{matrix} CPh{:}C(OH)\cdot C{=}CPh \\ \quad\quad\quad\quad\quad\quad O \\ CO\text{———}O \quad CO_2H \end{matrix}$ (II.)

Derivatives of pulvinic acid are prepared, through the dinitriles of substituted ketipic acids, by condensation of oxalic esters with appropriately substituted phenylacetonitriles (Volhard, *loc. cit.*): $CH_2R\cdot CN + RO_2C\cdot CO_2R + NC\cdot CH_2R \rightarrow \begin{matrix} CHR\cdot CO\cdot CO\cdot CHR \\ | \quad\quad\quad\quad | \\ CN \quad\quad\quad CN \end{matrix} \rightarrow \begin{matrix} O\text{—}CO \\ | \quad | \\ CR{:}C\cdot C{:}CR \\ | \quad | \\ CO\text{—}O \end{matrix}$. Esterification of the carboxyl group is effected by potassium hydroxide and methyl or ethyl alcohol, etherification of the hydroxyl group by treatment with diazomethane or diazoethane. The following are described: *di*-p-*tolylketipic dinitrile*, m. p. 257° after partial decomp. above 240°; *di*-p-*tolylketipic dilactone*, decomp. 275—276°; pp′-*dimethylvulpinic acid*, m. p. 190° (*methyl ether*, m. p. 172°); *ethyl di*-p-*tolylketipate monolactone*, m. p.

137—138° (*methyl ether*, m. p. 157°); *methyl di-p-tolylketipate monolactone ethyl ether*, m. p. 171°; pp'-*dimethylpulvinamide*, m. p. 245—248° after sintering; *di-p-chlorophenylketipic dinitrile*, darkening at 235°, decomp. at 273°; *di-p-chlorophenylketipic dilactone*, sintering at 231°, decomp. 236°; pp'-*dichlorovulpinic acid*, sintering at 210°, decomp. at 214—216° (*methyl ether*, m. p. 177°, *ethyl ether*, m. p. 146—147°); pp'-*dichloropulvinic acid* [*amide*, sintering at 230°, m. p. 237—238° (decomp.)]; *ethyl di-p-chlorophenylketipate monolactone*, m. p. 137—138° (*methyl ether*, sintering at 157—158°, m. p. 175°); vulpinic acid (*benzoyl* derivative, m. p. 176°, *acetyl* derivative, m. p. 148°, *phenylacetyl* derivative, m. p. 172°). Oxidation of the vulpinic acid methyl ether with ozone and decomposition of the product with water yields oxalic, benzoic, and phenylglyoxylic acids, also obtained by oxidation with potassium permanganate.

M. CLARK.

Conversion of oximes into nitriles by means of potassium cyanide. M. PASSERINI (Gazzetta, 1926, **56**, 122—126).—Potassium cyanide acts on the oximes of aldehydes but not of ketones, yielding nitriles. That the reaction is not a direct dehydration, but rather an elimination of water from an intermediate, labile, additive compound of the oxime with the potassium cyanide, is indicated by the assumption of a red colour by the liquid during the reaction and by the fact that both α- and β-oximes react in this way. Thus, the α- and β-isomerism is not possible with the additive product, which hence cannot contain the double linking between the carbon and nitrogen of the oxime. The action of the potassium cyanide is a specific one and is not due to either the alkalinity of the salt or the hydrocyanic acid liberated during the reaction. Although good yields of the nitriles are obtained, part of the oxime displaces the hydrocyanic acid of the cyanide, giving a potassium salt incapable of conversion into the nitrile. By this reaction, α-benzaldoxime was converted into benzonitrile, α- or β-anisaldoxime into anisonitrile, and 2-hydroxy-1-naphthaldehyde into the efflorescent *2-hydroxy-1-naphthonitrile*, m. p. 154—155°.

T. H. POPE.

Photochemical reactions of derivatives of *o*-nitrobenzylideneacetal. I. TANASESCU and H. TANASESCU (Bul. Soc. Stiint. Cluj, 1925, **2**, 369—382; from Chem. Zentr., 1926, **1**, 632—633).—*o-Nitrobenzylideneglycol*, b. p. 174°/12 mm. (prepared by heating *o*-nitrobenzaldehyde and glycol at 150°) is converted by light into a *product*, $C_9H_9O_4N$, m. p. 128° (*benzoyl* derivative, m. p. 103—104°), which is hydrolysed to *o*-nitrosobenzoic acid and glycol, and to which the formula $\begin{matrix}CH_2\cdot O\\CH_2\cdot O\end{matrix}>C(OH)\cdot C_6H_4\cdot NO$ is assigned. The *amphi*-form of di-*o*-nitrobenzylidene-erythritol is more stable to light than is the *anti*-form, but both are transformed into the same *product*, $C_{18}H_{16}O_8N_2$, probably $NO_2\cdot C_6H_4\cdot CH<\begin{matrix}O\cdot CH-CH-O\\O\cdot CH_2\ \ CH_2\cdot O\end{matrix}>C(OH)\cdot C_6H_4\cdot NO$, m. p. 120° (*benzoyl* derivative, m. p. 92—93°), which is hydrolysed to *o-nitrobenzylidene-erythritol*, m. p. 114°.

F. M. HAMER.

Isomerisation of disubstituted aldehydes to ketones. S. DANILOV and E. VENUS-DANILOVA (Ber., 1926, **59**, [*B*], 1032—1043).—Diphenylacetaldehyde, from hydrobenzoin, gives deoxybenzoin in 80% or 60% yield when treated with concentrated sulphuric acid at −12° to −8° or with boiling 65% acid; the aldehyde, prepared according to Béhal and Sommelet (A., 1904, i, 222), affords the ketone in 30% or 74% yield with concentrated sulphuric acid at −5° to +15° or boiling 55% acid. Diphenylacetaldoxime and boiling 50% acid give deoxybenzoin in 60% yield. Deoxy-*p*-toloin is obtained in 84%, 74%, and 80% yield from di-*p*-tolylacetaldehyde and concentrated sulphuric acid at −15° to −8°, boiling 60% acid, or boiling 50—60% acid. Incomplete conversion accompanied by production of hydrocarbon is observed with a mixture of water, alcohol, and sulphuric acid at 125—145°. Di-*p*-tolylacetaldehydesemicarbazone and boiling 50% sulphuric acid afford 73% of deoxy-*p*-toloin.

Di-*p*-tolylvinyl ethyl ether is obtained with some deoxy-*p*-toloin by the action of magnesium *p*-tolyl bromide on ethyl ethoxyacetate. Deoxy-*p*-toloin is converted by alkali hydroxide into toluene and *p*-tolylacetic acid.

H. WREN.

Carbon rings. IV. Preparation of *cyclo*nonanone from sebacic acid. V. Preparation of a 9-membered ring from an 8-membered ring. L. RUZICKA and W. BRUGGER (Helv. Chim. Acta, 1926, **9**, 389—398, 399—408; cf. Zelinsky, A., 1907, i, 780; Willstätter, *ibid.*, i, 936, 1018).—IV. Distillation of the tar obtained by decomposition of thorium sebacate (cf. this vol., 619) yields a fraction, b. p. 65—120°/12 mm., from which four ketonic components are separated by treatment with an aqueous-alcoholic solution of sodium hydrogen sulphite. The ketone mixture regenerated from the crystalline additive compound is separated by distillation into a fraction, b. p. 63—88°/12 mm., from which *cyclo*heptanone is isolated as the semicarbazone, and into a fraction, b. p. 88—105°/12 mm., from which the semicarbazone of methyl octyl ketone is obtained. The ketone mixture which failed to react with sodium hydrogen sulphite is separated by distillation into a fraction, b. p. 90—100°/12 mm., from which the semicarbazone of *cyclo*nonanone is obtained, and a higher-boiling fraction, b. p. 100—110°/12 mm., from which an unidentified *semicarbazone*, m. p. 173—175°, is isolated. The approximate yields of *cyclo*heptanone, methyl octyl ketone, *cyclo*nonanone, and the unknown ketone (or mixture of ketones) amount to 0·5%, 0·7%, 1·2—1·5%, and 0·5%, respectively.

Isolation of pure *cyclo*nonanonesemicarbazone from the crude mixture of ketones is effected by crystallisation of the semicarbazone mixture from methyl alcohol or benzene. The product thus obtained shows the apparently constant m. p. 105° given by previous investigators (*loc. cit.*) for the semicarbazone of *cyclo*nonanone. Oxidation of such a product, however, gives pimelic acid in addition to azelaic acid, indicating admixture with *cyclo*heptanone. Further crystallisation from dilute solution in benzene rapidly raises the m. p. to that of the pure compound, 178—179°.

V. *cyclo*Hexanonecyanohydrin reacts with thionyl chloride to give *cyano*cyclo*hexene*, b. p. 81°/12 mm., reduced by sodium and ethyl or amyl alcohol to *cyclo*hexylmethylamine (cf. Wallach, A., 1907, i, 616). Distillation of the product obtained by reaction of the amine with nitrous acid (Demjanov, A., 1904, i, 410) yields a fraction boiling below 165°/720 mm., which contains an unsaturated hydrocarbon recognised by its oxidation to pimelic acid as *cyclo*heptene (1 part). The higher-boiling fraction, b. p. 165—190°/720 mm., consists of *cyclo*heptanol (3 parts), isolated as the phenylurethane.

*cyclo*Octanonecyanohydrin is similarly converted through *cyano*cyclo*octene*, b. p. 100—115°/12 mm., into cyclo*octylmethylamine*, b. p. 92—94°/12 mm. (*benzoyl* derivative, m. p. 70°). Distillation of the product obtained by reaction of the amine with nitrous acid yields two fractions, b. p. 60—90°/12 mm. (2 parts) and 90—120°/12 mm. (3 parts), respectively. Distillation of the lower-boiling fraction over sodium gives 1-*methyl*-Δ^1-cyclo*octene*, b. p. 165—169°/730 mm., d_4^{20} 0·8487, n_D^{20} 1·4691, yielding, on oxidation with permanganate, suberic acid and *η-ketononoic acid*, further oxidised by sodium hypobromite to the first-named acid. Oxidation of the hydrocarbon with ozone and decomposition of the product with water gives the same products accompanied by *η-ketononaldehyde* (*disemicarbazone*, m. p. 182—183°). The higher-boiling fraction is separated by esterification of the primary alcohol with phthalic anhydride in boiling benzene solution into cyclo*octylcarbinol*, b. p. 114—116°/22 mm. (3 parts), and *cyclo*nonanol (2 parts). Oxidation of *cyclo*octylcarbinol gives cyclo*octylcarboxylic acid*, b. p. 140—160°/12 mm. (*amide*, m. p. 191—191·5°), and suberic acid. Oxidation of *cyclo*nonanol gives cyclo*nonanone*, m. p. 0°, b. p. 93—95°/12 mm., d_4^{17} 0·9587, n_D^{17} 1·4730 (*semicarbazone*, m. p. 179°). The transition from the 8- to 9-ring thus proceeds less smoothly than that from the 6- to 7-ring. M. Clark.

Carbon rings. VI. Relative ease of formation, relative stability, and spatial structure of saturated carbon rings. L. Ruzicka, W. Brugger, M. Pfeiffer, H. Schinz, and M. Stoll (Helv. Chim. Acta, 1926, **9**, 499—520).—cyclo*Heptadecane*, m. p. 64—65°, and cyclo*pentadecane*, m. p. 60—61°, obtained by the action of sodium ethoxide on the semicarbazones of the corresponding cyclic ketones, are unchanged by treatment with fuming hydriodic acid and red phosphorus at 250°. The cyclic ketones with 7- to 9- and 12- to 18-membered carbon rings on treatment with concentrated hydrochloric acid at 180—190° show partial polymerisation and partial carbonisation without ring-fission or production of isomeric compounds. *cyclo*Heptadecanone, passed over thorium oxide at 400—420°, is similarly unchanged except by partial carbonisation. The stability of rings containing up to 18 carbon atoms is therefore comparable with that of the 5- and 6-membered rings. In contrast to the comparatively unstable 3- and 4-rings, the compounds containing more than 7 atoms in the ring are so far accessible by only one method and, in general, in small yield (cf. this vol., 615). The ease of formation bears no direct relation either to the number of carbon atoms in the ring or to the stability of the compound concerned. The densities and molecular volumes at 20° are given for normal aliphatic hydrocarbons and ketones as well as for the corresponding cyclic compounds up to the 17-ring derivatives. The densities of the aliphatic compounds rise progressively, although more slowly as the series is ascended. The densities of the cyclic compounds rise to a maximum value and afterwards decline. The molecular volumes of the aliphatic compounds show steady increase with the number of carbon atoms, giving an average value of 16·2 for each CH_2 group. Those of the cyclic compounds increase less rapidly, giving a mean value for the CH_2 group varying from 20·4 in the 4-ring to 16·1 in the 15- and 17-rings. A lack of uniformity in spatial structure between the lower and higher rings is therefore postulated. From the stability of the higher rings, taken in conjunction with this factor, it is concluded that ring compounds from the 6-ring upwards are without strain, owing to disposition of the carbon atoms in more than one plane. The ease of formation of a ring-compound is regarded as the resultant of two component factors favouring, respectively, the formation of small rings and of rings free from strain. M. Clark.

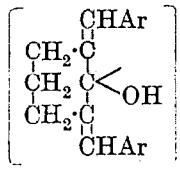
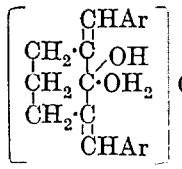
Catalytic hydrogenation of the carbonyl group in aromatic compounds under pressure in the presence of copper. II. B. Kubota and T. Hayashi (Bull. Chem. Soc. Japan, 1926, **1**, 67—70).—Treatment of acetophenone with hydrogen under 66 atm. in presence of copper at 140° gives 4% of phenylmethylcarbinol, whilst at 160° ethylbenzene and diphenyldimethylethane are the products. Similar treatment of benzophenone at 120° and under 50 atm. gives rise to 98% of diphenylcarbinol and some diphenylmethane; at 190° and under 52 atm., diphenylmethane and tetraphenylethane are formed. Camphor, treated at 120—150° under 10—92 atm., gives yields of 71—79% of *iso*borneol and 21—29% of borneol, the lower temperatures of reduction giving the greater yields of borneol. This last hydrogenation takes place in a gas–solid system.
B. W. Anderson.

Condensation products of aliphatic-aromatic ketones with polyalcohols. J. Altwegg and E. F. Chermette.—See B., 1926, 462.

Catalytic action of reduced copper on pinacones. S. Yamaguchi (Bull. Chem. Soc. Japan, 1926, **1**, 64—66).—Benzopinacone, when passed over reduced copper at 200°, is converted almost entirely into benzopinacolin. Similarly treated, acetophenonepinacone yields mainly acetophenone.
B. W. Anderson.

Heteropolar carbon compounds. II. Halochromy of acylated aminochalkones and related compounds. W. Dilthey and C. Berres (J. pr. Chem., 1926, [ii], **112**, 299—313; cf. this vol, 177; Pfeiffer, A., 1925, i, 408).—Acylaminochalkones (aryl acylaminostyryl ketones) and acylaminodistyryl ketones form monoperchlorates which are more deeply coloured than those of the corresponding nitrogen-free ketones and are figured as oxonium

salts (cf. Pfeiffer, *loc. cit.*). In the case of di-(*p*-acetamidobenzylidene)*cyclo*hexanone, a yellow hydrated salt and a violet salt are obtained, which according to Pfeiffer's views would be the ammonium and the oxonium salt, respectively. If, however, the colour change is due to the presence of water in the molecule, another explanation must be sought, and it is suggested that the violet perchlorate has the structure (I), whilst the yellow perchlorate is repre-

(I.)  ClO_4  ClO_4 (II.)

sented by (II), the hypsochromic effect being due to co-ordinative saturation of the ketonic carbon atom.

[With A. Lachs and P. Schier.]—Phenyl *p*-acetamidostyryl ketone yields a *monoperchlorate* (decomp. 206—210°) which on recrystallisation from acetic acid containing no perchloric acid is converted into the *compound* $3Ch,2HClO_4$ (Ch=the chalkone molecule). *Compounds* $2Ch,H_2SnCl_6$, m. p. 186—190°, and $3Ch,HCl,ZnCl_2$, m. p. 227°, are described. Phenyl *p*-benzamidostyryl ketone forms a *perchlorate*, and with antimony pentachloride a *compound*, $Ch,HSbCl_6$. *Phenyl* p-*formamidostyryl ketone*, m. p. 171—172°, gives a *zinc chloride* compound, $3Ch,2ZnCl_2$, and a *perchlorate*, decomp. 190—193°. From *p*-anisyl *p*-acetamidostyryl ketone are obtained the *compounds* $2Ch,H_2SnCl_6$, m. p. 200—210°, $Ch,HClO_4$, m. p. 195—198° (decomp.), $3Ch,2HClO_4$, m. p. 210° (decomp.), and $Ch,ZnCl_2$, m. p. 250° (decomp.). The normal perchlorate of *p*-anisyl *p*-benzamidostyryl ketone melts at 175—176° (decomp.). p-*Anisyl* p-*formamidostyryl ketone*, m. p. 163—164° [*perchlorate*, m. p. 190° (decomp.)], and the *perchlorate* and *chlorostannate* of phenyl *m*-acetamidostyryl ketone are described. 3-Acetamidodistyryl ketone, 3-*acetamido*-4'-*methoxydistyryl ketone*, m. p. 177°, 4-*acetamidodistyryl ketone*, m. p. 178—179°, and 4-*acetamido*-4'-*methoxydistyryl ketone*, m. p. 164—165°, all give *monoperchlorates*. From di-(*p*-acetamidobenzylidene)-*cyclo*hexanone are obtained a yellow *perchlorate* (decomp. 239°) from cold solutions, or a violet *perchlorate*, m. p. 239° (decomp.) from hot solutions. The yellow salt contains $1H_2O$, becomes violet when dried, and may be obtained from the violet salt by exposure to a cold, moist atmosphere.

C. Hollins.

Isomeric alkyl derivatives of *cyclo*hexan-2-ol-1-one. M. Bergmann and M. Gierth (Annalen, 1926, **448**, 48—76).—When *cyclo*hexan-2-ol-1-one is recrystallised from methyl alcohol or distilled under reduced pressure (b. p. 83—86°/13 mm., 50—56°/0·4 mm., *phenylhydrazone*, m. p. 121—121·5°) its m. p. is raised from 92—98° to 130°, without change in composition or mol. wt. A liquid, freshly-distilled sample changed in 14 min. from n_D^{21} 1·4711 to 1·4785. The isolation of two distinct series of alkyl ethers proves that these variations are due to the presence of a tautomeric *cyclo*acetal form, 1-*hydroxy*-Δ^1-cyclo*hexene oxide*. When *cyclo*hexanolone, or its methyl-*cyclo*acetal, is heated to 100° with *N*-methyl-alcoholic hydrogen chloride, 2-*methoxy*cyclo*hexanone*, b. p. 72—73°/14 mm., d_4^{20} 1·020, n_D^{20} 1·4537, is obtained. This is unimolecular in solution; it decomposes on keeping, reduces Fehling's solution in the cold, and yields a *phenylhydrazone*, m. p. 94—96°, and a p-*nitrophenylhydrazone*, m. p. 126·5—127°. It is hydrolysed by *N*-hydrochloric acid at 100° to the hydroxyketone. 2-*Ethoxy*cyclo*hexanone*, b. p. 80—83°/14 mm., n_D^{22} 1·4519, d_4^{22} 0·9969, gives a p-*nitrophenylhydrazone*, m. p. 144°. The compound described by Kötz (A., 1913, i, 1201) as methoxy-*cyclo*hexanone is the *methyl*cyclo*acetal* (1-*methoxy*-Δ^1-cyclo*hexene oxide*), since it is bimolecular in solution (A., 1924, i, 490), does not reduce Fehling's solution, and forms an iodine–potassium iodide *compound*, $(C_7H_{12}O_2)_2I_4,KI$ (cf. *ibid.*, 618). It is also obtained on treating 2-bromo*cyclo*hexanone with methyl alcohol and silver carbonate. The corresponding 1-*ethoxy*-Δ^1-cyclo*hexene oxide*, described by Kötz as ethoxy*cyclo*hexanone, 1-iso*butoxy*-, m. p. 123·5° (corr.), and 1-*benzyloxy*-Δ^1-cyclo*hexene oxide*, m. p. 160° (corr.), have similar properties. 2-*Acetoxy*-cyclo*hexanone*, m. p. 41—42° (*phenylhydrazone*, m. p. 97—98°), and 2-*benzoxy*cyclo*hexanone*, m. p. 87° (cf. Kötz *loc. cit.*) (*phenylhydrazone*, m. p. 112°; p-*nitrophenylhydrazone*, m. p. 158—160°), are unimolecular in solution. *Acetol ethyl*cyclo*acetal*, $OEt\cdot CMe<\begin{matrix}CH_2\\O\end{matrix}$, b. p. 71—74°/1·5 mm., m. p. 73—73·5° [iodine–potassium iodide *compound*, $(C_5H_{10}O_2)_2I_4,KI$], *acetol* n-*propyl*cyclo*acetal*, b. p. 94—96°/1·5 mm., 98—99°/3·5 mm., m. p. 73°, n_D^{20} 1·4319, *acetoin ethyl*cyclo-*acetal*, $OEt\cdot CMe<\begin{matrix}CHMe\\O\end{matrix}$, b. p. 71—81°/1·5 mm., m. p. 74°, and *acetoin* n-*propyl*cyclo*acetal*, b. p. 80—82·5°/1·7 mm., n_D^{20} 1·4345, are all bimolecular in solution and unimolecular in the form of vapour.

H. E. F. Notton.

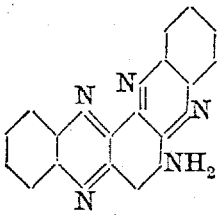
Nitration of benzil. F. D. Chattaway and E. A. Coulson (J.C.S., 1926, 1070—1073).—Benzil is nitrated by a large excess of fuming nitric acid to a product of m. p. about 107°. This was formerly described as *mm'*-dinitrobenzil (Klinger and Martinoff, A., 1912, i, 571; Barnett and Kay, *ibid.*, 1922, i, 844), but is now shown, by fractional crystallisation, to be a mixture of about 70% of mm'-*dinitrobenzil* (m. p. 132°), 20% of om'-*dinitrobenzil* (m. p. 149°), and 10% of oo'-*dinitrobenzil* (m. p. 208°). A. Davidson.

Action of sodamide on some organic compounds. I. Kasiwagi (Bull. Chem. Soc. Japan, 1926, **1**, 66—67).—Sodamide reacts with benzil to give a good yield of benzilic acid and with furfuraldehyde to give pyromucic acid and furfuryl alcohol; with benzaldehyde, benzyl alcohol and benzoic acid (not benzamide) are formed. At 80° sodamide and acenaphthenequinone react violently and naphthalene is formed. B. W. Anderson.

Production of benzanthrone derivatives. L. Cassella und Co.—See B., 1926, 434.

Derivatives of *o*-benzoquinone. F. Kehrmann and N. Poehl (Helv. Chim. Acta, 1926, **9**, 485—491; cf. A., 1925, i, 304).—3 : 5-*Diacetamidopyrocatechol*

diacetate, m. p. 185°, dissolved in the minimum quantity of dilute sodium hydroxide, undergoes hydrolysis of the acetoxy-groups, and is oxidised by immediate treatment with potassium dichromate in acid solution or with nitrous acid to 3 : 5-*diacetamido*-o-*benzoquinone*, m. p. 220°. With hydroxylamine sulphate the quinone gives 3 : 5-*diacetamido*-o-*benzoquinone*-1-*oxime*, reduced by tin and hydrochloric acid to 2 : 4 : 6-triaminophenol. Pyrogallol triacetate is converted by the action of nitric acid (*d* 1·52) at 0° into 4 : 6-*dinitropyrogallol monoacetate*, m. p. 130°. Reduction with tin and hydrochloric acid gives 4 : 6-diaminopyrogallol (*penta-acetyl* derivative, m. p. 265°), oxidised in ammoniacal solution by a current of air to 2-*amino*-5 : 6-*dihydroxy*-p-*benzoquinone*-1-*imine*, decomp. at about 200°. This compound condenses with *o*-phenylenediamine, giving, probably, 7 : 9-diamino-6-hydroxyphenazine, which condenses with another molecule of *o*-phenylenediamine under oxidising conditions, giving the *aminobenzodiphenazine* (annexed formula), decomp. at about 310° (*hydrochloride*, *chloroplatinate*, *acetyl* derivative, decomp. at about 320°). Condensation of the quinoneimine with 3 : 4-tolylenediamine, in a similar manner, gives an *aminobenzoditoluazine*, $C_{20}H_{15}N_5$, decomp. at about 320° (*acetyl* derivative, m. p. 245°, *chloroplatinate*).



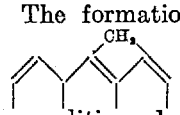
M. CLARK.

Duroquinone and some derivatives of durene. L. I. SMITH and F. J. DOBROVOLNY (J. Amer. Chem. Soc., 1926, 48, 1420—1423).—Dinitrodurene is obtained in 70—80% yield by adding nitric acid (*d* 1·5) to a mixture of sulphuric acid and a solution of pure durene in chloroform. It is necessary to work with small batches, and to separate the chloroform solution of the nitro-compound immediately, to prevent loss by formation of tarry products. Reduction of dinitrodurene with stannous chloride in glacial acetic and hydrochloric acids affords the *stannic chloride double salt* of *diaminodurene hydrochloride*, $2C_{10}H_{12}(NH_2{\cdot}HCl)_2,SnCl_4$, in 85% yield, which is oxidised direct to duroquinone by concentrated aqueous ferric chloride and hydrochloric acid. Duroquinol has m. p. 233° after sintering at about 220° (*diacetate*, m. p. 207°). When treated with excess of bromine in acetone, duroquinone yields a *dibromide*, pale yellow, m. p. 73—74°. *Diacetamidodurene*, m. p. above 310°, after sintering and darkening about 300°, is described. F. G. WILLSON.

Mechanism of Fichter's synthesis of dihydroxydialkylquinones. F. KÖGL and A. LANG (Ber., 1926, 59, [*B*], 910—913).—Dihydroxydiethyl-*p*-benzoquinone is obtained in 29% yield by the action of sodium ethoxide on an ethereal solution of ethyl oxalate and octane-δε-dione. Dihydroxydi*iso*propyl-*p*-benzoquinone is derived similarly from βη-dimethyloctane-δε-dione. It is therefore probable that αβ-diketones are formed initially from the fatty esters under the influence of sodium in Fichter's synthesis of dihydroxydialkylquinones (cf. A., 1913, i, 279) and subsequently condense with ethyl oxalate. In support, it is shown that the yields are increased considerably if the action between fatty ester and sodium is first permitted to occur, the product is then oxidised by dry oxygen, and the ethyl oxalate added subsequently. H. WREN.

[Vat] dyes [from diarylaminobenzoquinones]. SOC. CHEM. IND. IN BASLE.—See B., 1926, 479.

Catalytic hydrogenation under pressure in the presence of nickel salts. X. Acenaphthenequinone. J. VON BRAUN and O. BAYER (Ber., 1926, 59, [*B*], 920—923; cf. Skita, this vol., 174).—Hydrogenation of acenaphthenequinone, which has not been purified through the hydrogen sulphite compound, proceeds rapidly in tetrahydronaphthalene solution below 180°, yielding successively dihydroxyacenaphthylene, dihydroxyacenaphthene, hydroxyacenaphthene, and acenaphthenone, which is thus readily accessible. Further reduction at 240° affords *acenaphthenol*, m. p. 146° (corresponding *phenylurethane*, m. p. 137°), acenaphthylene, acenaphthene, and tetrahydroacenaphthene. H. WREN.

Reduction of α-methylanthraquinones by zinc dust and the non-existence of so-called anthracylenes. J. VON BRAUN and O. BAYER (Ber., 1926, 59, [*B*], 914—919).—1-Methylanthraquinone is converted by protracted reduction with zinc dust and ammonia into methyldihydroanthrol, which loses water when distilled and passes into 1-methylanthracene. If action is less prolonged, the product contains 1-*methylanthrone*, m. p. 126—127° (prepared also by catalytic hydrogenation of 1-methylanthraquinone in the presence of nickel at 150—170°), and *dimethyltetrahydrodianthrol*, m. p. 147°. Since the anthrone form is unusually stable, the methyl group is considered to be vicinal to the oxygenated group in these compounds. The formation of anthracylenes with the group  could not be detected. Under similar conditions, 1 : 3-dimethylanthraquinone affords 1 : 3-*dimethylanthrone*, m. p. 119·5°, *tetramethyltetrahydrodianthrol*, m. p. 147°, and non-crystalline dimethyldihydroanthrol, which passes very readily into 1 : 3-dimethylanthracene (picrate, m. p. 136°). 1 : 4-Dimethylanthraquinone is somewhat less readily reduced by zinc dust and ammonia, yielding 1 : 4-*dimethyldihydroanthrol*, m. p. 134—136° [which affords 1 : 4-*dimethylanthracene*, m. p. 74° (*picrate*, m. p. 140°)], and 1 : 4-*dimethylanthrone*, m. p. 113°. H. WREN.

Geometrical stereoisomerism in the *cyclo*hexane series. VI. Menthols and menthones. P. BEDOS (Bull. Soc. chim., 1926, [iv], 39, 674—690).—The two isomeric 2-chloro-5-methyl*cyclo*hexanols react with magnesium *iso*propyl bromide as with magnesium methyl iodide (this vol., 280), yielding two isomeric menthols, which were characterised by their *allophanates*, m. p. 133° and 177°, but the pure menthols could not be isolated from the reaction product. Similarly, the action of magnesium *iso*propyl bromide on methyl-Δ^3-*cyclo*hexene (cf. this vol., 395) yields a single *menthol*, b. p. 92°/14 mm., d_{20}^{22} 0·901, n_D^{20} 1·45786 (*phenylurethane*, m. p. 109—110°; *allo-*

phanate, m. p. 177°), identical with that which is the main product with the 2-chloro-5-methyl*cyclo*hexanol of b. p. 103—105°/14 mm. This menthol is regarded as possessing the hydroxyl and *iso*propyl groups in *cis*-relationship. The isomeric menthol (allophanate, m. p. 133°), obtained from the 2-chloro-5-methyl-*cyclo*hexanol of b. p. 95—97°/14 mm., will possess the corresponding *trans*-structure. Attempts to regenerate the menthols from the corresponding allophanate by hydrolysis with potassium hydroxide yielded the same *urethane*, $C_{11}H_{21}O_2N$, m. p. 117—118°; on heating in a vacuum (cf. Grandière, A., 1924, i, 625), profound decomposition took place. The menthol obtained from any of these three sources on oxidation with chromic acid in acetic acid solution yields the same inactive *menthone*, b. p. 81—82°/13 mm., d_{16}^{16} 0·891, n_D^{16} 1·4444, which, unlike the menthone obtained by Wallach and others, yields no crystalline derivatives. The liquid *oxime* (cf. Einhorn and Klages, A., 1902, i, 74) has b. p. 124—125°/10 mm., d_{13}^{13} 0·9502, n_D^{13} 1·4787, and on reduction with sodium and alcohol yields the same menthylamine, b. p. 79—80°/10 mm., d_{25}^{25} 0·849, n_D^{25} 1·45116 (*phenylcarbamide*, m. p. 122°), independently of the source from which the original menthone was obtained. This menthylamine yields no crystalline picrate (cf. Brunel, Bull. Soc. chim., 1905, **33**, 500) and is apparently the second inactive amine required by theory. Further evidence that the inactive menthone is a single substance and not a mixture of stereoisomerides is afforded by the fact that on reduction, either with sodium in aqueous ether or with hydrogen and platinum oxide catalyst in acetic acid, it yields the same menthol, b. p. 90—92°/15 mm. (allophanate, m. p. 177°). R. BRIGHTMAN.

Action of menthol on the chlorides of phosphorus. T. MITOBEDZKI and J. H. KOLITOWSKA (Rocz. Chem., 1926, **6**, 67—96).—The reactions between menthol and phosphorus chlorides were studied with a view to establish the analogy between hydrolysis and alcoholysis. The first product of the reaction with phosphorus trichloride is *trimenthyl phosphite*, $P(OC_{10}H_{19})_3$, m. p. 44—45°, which, with the hydrogen chloride liberated, yields sec.-d-*menthyl chloride*, and, as by-products, *d*-menthene and tertiary menthyl chloride. With phosphorus oxychloride, menthol yields mainly *trimenthyl orthophosphate*, m. p. 86°, $[\alpha]_D$ −100°, also obtained from phosphorus oxychloride and sodium menthoxide. A small fraction of this ester then reacts further with hydrogen chloride, yielding menthyl chloride. Phosphorus pentachloride in molecular proportions with menthol yields only secondary menthyl chloride; with excess of menthol, the phosphorus oxychloride formed gives trimenthyl orthophosphate. With menthol, triphenyl dichlorophosphate yields menthyl chloride and menthyldiphenyl dichlorophosphate. These reactions indicate that menthol behaves similarly to water in the above respects.

R. TRÜSZKOWSKI.

Rate of oxidation of unsaturated compounds [terpenes] by perbenzoic acid. H. MEERWEIN.—See this vol., 722.

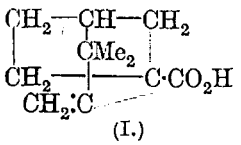
Dihydroxydiphenylcaoutchouc and its dimethyl ether. H. L. FISHER, H. GRAY, and E. M. MCCOLM (J. Amer. Chem. Soc., 1926, **48**, 1309—1312).—Caoutchouc dibromide is converted quantitatively into Weber's "tetroxyphenylpolyprene," m. p. 195—205° after shrinking at 190° (A., 1900, i, 353), when heated with phenol and ferric chloride. As this dissolves readily in cold aqueous alkali, it must be formulated as a *dihydroxydiphenylcaoutchouc*, $[C_5H_8(C_6H_4{\cdot}OH)_2]_x$, and this is supported by its conversion, on treatment with methyl sulphate in presence of alkali, into the *dimethyl ether*, m. p. 151—156°. F. G. WILLSON.

Manasse's α- and β-hydroxycamphors. J. BREDT and H. AHRENS (J. pr. Chem., 1926, [ii], **112**, 273—298).—The reduction of *dl*-camphorquinone with zinc dust and acetic acid (cf. Manasse, A., 1903, i, 42) gives a mixture of *dl*-α- and *dl*-β-hydroxycamphors, m. p. 203—205°, from which, by the action of methyl alcohol and hydrogen chloride, may be obtained a crystalline dl-β-*methyl ether*, m. p. 133—134°, b. p. 344° or 160°/4 mm. The optically active isomeride, m. p. 149—150°, $[\alpha]_D^{18}$ +174·2°, is prepared similarly from Manasse's hydroxycamphor or from pure active β-hydroxycamphor. They are bimolecular, fail to react with semicarbazide or with Grignard reagents, and have probably the structure $C_8H_{14}<\begin{matrix}CH-O-C(OMe)\\ C(OMe)\cdot O\cdot CH\end{matrix}>C_8H_{14}$. The active ether is hydrolysed by concentrated hydrochloric acid at the ordinary temperature to pure, active, unimolecular β-hydroxycamphor, m. p. 211—212° [semicarbazone, m. p. 223—224° (Manasse, 203—204°); *acetate*, m. p. 63—64°; *chloride*, m. p. 207—208°]. Manasse's hydroxycamphor gives the same chloride, but in only half the yield, and may be converted, by successive treatment with thionyl chloride and methyl alcohol, into the solid β-methyl ether, m. p. 149—150°, and an oily α-methyl ether, b. p. 70—72°/2 mm., which is obtained also by direct etherification with methyl alcohol and hydrogen chloride. Unlike the β-ether, the α-ether is not hydrolysed by cold hydrochloric acid; it reacts normally with magnesium phenyl bromide to give the tertiary *alcohol*, $C_8H_{14}<\begin{matrix}CH\cdot OMe\\ CPh\cdot OH\end{matrix}$, b. p. 143—144°/2 mm. The bimolecular β-ether is completely converted by boiling methyl alcohol and hydrogen chloride into a unimolecular *ether*, $C_8H_{14}<\begin{matrix}CH\cdot OMe\\ CO\end{matrix}$, b. p. 81°/4 mm., obtainable also from the mixed hydroxycamphors or from pure β-hydroxycamphor by treatment with sodium and methyl iodide.

α-Hydroxycamphor, m. p. 168—169° (semicarbazone, m. p. 182—183°), is isolated from the mother-liquors in the preparation of the bimolecular β-methyl ether from Manasse's hydroxycamphors. Alternatively, the two constituents may be separated by fractional crystallisation of the mixed semicarbazones. From the semicarbazone of m. p. 183—184° oxalic acid liberates an α-hydroxycamphor, m. p. 196—197° (140—142° after keeping a day), which gives with thionyl chloride a very reactive unimolecular *chloride*,

$C_8H_{14}<\begin{matrix}CH\\|\\CCl\end{matrix}>O$. From the semicarbazone of m. p. 211—211·5° there is obtained β-hydroxycamphor, m. p. 209—210°. C. HOLLINS.

Camphor and terpenes. III. Transformations in the camphor series. J. HOUBEN and E. PFANKUCH (Ber., 1926, **59**, [*B*], 956—962).—Camphane-2-carboxylic acid is converted by the successive action of phosphorus pentachloride and sodium hydroxide into *camphene-1-carboxylic acid* (I), m. p. 109—110°, characterised by oxidation to camphenonic acid, conversion by hydrogen chloride in ether–light petroleum into 2-*chlorocamphane-2-carboxylic acid*, m. p. 146° (decomp.), by catalytic reduction to dihydrocamphene-1-carboxylic acid and by the impossibility of chlorinating the *chloride*, b. p. 108°/21 mm., of the latter acid. It behaves as a simple racemate resolvable by brucine. Previous observations (Houben and Willfroth, A., 1913, i, 970, 1196) were obscured by the presence of mixtures of the racemic and active forms; the "isomeric camphenecarboxylamide" then observed is identified as camphane-2-carboxylamide, probably due to incomplete nuclear chlorination of the initial material.



(I.)

Camphene-1-carboxylamide, suspended in dry ether, is transformed by dry hydrogen chloride into the *hydrochloride* without affecting the carbon skeleton or double linking; with concentrated aqueous hydrochloric acid, 2-*chlorocamphane-2-carboxylamide hydrochloride* is produced, which is immediately hydrolysed by water to 2-chlorocamphane-2-carboxylamide, in which an *exo*-compound cannot be present in more than small amount.

2-Chlorocamphane-2-carboxyl chloride has $[\alpha]_D$ +19·1° in benzene. H. WREN.

Action of hydrogen chloride on nopinene. O. ACHMATOWICZ (Rocz. Chem., 1926, **6**, 59—66).—Hydrogen chloride combines with nopinene to give bornyl chloride and terpinyl or terpene chloride. This result is explicable on the basis of Stawiński's theory (*ibid.*, 1923, **3**, 200) of the analogy between conjugated double linkings and rings, whilst Wagner's theory (1899) does not afford a satisfactory explanation. R. TRUSZKOWSKI.

Sesquiterpenes. R. VESTERBERG (Svensk Kem. Tidskr., 1925, **37**, 219—226; from Chem. Zentr., 1926, I, 132—133).—A semi-fossilised Borneo resin when heated at 400° with activated nickel gave methane, hydrogen, and an oil, which after purification yielded a *sesquiterpene*, $C_{15}H_{24}$, b. p. 90—92°/1 mm., d_4^{19} 0·9153, n_D^{19} 1·5120, α_D^{22} 1·52°. By distillation with sulphur it gave an oily naphthalene *derivative*, having d_4^{19} 0·0798, n_D^{15} 1·5858. The *picrate* has m. p. 115°. The naphthalene derivative agreed in its properties with cadalene. Dammar resin, presumed to be analogous to the fossil resin, on similar treatment yielded a sesquiterpene of b. p. 97—98°/2 mm., d_4^{18} 0·9120, n_D^{21} 1·5100. When heated with sulphur, it gave a naphthalene hydrocarbon having constants different from those of cadalene. G. W. ROBINSON.

Isomerism between dimeric ketens and *cyclo*butadiones. III. G. SCHROETER [with E. FINCK] (Ber., 1926, **59**, [*B*], 973—991; cf. A., 1917, i, 145; 1920, i, 852).—*Methyl acetonetetracarboxylate*, m. p. 59—60° (*copper*, *nickel*, *cobalt*, *lead*, *mercury*, *calcium*, *strontium*, *barium*, *ferrous*, and *ferric* salts), is obtained in 40% yield from carbonyl chloride and methyl sodiomalonate in the presence of benzene. Side reactions are due to initial formation of the chloride, $(CO_2Me)_2CH{\cdot}COCl$, which partly decomposes into methyl methanetricarboxylate and the ester di- or tri-chloride, and to the condensation of the acetonetetracarboxylate with unchanged malonate to *methyl* iso*butylenehexacarboxylate*, $(CO_2Me)_2C{:}C[CH{\cdot}(CO_2Me)_2]_2$, m. p. 114—115°. *Methyl acetoneaniltetracarboxylate* has m. p. 102°. Methyl acetonetetracarboxylate is converted by sulphuric acid (10% SO_3) into *methyl* 2-*methoxy*-4 : 6-*pyronone*-3 : 5-*dicarboxylate*, m. p. 122—123° (*sodium*, *potassium*, *barium*, *calcium*, *strontium*, *magnesium*, *lead*, *zinc*, *cadmium*, *copper*, *cobalt*, *nickel*, *ferrous*, *ferric*, and *silver* salts), instead of the expected *cyclo*butane derivative. It is converted by methyl alcohol into methyl acetonetetracarboxylate, by phenylhydrazine into the *monophenylhydrazide*, $CH(CO_2Me)_2{\cdot}CO{\cdot}CH(CO_2Me){\cdot}CO{\cdot}NH{\cdot}NHPh$, m. p. 90—91°, by aniline in benzene into the corresponding *monoanilide*, m. p. 114—115° (*sodium* and *copper* salts), by undiluted aniline into a *compound*, $C_{20}H_{20}O_5N_2$, m. p. 132—133° (decomp.), and by water probably into methyl acetonetricarboxylate, which affords methyl malonate when distilled. The sodium, potassium, or barium salt of methyl methoxypyrononedicarboxylate is decomposed by boiling water into carbon dioxide, sodium methyl malonate, methyl malonate, and acetic acid. Towards pyridine and quinoline, methyl 2-methoxy-4 : 6-pyronone-3 : 5-dicarboxylate acts as a methylating agent, giving the methylpyridinium *salt* of methyl 2 : 6-dihydroxy-1 : 4-benzopyrone-3 : 5-dicarboxylate, m. p. 128—129° (decomp.), and thence 1-methylpyridine [1-*methylquinolinium chloroplatinate*, m. p. 230° (decomp.), is described]. *Methyl* 2 : 6-*dihydroxy*-1 : 4-*benzopyrone*-3 : 5-*dicarboxylate*, m. p. 183—185° (decomp.), and its trihydrate were prepared [*monosodium*, *disodium*, *monobarium* (+2H_2O), *dibarium* (+H_2O), *aniline*, m. p. 144—145° (decomp.), and *pyridine* salts].

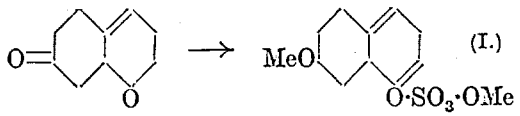
The isolation of pyronone derivatives from methyl acetonetetracarboxylate raises doubts about the structure of the compounds derived similarly from *s*-dialkylacetonedicarboxylic esters (*loc. cit.*). The production of 2 : 4-diethyl*cyclo*butane-1 : 3-dione from ethyl diethyl*cyclo*butadionecarboxylate and barium hydroxide cannot, however, be a secondary process, since the normal and basic *barium* salts of acetonedicarboxylic and *s*-diethylacetonedicarboxylic acids decompose under similar conditions into carbon dioxide and acetic acid or dipropyl ketone without a trace of *cyclo*butandione derivatives. It is suggested that a type of desmotropy exists between alkoxypyronones and *cyclo*butadionecarboxylic esters analogous to that observed between *C*- and *O*-acyl derivatives of β-diketones. This conception explains the production of trialkylacetonedicarboxylic esters by alkylation of dialkyl*cyclo*butadionecarboxylic

esters, the action of chloroformic esters on the latter substances to produce what are now considered pyronone compounds, and the action of bromine on Dieckmann's compound, $CO<\begin{matrix}CR\text{———}\\CR(CO_2R')\end{matrix}>C\cdot O\cdot CO_2R'$ (cf. A., 1922, i, 1156; Staudinger, *ibid.*, 1924, i, 295). H. WREN.

Cyclic derivatives of acetonedicarboxylic acid. R. MALACHOWSKI (Rocz. Chem., 1926, 6, 27—44).—6-*Hydroxy*-4-*acetoxy*-1 : 2-*benzopyrone*, m. p. 91—92° (*quinoline* salt, m. p. 167—168°), is prepared from acetonedicarboxylic anhydride, and yields with alcohol *ethyl hydrogen* β-*acetoxyglutaconate*, $CO_2Et\cdot CH_2\cdot C(OAc):CH\cdot CO_2H$, m. p. 79—80°. From the *silver* salt of the above pyrone are prepared 4 : 6-*diacetoxy*-1 : 2-*benzopyrone*, an oil, and 4-*acetoxy*-6-*benzoxy*-1 : 2-*benzopyrone*, m. p. 111·5—112·5°. β-*Hydroxy*-β-*acetoxyglutaric anhydride*, m. p. 115—116°, is prepared by the fusion of the above hydroxyacetoxypyrone, whilst the *pyridine* salt, m. p. 143°, of the latter is shown to be derived from 3-*acetyl*-1 : 2-*benzopyrone*, yielding with acids 4 : 6-*dihydroxy*-3-*acetyl*-1 : 2-*benzopyrone*, m. p. 125—126°, which again on heating with concentrated sulphuric acid gives triacetolactone 5-carboxylic acid (4-keto-6-methyl-3 : 4-dihydro-1 : 2-benzopyrone-5-carboxylic acid). 3-*Bromo*-4 : 6-*dihydroxy*-1 : 2-*benzopyrone*, m. p. 149—150°, and 3-*bromo*-6-*hydroxy*-4-*acetoxy*-1 : 2-*benzopyrone*, m. p. 107—108°, are obtained from the corresponding pyrone derivatives. The following further compounds are described: *phenylhydrazones* of 6-*hydroxy*-4-*acetoxy*-1 : 2-*benzopyrone*, m. p. 166—167°, of 4 : 6-*dihydroxy*-1 : 2-*benzopyrone*, m. p. 176—177°, of αβ-*dihydroxyglutaric acid*, m. p. 149°, 3-*bromo*-4 : 6-*dihydroxy*-, m. p. 187—188°, and 3-*bromo*-6-*hydroxy*-4-*acetoxy*-5-*cinnamylidene*-1 : 2-*benzopyrone*, m. p. 189—191°. R. TRUSZKOWSKI.

7-Methoxy-3-(6′-bromohomopiperonyl)-2-methyl-1 : 4-benzopyrone. W. BAKER (J.C.S., 1926, 1074—1076).—6-Bromopiperonal, on condensation with ethyl cyanoacetate in presence of piperidine followed by the hydrolysis of the resulting *ester*, m. p. 31°, yields 6-*bromopiperonylidenecyanoacetic acid*, m. p. about 300° (decomp.), which forms α-cyano-β-piperonylpropionic acid on reduction with sodium amalgam. β-Piperonylpropionitrile, when brominated in glacial acetic acid, forms the 6-*bromo*-derivative, m. p. 81°, which, on keeping in presence of hydrogen bromide and acetic acid, yields the corresponding *amide*, m. p. 151°. By condensation with resorcinol (Hoesch synthesis), the bromonitrile gives 6′-*bromohomopiperonylresacetophenone*, m. p. 163°, which by successive acetylation, hydrolysis, and methylation gives 7-methoxy-3-(6′-bromohomopiperonyl)-2-methyl-1 : 4-benzopyrone, m. p. 206—207°. This synthesis establishes the position of the bromine atom (cf. A., 1925, i, 925). J. S. H. DAVIES.

Oxonium derivatives of benzopyran. F. KEHRMANN and M. RIEDER (Helv. Chim. Acta, 1926, 9, 491—499).—The bases of the condensation products of acetylacetone, methylacetylacetone, benzoylacetone, and dibenzoylmethane with resorcinol, phloroglucinol, or pyrogallol (A., 1901, i, 559, 603; 1903, i, 272), on treatment with methyl sulphate, undergo simultaneous methylation and conversion into the methyl sulphate oxonium salt, according to the scheme (I). Further oxonium salts are prepared

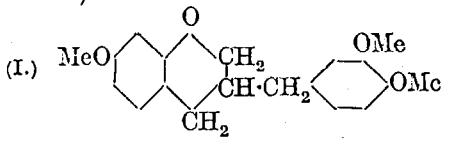


(I.)

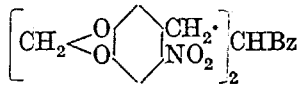
from the aqueous solutions of these compounds. Precipitation with sodium acetate yields the ψ-base. Solutions of the 7-monomethoxy-derivatives are characterised by marked fluorescence, which, in general, entirely disappears on introduction of further methoxyl groups. The stability of the salts towards water is increased by the introduction of alkoxy- or aryl groups, in particular by introduction of methoxyl groups. The following are described: 7-*methoxy*-2 : 4-*dimethylbenzopyrylium chloroaurate*; 5 : 7-*dimethoxy*-2 : 4-*dimethylbenzopyrylium chloroaurate*; 7-*methoxy*-2 : 3 : 4-*trimethylbenzopyrylium chloroaurate*; 7-*methoxy*-4-*phenyl*-2-*methylbenzopyrylium perchlorate, chloroplatinate, nitrate, bromide*; 7 : 8-*dimethoxy*-4-*phenyl*-2-*methylbenzopyrylium perchlorate, nitrate, bromide, dichromate, chloroplatinate*; 5 : 7-*dimethoxy*-4-*phenyl*-2-*methylbenzopyrylium perchlorate, chloroplatinate*; 7-*methoxy*-2 : 4-*diphenylbenzopyrylium methyl sulphate, perchlorate, bromide, nitrate, chloroplatinate*, and non-crystalline *anilide*; 7 : 8-*dimethoxy*-2 : 4-*diphenylbenzopyrylium methyl sulphate, perchlorate, chloroplatinate*; 5 : 7-*dimethoxy*-2 : 4-*diphenylbenzopyrylium methyl sulphate, bromide, nitrate, perchlorate, chloroplatinate*. 1 : 2 : 4-Trihydroxybenzene condenses with benzoylacetone in glacial acetic acid under the influence of hydrogen chloride, giving 6 : 7-*dihydroxy*-4-*phenyl*-2-*methylbenzopyrylium hydrochloride*. The *base*, decomp. 210—220°, isolated by precipitation of an aqueous alcoholic solution of the hydrochloride with sodium acetate, yields, through the methylation product, 6 : 7-*dimethoxy*-4-*phenyl*-2-*methylbenzopyrylium chloroplatinate, perchlorate, bromide, nitrate*. M. CLARK.

Synthesis of brazilin and hæmatoxylin and their derivatives. I. Veratrylidene-7-methoxychromanone, and a new synthesis of some benzopyrylium salts. W. H. PERKIN, jun., J. N. RÂY, and R. ROBINSON (J.C.S., 1926, 941—953; cf. Perkin and Robinson, Proc. C.S., 1912, **28**, 7).—Optimal conditions for the monomethylation of resorcinol are given. *m*-Methoxyphenol, b. p. 240—242°, condenses with β-chloropropionic acid (less satisfactorily with the β-bromo- and β-iodo-acids) to form β-*m*-methoxyphenoxypropionic acid, and with ethylene chlorohydrin and alcoholic sodium ethoxide to yield *m*-β-hydroxyethoxyanisole, b. p. 290°/15 mm. The latter compound is converted by phosphorus tribromide in benzene into a *substance*, m. p. 65°, which is probably the ethylene ether of *m*-methoxyphenol. 7-Methoxychromanone, m. p. 56°, b. p. 197°/30 mm. [semicarbazone, m. p. 222° (decomp.)], is best prepared by the action of phosphoric anhydride on methoxyphenoxypropionic acid in boiling benzene. The product is condensed with veratraldehyde in acetic acid in a current of hydrogen chloride, and the resulting 3-veratrylidene-7-methoxychromanone, m. p.

141° (*hydrochloride* described), is reduced by hydrogen and palladous chloride to 3-*homoveratryl*-7-*methoxychroman* (I), m. p. 96—97° (cf. Pfeiffer and Emmer, A., 1920, i, 561, who claim to have obtained the dihydroketone).

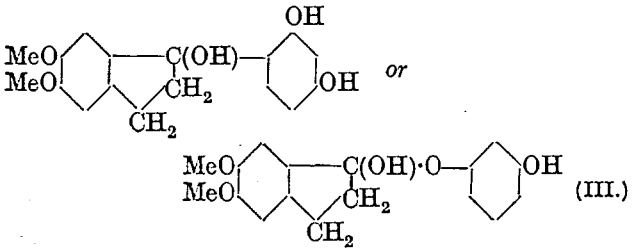
(I.) 

When homopiperonyl bromide is added to the sodium derivative obtained from acetophenone and sodamide, the product is a yellow *oil*, which on nitration yields dinitrodihomopiperonylamine; but if care be taken to remove ammonia before adding the bromide, the nitration gives the expected *di*-ω-6-*nitropiperonyl*isobutyrophenone (II), m. p. 160—161°.

(II.) 

Veratraldehyde is converted by alcoholic potassium hydroxide into veratric acid, homoveratryl alcohol, and 3 : 4-dimethoxycinnamic acid (cf. Perkin and Stoyle, J.C.S., 1923, **123**, 3174).

2-*Bromo*-5 : 6-*dimethoxy*-1-*hydrindone*, m. p. 157°, prepared by bromination of dimethoxyhydrindone, reacts with aqueous-alcoholic potassium cyanide to give the 2-*cyano*-compound, m. p. 174°, and, when less water is used, a *substance*, m. p. 256—257°. The nitrile is converted by alcoholic hydrogen chloride into *ethyl* 5 : 6-*dimethoxy*-1-*hydrindone*-2-*carboxylate*, m. p. 138° (decomp.). 5 : 6-*Dimethoxy*-1-*hydrindone*-*resorcinol* (III), m. p. 78°, and a *by-product*, m. p. 227°, are obtained by the action of hydrogen chloride on a solution of dimethoxyhydrindone and resorcinol in acetic acid.

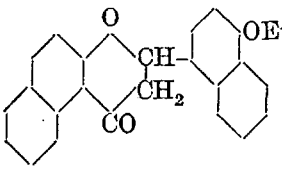


(III.)

A new synthesis of benzopyrylium salts by the action of anhydrous ferric chloride on a solution of an arylidene derivative of a cyclic ketone is found to have limited application. Veratrylidene-7-methoxychromanone gives 2 : 3-[7-*methoxychromeno*(4 : 3)]-6 : 7-*dimethoxybenzopyrylium ferrichloride*, m. p. 213°; 2-*veratrylidene*-1-*hydrindone*, m. p. 175°, is converted into 2 : 3-*indeno*(1 : 2)-6 : 7-*dimethoxybenzopyrylium ferrichloride*, m. p. 237—238°; 2-veratrylidene-5 : 6-dimethoxy-1-hydrindone into 2 : 3-[5 : 6-*dimethoxyindeno*(1 : 2)]-6 : 7-*dimethoxybenzopyrylium ferrichloride*, m. p. 246—247°; 2-piperonylidene-5 : 6-dimethoxy-1-hydrindone into 2 : 3-[5 : 6-*dimethoxyindeno*(1 : 2)]-6 : 7-*methylenedioxybenzopyrylium ferrichloride*, m. p. 270° (decomp.); 2-(2 : 3-*dimethoxybenzylidene*)-1-*hydrindone*, m. p. 124°, into 2 : 3-*indeno*-(1 : 2)-5 : 6-*dimethoxybenzopyrylium ferrichloride*, m. p. 168°; and 2′ : 3′ : 5 : 6-*tetramethoxy*-2-*benzylidene*-1-*hydrindone*, m. p. 183—184°, into 2 : 3-[5 : 6-*dimethoxyindeno*(1 : 2)]-5 : 6-*dimethoxybenzopyrylium ferrichloride*, m. p. 211°. The reaction fails with 2-*m*-*methoxybenzylidene*-5 : 6-*dimethoxy*-1-*hydrindone*, m. p. 164—165°, 2-anisylidene-5 : 6-dimethoxy-1-hydrindone, 3 : 4-*dimethoxystyryl veratryl ketone*, m. p. 116°, and 2-*veratrylidene*-4 : 6-*dimethoxycoumaranone*, m. p. 175°. 2 : 3-[5 : 6-*Dimethoxyindeno*(1 : 2)]-8-*methoxybenzopyrylium ferrichloride*, m. p. 250° (decomp.), is prepared by the action of hydrogen chloride on a solution of *o*-vanillin and dimethoxyhydrindone in acetic acid.

[A protest is entered against the continued use of "piperonyl" to connote the radical $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}$, which should be called "homopiperonyl."] C. HOLLINS.

2-Hydroxy-α-naphthyl methyl ketone. J. TAMBOR, G. PLATTNER, and C. ZÄCH (Helv. Chim. Acta, 1926, 9, 463—466).—An alcoholic solution of 2-hydroxynaphthyl methyl ketone condenses with benzaldehyde in presence of sodium hydroxide, giving β-*naphthaflavanone* (5 : 6-*benzo*-β-*flavanone*), m. p. 117° (cf. A., 1898, i, 373; 1899, i, 370). The *bromo*-derivative, m. p. 148°, obtained by bromination of the flavanone in carbon disulphide solution in sunlight or at 30—35°, is decomposed in alcoholic solution by sodium hydroxide, yielding β-naphthaflavone (A., 1914, i, 315). An alcoholic solution of 2-hydroxynaphthyl methyl ketone condenses with 1-aldehydo-4-ethoxynaphthalene, in presence of sodium hydroxide, giving 4′-*ethoxy*-5 : 6-2′ : 3′-*dibenzo*-β-*flavanone* (annexed formula), m. p. 213°, and a smaller yield of 2-*hydroxy*-α-*naphthyl* β-4-*ethoxy*-α-*naphthyl*-*ethenyl ketone*, m. p. 144°. Condensation in absolute alcohol gives the latter as main product with a small yield of the flavanone, into which it is converted by treatment in hot alcoholic solution with excess of aqueous sodium hydroxide.



M. CLARK.

Phenolphthalol: preparation, and reaction towards oxydases and peroxydases. G. D. BUCKNER (Amer. J. Physiol., 1925, **74**, 354—358).—Phenolphthalol, an improved method for the preparation of which is described, is a satisfactory reagent for oxydases and peroxydases, but is not preferable to phenolphthalin. Human blood can be detected at a dilution of 1 in 5×10^6.

A. A. ELDRIDGE.

Absorption spectra of resorcinolbenzein. W. R. ORNDORFF, R. C. GIBBS, and C. V. SHAPIRO (J. Amer. Chem. Soc., 1926, **48**, 1327—1333; cf. this vol., 60).—Resorcinolbenzein in absolute alcoholic solution shows nine absorption bands, the greater complexity of the spectrum as compared with that of benzaurin (*loc. cit.*) being ascribed to the pyrone ring of the former. The colour of alcoholic solutions of resorcinolbenzein does not fade. The absorption spectra of solutions of resorcinolbenzein in alcoholic hydrogen chloride, 93% sulphuric acid, and aqueous potassium hydroxide indicate the respective formation of the hydrochloride, sulphate, and potassium

salt. Pure resorcinolbenzein (cf. Kehrmann and Dengler, A., 1909, i, 249; Pope, J.C.S., 1914, **105**, 251), m. p. 328—329° in a sealed tube, does not lose a mol. of water when heated at 140° (cf. Meyer and Gerloff, A., 1924, i, 509). F. G. WILLSON.

Synthesis in the thianthren series. II. M. SEN and J. N. RÂY (J.C.S., 1926, 1139—1142; cf. *ibid.*, 1921, **119**, 1959).—1 : 4 : 5 : 8-*Tetramethylthianthren*, m. p. 242°, obtained by the interaction of sulphur monochloride and *p*-xylene in presence of aluminium–mercury couple, forms a *disulphone*, m. p. above 290°. 3 : 7-*Dimethoxy*-2 : 6-*dihydroxythianthren*, m. p. 202°, prepared similarly from guaiacol, forms a yellow *sodium* salt and a *diacetyl* derivative, m. p. 165°. The *azo*-compounds derived from diazotised diaminothianthren and β-naphthol, resorcinol, and sulphanilic acid are described. The thianthren derivatives, obtained by the general method from bromobenzene, *p*-chlorophenol, *p*-cresol, *p*-tolyl methyl ether, the dimethyl ethers of quinol and resorcinol, could not be obtained free from sulphur. Bromobenzene differs from iodobenzene in that the halogen is not displaced during the reaction.

J. S. H. DAVIES.

Synthesis of naphthathioxins. R. CHILD and S. SMILES (J.C.S., 1926, 957).—Di-β-naphthyl ether, heated with sulphur and a trace of iodine at 280°, or treated with sulphur chloride and aluminium chloride, gives small yields of αα′-naphthathioxin, m. p. 165°, but similar reactions with α-naphthyl β-naphthyl ether (αβ′-dinaphthyl ether) failed. 4-Chloro-1-hydroxy-β-naphthyl 2-hydroxy-α-naphthyl sulphide (Lesser and Gad, this vol., 167) is readily prepared by the interaction of β-naphthol and 4-chloro-α-naphthol 2-sulphur bromide (4-chloro-2-bromothiol-α-naphthol), which is obtained from the corresponding disulphide by the action of bromine in carbon tetrachloride. This αβ′-sulphide, when treated with dehydrating agents, yields a substance, m. p. 157°, which is probably a naphthathioxin.

C. HOLLINS.

Formation of 2-hydroxypyrroline-5-carboxylic acid from glutamic acid and the conversion of the former compound into 2-hydroxypyrrolidine-2-carboxylic acid. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1926, **153**, 88—92).—Glutamic acid when heated with aniline at 205—210° is converted into 2-*hydroxypyrroline*-5-*carboxylic acid*, m. p. 180°. This compound differs markedly from the isomeric 2-pyrrolidone-5-carboxylic acid, in particular giving the reactions for an unsaturated linking and also an intense coloration with *p*-dimethylaminobenzaldehyde. With hydrogen in presence of platinum-black, it is reduced to 2-*hydroxypyrrolidine*-5-*carboxylic acid* (hydroxyproline), m. p. 204·5°. W. O. KERMACK.

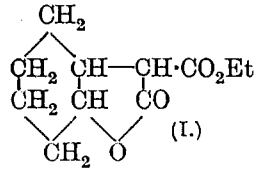
Ultra-violet absorption of a series of eight organic substances of the 4-pyridone type, in water solution. E. R. RIEGEL and M. C. REINHARD (J. Amer. Chem. Soc., 1926, **48**, 1334—1345).—Ultra-violet absorption spectra (to 2100 Å.) of 4-pyridone, *N*-methyl-4-pyridone, 1 : 4-benzopyrone (group A), chelidamic acid, *N*-methylchelidamic acid, chelidonic acid (group B), 4-hydroxypiperidine, and *N*-methyl-4-hydroxypiperidine (group C), in aqueous solution are recorded. Compounds of groups A and B show selective absorption, whilst this property is practically absent in group C. The persistence of the absorption by compounds of group A is about three times that shown by those of group B, whilst the absorption of the latter is shifted towards the red, by the introduction of the carboxyl groups, in accordance with Hartley's rule, as compared with that of group A. F. G. WILLSON.

Preparation of 5-hydroxy-*N*-methyloxindole etc. E. MERCK.—See B., 1926, 434.

Manufacture of a new iodine-substituted oxindole. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1926, 514.

Manufacture of poly-iodine-substituted isatins. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1926, 514.

Preparation of 2-ketodihydro- and 2-ketohexahydro-indole-3-propionic acids and some of their halogen derivatives. Thyroid activity. V. E. C. KENDALL, A. E. OSTERBERG, and B. F. MACKENZIE (J. Amer. Chem. Soc., 1926, **48**, 1384—1401).—Condensation of *cyclo*hexene oxide in presence of sodium ethoxide with ethyl malonate affords the *ethyl* ester, (I), b. p. 199°/30 mm., of 2-*keto-octahydrobenzfuran*-3-*carboxylic acid*, m. p. 120°, with loss of carbon dioxide. The sodium derivative of (I) condenses, in benzene suspension, with β-bromopropionic acid, and the product yields, on hydrolysis, the *dicarboxylic acid*, (II), m. p. 199° (decomp.),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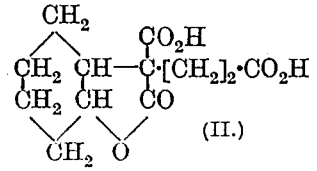
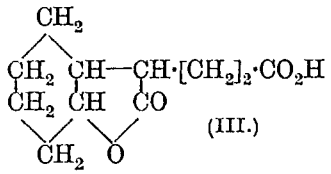
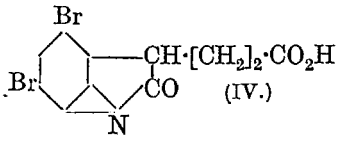

(II.)

which, when heated at 200°, is converted into 2-*keto-octahydrobenzfuran*-3-β-*propionic acid*, (III), m. p. 81°. Oxidation of the latter, as the magnesium salt, with aqueous bromine affords 2-*keto*cyclo*hexane*-α-*glutaric acid*, m. p. 131° (*phenylhydrazone*, m. p. 146°, losing water when boiled in xylene, with formation of the corresponding *pyridazinone*, m. p. 126°; *phenylhydrazone* of the *ethyl* ester, unstable, m. p. 110°), and this, when heated in a vacuum at 200°, is converted into the *lactone*, 2-*ketohexahydrobenzfuran*-3-β-*propionic acid*, m. p. 100° (*ethyl* ester, b. p. 195—200°/8 mm.), whilst it is converted, by the action of alcoholic ammonia at 100°, into 2-*keto*-2 : 3 : 4 : 5 : 6 : 7-*hexahydroindole*-3-β-*propionic acid*, m. p. 173°. The latter cannot be obtained by the action of ammonia on the above lactone, but is converted, when boiled with concentrated aqueous sodium hydroxide, into the above keto*cyclo*hexane-glutaric acid. Treatment of the ketohexahydroindolepropionic acid with bromine in boiling glacial acetic acid affords 4 : 6 : 7-*tribromo*-2-*ketodihydro*-


(III.)

indole-3-β-*propionic acid*, m. p. 189°. This loses 1 mol. of hydrogen bromide when treated in alcoholic solution with 0·1*N*-aqueous sodium hydroxide; treatment with zinc dust in boiling acetic acid (etc.) affords 4 : 6-*dibromo*-2-*ketodihydroindole*-3-β-*propionic acid*, m. p. 245°, whilst boiling acetic acid in presence of sodium acetate converts it into 4 : 6-*dibromo*-2-*keto*-2 : 3-*dihydro*tricyclo*indole*-3-β-*propionic acid*, (IV), m. p. 219°. The latter is converted, when boiled with aqueous sodium hydroxide, into α-(4 : 6-*dibromo* - 2 : 3 - *imino* - *phenyl*)*glutaric acid*, m. p. 219°, and is reduced by sodium amalgam and water to 2-*ketodihydroindole*-3-β-*propionic acid*, m. p. 174°, which yields, when treated with iodine in aqueous alkali, α-(2 : 3-*iminophenyl*)*glutaric acid*, m. p. 199°, and when heated at 175° or boiled with acetic anhydride, is converted into 2-*keto*-2 : 3-*dihydro*tricyclo*indole*-3-β-*propionic acid* (+0·5H_2O), m. p. 90°, or, anhydrous, m. p. 116°. Treatment of 2-ketodihydroindole-3-β-propionic acid with iodine in glacial acetic acid, in presence of sulphuric and iodic acids, affords α-(4-*iodo*-2 : 3-*iminophenyl*)*glutaric acid*, m. p. 162°, followed by resolidification and decomposition at 250°, and α-(4 : 6-*di-iodo*-2 : 3-*iminophenyl*)*glutaric acid*, m. p. 252°. When boiled in aqueous solution, the former is converted into 6-*iodo*-2-*keto*-2 : 3-*dihydro*tricyclo*indole*-3-β-*propionic acid*, m. p. 251°, and this, on reduction with iodine and phosphorus in glacial acetic acid, affords 6-*iodo*-2-*keto*-2 : 3-*dihydroindole*-3-β-*propionic acid*, m. p. 172°. 4 : 6-*Di-iodo*-2-*keto*-2 : 3-*dihydro*tricyclo*indole*-3-β-*propionic acid*, m. p. 242°, is obtained by boiling the above di-iodo-derivative with glacial acetic acid in presence of concentrated sulphuric acid, and is converted, as above, into 4 : 6-*di-iodo*-2-*keto*-2 : 3-*dihydroindole*-3-β-*propionic acid*, m. p. 244°.



(IV.)

F. G. WILLSON.

Preparation of dicyclic bases [tetrahydroquinolines]. J. D. RIEDEL.—See B., 1926, 513.

Synthetical work on the *iso*quinoline alkaloids. I. Substituted *o*-carboxyphenylethylamines. G. E. EDWARDS (J.C.S., 1926, 740—749).—*r*-Laudanosine, m. p. 115°, is prepared easily by reduction of papaverine methosulphate with zinc dust and alcoholic sulphuric acid. Its oxidation product, 1-hydroxy-6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline (Pyman, *ibid.*, 1909, **95**, 1272), could not be benzoylated (cf. Freund, A., 1889, 977), but condenses with homopiperonylonitrile to give 6 : 7-*dimethoxy*-1-(3′ : 4′-*methylenedioxy*-ω-*cyanobenzyl*)-2-*methyltetrahydro*isoquinoline, m. p. 171°, which is converted by formaldehyde, methylal, or methylene iodide into high-melting bases not of the tetrahydro*epi*berberine type. Piperonyl bromide and sodium ethoxide react to form *piperonyl ethyl ether*, b. p. 130—133°/13 mm. Homopiperonylonitrile, m. p. 49°, is obtained from *piperonylpyruvic acid oxime*, m. p. 174—175°, by the action of acetic anhydride.

For the synthesis of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylamine*, m. p. 225° (*picrate*, m. p. 292—294°; *lactone hydrochloride*, m. p. 248°; *acetyl* derivative of the lactone, m. p. 155°), meconinenitromethane is reduced with stannous chloride and hydrochloric acid. A better yield results from the following series of reactions. Meconineacetic acid, from opianic acid and malonic acid (Liebermann, A., 1887, 47), is converted by way of the *acid chloride*, m. p. 158—159°, into the *amide*, m. p. 223—224°, which with sodium hypochlorite gives the required base; or into the *hydrazide*, which with nitrous acid gives the *azide*, m. p. 94°, and thence by Curtius' reaction the *lactone* of *ethyl* β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylcarbamate*, m. p. 131°. This is hydrolysed by hot 15% sodium hydroxide solution to give the required amino-acid, or by concentrated hydrochloric acid at 150° to give β-*hydroxy*-β-(2-*carboxy*-3 : 6-*dihydroxyphenyl*)*ethylamine*, m. p. 138—140° (*hydrochloride*, m. p. 262—265°). The *benzylidene* derivative, m. p. 125°, of the dimethoxylactone base forms a *methiodide*, m. p. 180°, which is hydrolysed by hot 95% ethyl alcohol to the *lactone* of β-*hydroxy*-β-(2-*carboxy*-3 : 4-*dimethoxyphenyl*)*ethylmethylamine hydriodide*, m. p. 220—222° (*hydrochloride*, m. p. 233°; *nitroso*-compound, m. p. 108°; *benzoyl* derivative, m. p. 106°; free *amino-acid*, m. p. 190—192°).

m-*Meconineacetic acid*, m. p. 230—231° (*acid chloride*, m. p. 103—104°; *amide*, m. p. 240—241°; *ethyl* ester, m. p. 133°; *methyl* ester, m. p. 129°), is similarly converted via the *azide*, m. p. 100° (decomp.), and the *lactone-carbamic* ester, m. p. 177—178°, into β-*hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylamine*, m. p. 204—205° (*benzylidene* compound, m. p. 146°, forms a *methiodide*), and β-*hydroxy*-β-(2-*carboxy*-4 : 5-*dimethoxyphenyl*)*ethylmethylamine*, m. p. 199—204° (decomp.) (*lactone*, m. p. 230—231°).

C. HOLLINS.

Synthesis of 1 : 2-dihydro-2-methylquinoline. A correction. F. A. MASON (J.C.S., 1926, 955—956).—The compound previously described as "1 : 2-dihydroquinaldine" (*ibid.*, 1925, **127**, 1032) is found to be 2-methylquinoline. C. HOLLINS.

Crystalline methylene bases of the quinoline series. I. E. ROSENHAUER [with H. HOFFMANN and H. UNGER] (Ber., 1926, **59**, [*B*], 946—948; cf. Mills and Raper, this vol., 77).—1-*Methyl*-2-*methylenedihydroquinoline*, m. p. 71—72°, is obtained by cautious addition of dilute sodium hydroxide to an aqueous solution of 2-methylquinoline methosulphate, followed by immediate extraction of the base with ether. The quaternary iodides from 2 : 4-di- and 2 : 4 : 6-tri-methylquinoline yield similar methylene *bases*, m. p. 60° and 43—45°, respectively. H. WREN.

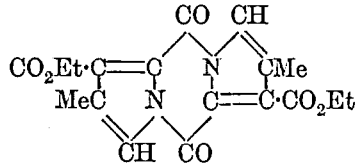
Preparation of a hydroxy-Bz-tetrahydroquinoline. J. D. RIEDEL.—See B., 1926, 513.

Derivatives of tetrahydrocarbazole. V. Carboxylic acids. (MISS) W. M. COLLAR and S. G. P. PLANT (J.C.S., 1926, 808—810).—*Tetrahydrocarbazole*-6-*carboxylic acid*, m. p. 282° (*methyl* ester, m. p. 158°; *ethyl* ester, m. p. 119°), is obtained by boiling cyclo*hexanone*-p-*carboxyphenylhydrazone*, m. p. 236°, with dilute sulphuric acid. In a similar manner the o-*carboxyphenylhydrazone*, m. p. 162°, gives *tetrahydrocarbazole*-8-*carboxylic acid*, m. p. 203° (*methyl* ester, m. p. 124°; *ethyl* ester, m. p. 76°), whilst from

the m-*carboxyphenylhydrazone*, m. p. 176° (decomp.), is obtained a mixture of *tetrahydrocarbazole*-5- and -7-*carboxylic acids*, separable by fractional crystallisation into an acid of m. p. 287° (*methyl* ester, m. p. 155°; *ethyl* ester, m. p. 146°) and an acid of m. p. 210° (*methyl* ester, m. p. 93°). The higher-melting acid predominates in the mixture. C. HOLLINS.

Doebner's reaction. V. R. CIUSA and G. BARATTINI (Gazzetta, 1926, **56**, 131—134).—It has been shown previously (A., 1921, i, 195) that the reaction between β-naphthylamine, pyruvic acid, and an aromatic aldehyde yields, besides α-aryl-β-naphthacinchonic acid as principal product, also the corresponding tetrahydrogenated compound, which may be readily converted into the non-hydrogenated compound by treatment with alkaline permanganate solution. The opposite change, viz., the conversion of the non-hydrogenated into the hydrogenated compound, has now been effected, in the case of α-phenyl-β-naphthacinchonic acid and α-phenyl-β-naphthaquinoline by reduction with sodium amalgam. Further, the tetrahydrogenated acid, when heated with soda-lime, undergoes decarboxylation and dehydrogenation to the non-hydrogenated base. If, on the other hand, α-phenyltetrahydro-β-naphthacinchonic acid is heated in a vacuum at a temperature slightly above its m. p. as long as carbon dioxide is liberated, the hydrogenated base is obtained. T. H. POPE.

Some transformations of ethyl 3-methylpyrrole-4-carboxylate. H. FISCHER and O. WIEDEMANN (Z. physiol. Chem., 1926, **155**, 52—71).—*Ethyl* 3-*methylpyrrole*-4 : 5-*dicarboxylate*, m. p. 63°, and 5-*carbomethoxy*-4-*carbethoxy*-3-*methylpyrrole*, m. p. 59°, are obtained by the action of alcohol and hydrogen chloride, and ethereal diazomethane, respectively, on 4-carbethoxy-3-methylpyrrole-5-carboxylic acid. Above its m. p., the latter affords *ethyl* 3-*methylpyrrole*-4-*carboxylate*, m. p. 73°, whilst treatment with hydrocyanic acid and hydrogen chloride yields *ethyl* 2-*aldehydo*-3-*methylpyrrole*-4-*carboxylate*, m. p. 121° (*phenylhydrazone*, m. p. 154°; *semicarbazone*, m. p. 224°; *azlactone*, m. p. 192°; *oxime*, m. p. 167°, from which the corresponding *nitrile*, m. p. 135°, is obtained by boiling with acetic anhydride), and this, with sodium ethoxide and hydrazine, affords 2 : 3-dimethylpyrrole. Condensation of ethyl 3-methylpyrrole-4-carboxylate with the above aldehyde in presence of hydrochloric acid affords *bis*-(4-*carbethoxy*-3-*methylpyrryl*)*methene*, orange, m. p. 129° (*hydrochloride*, red, m. p. 195°). The *methene hydrochloride*, reddish-yellow, m. p. 218° after sintering at 190°, obtained similarly from the aldehyde and ethyl 2 : 4-dimethylpyrrole-3-carboxylate, is described. 2-*Aldehydo*-3-*methylpyrrole*-4-*carboxylic acid*, m. p. 255° (sublimes at 230—240°), yields 2-*aldehydo*-3-*methylpyrrole*, m. p. 95°, when heated at 190—200° under reduced pressure. Condensation of ethyl 3-ethylpyrrole-4-carboxylate with acetonitrile in ethereal hydrogen chloride affords *ethyl* 2-*acetyl*-3-*methylpyrrole*-4-*carboxylate*, m. p. 117°, which, with sodium ethoxide and hydrazine, yields 3-*methyl*-2-*ethylpyrrole* [*picrate* (aldehyde : picric acid = 2 : 1), m. p. 137°]. 2-*Acetyl*-3-*methylpyrrole*-4-*carboxylic acid*, m. p. 272° (sublimes 250—260°), yields 2-*acetyl*-3-*methylpyrrole*, m. p. 98°, when heated. Condensation of ethyl 3-methylpyrrole-4-carboxylate with chloroacetonitrile affords similarly *ethyl* 2-*chloroacetyl*-3-*methylpyrrole*-4-*carboxylate*, m. p. 115°. When heated with acetic anhydride and sodium acetate, 4-carbethoxy-3-methylpyrrole-5-carboxylic acid affords the "*pyrocoll*," (I), pale yellow, m. p. 168°.



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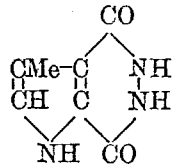


(II.)

When heated with alcoholic hydrazine hydrate, ethyl 3-methylpyrrole-4 : 5-dicarboxylate yields successively *ethyl* 3-*methylpyrrole*-5-*carbohydrazide*-4-*carboxylate*, m. p. 165° (*hydrochloride*; *benzoyl* derivative, m. p. 232°; *phenylthiosemicarbazide*, m. p. 185°; *glyoxal condensation product*, m. p. 330°; *condensation product* with *ethyl* 2-*aldehydo*-3-*methylpyrrole*-4-*carboxylate*, m. p. 221°), and the *pyrryldiketodiazine*, (II), sublimes 290—310° (slight decomp.), m. p. not below 360°. 4-*Carbohydrazido*-3-*methylpyrrole*-5-*carboxylic acid*, m. p. 235°, is obtained by the action of alcoholic hydrazine hydrate on the *potassium* salt of 4-carbethoxy-3-methylpyrrole-5-carboxylic acid. Treatment of the above hydrochloride with aqueous sodium nitrite affords the corresponding *azide* (exploding at 80°) which, when boiled with methyl alcohol, yields *methyl* 4-*carbethoxy*-3-*methylpyrrole*-5-*carbamate*, m. p. 108°. 3-*Methylpyrrole*-4 : 5-*dicarboxylic acid*, m. p. 221°, is described. Condensation of 3-methylpyrrole with magnesium ethyl bromide, followed by treatment with ethyl chloroformate, affords *ethyl* 3-*methylpyrrole*-2-*carboxylate*, m. p. 56°, which, on treatment with hydrocyanic acid and hydrogen chloride, affords *ethyl* 5-*aldehydo*-3-*methylpyrrole*-2-*carboxylate*, m. p. 107° (*semicarbazone*, m. p. 230°). Ethyl 3-methylpyrrole-4-carboxylate is obtained by distilling barium 4-carbethoxy-3-methylpyrrole-5-carboxylate. F. G. WILLSON.

Ethyl 2-methylpyrrole-3-carboxylate, its conversion into a stable tripyrrylmethane and tetrapyrrylethane, and other syntheses. H. FISCHER and F. SCHUBERT (Z. physiol. Chem., 1926, **155**, 72—95).—Application of the Gattermann aldehyde synthesis to ethyl 2-methylpyrrole-3-carboxylate, (I), (cf. Benary, A., 1911, i, 319) affords the *ethyl* ester, (II), m. p. 136°, of 5-*aldehydo*-2-*methylpyrrole*-3-*carboxylic acid*, m. p. 280° (decomp.). The *phenylhydrazone*, m. p. 143°, *oxime*, m. p. 159°, and *semicarbazone*, m. p. 263°, of (II) are described. Hydrogen in presence of platinum converts the latter into formaldehyde and 5-(3-*carbethoxy*-2-*methylpyrryl*)-*carbinol*, m. p. 102° (cf. Fischer and Stern, this vol., 303), which, when boiled with glacial acetic acid, affords *di*-5-(3-*carbethoxy*-2-*methylpyrryl*)*methane*, m. p. 333°, the latter being also obtained by condensing (I) with formaldehyde in presence of alcoholic hydrogen chloride, and by catalytic reduction of

(II) in glacial acetic acid. Treatment of (I) with malononitrile in ethereal hydrogen chloride affords *ethyl 5-cyanoacetyl-2-methylpyrrole-3-carboxylate*, m. p. 242° (decomp.), which was also prepared from the corresponding chloroacetyl derivative. Diazobenzenesulphonic acid couples with (I) to give a reddish-brown *dye*. Condensation of (II) with ethyl malonate in presence of methylamine affords *ethyl 2-methyl-5-(ω-dicarbethoxyvinyl)pyrrole-3-carboxylate*, m. p. 174°. Ethyl cyanoacetate yields similarly *ethyl 2-methyl-5-(ω-cyano-ω'-carbethoxyvinyl)pyrrole-3-carboxylate*, m. p. 175°, whilst malononitrile affords the corresponding *-5-(ω-dicyanovinyl)pyrrole*, m. p. 196°. Condensation with acetone, methyl ethyl ketone, and acetophenone affords β-5-(3-*carbethoxy-2-methylpyrryl)vinyl methyl*, m. p. 165°, *ethyl*, m. p. 167°, and *phenyl ketone*, m. p. 166°, respectively. Condensation of (I) with benzaldehyde, *p*-tolualdehyde, and *p*-nitrobenzaldehyde affords *di-(3-carbethoxy-2-methylpyrryl)phenyl-*, m. p. 231°, *-p-tolyl-*, m. p. 233°, and *-p-nitrophenyl-methane*, m. p. 254°.

Di-(3-carbethoxy-2-methylpyrryl)-p-dimethylaminophenyl-, m. p. 246°, *-phenylmethyl-*, m. p. 235°, *-methylethyl-*, m. p. 182°, *-methyl-*, m. p. 199·5°, and *-diphenyl-methane*, are obtained analogously from the appropriate aldehydes. *Di-(3-carbethoxy-2 : 4-dimethylpyrryl)-phenylmethyl-*, m. p. 221°, and *-diphenyl-methane*, m. p. 224°, are described. The action of chloroacetonitrile on di-(3-carbethoxy-2-methylpyrryl)dimethylmethane affords a *product*, m. p. 217°, identical with that obtained by the action of chloroacetonitrile on (I), whilst hydrocyanic acid and hydrogen chloride yield (II). Condensation of (I) with (II) affords *tri-(3-carbethoxy-2-methylpyrryl)-methane*, m. p. 246°, which, on treatment with hydrochloric acid, yields the corresponding *dipyrrylmethene*, yellow, m. p. 179—180° (decomp.) (*hydrochloride*, red, m. p. 198°), this being also obtained by the action of alcoholic hydrogen chloride on (II), and by condensing (I) with glyoxal in aqueous alcohol. In absolute alcohol, the latter condensation affords *tetra-(2-methyl-3-carbethoxypyrryl)methane*, m. p. 273°. Treatment of (II) with bromine in acetic acid affords *di-(4-bromo-3-carbethoxy-2-methylpyrryl)methene*, light red, m. p. 214° [(*hydrobromide*, violet, m. p. 185° (decomp.)], of which complex *nickel*, *copper*, *zinc*, and *cobalt* salts are described. Condensation of pyrrole-2-aldehyde with ethyl cyanoacetate, ethyl malonate, and malononitrile affords *2-(ω-cyano-ω'-carbethoxyvinyl)-*, m. p. 139°, *2-(ω-dicarbethoxylvinyl)-*, m. p. 132°, and *2-(ω-dicyanovinyl)-pyrrole*, m. p. 136°, respectively. F. G. WILLSON.

Friedel-Crafts syntheses of pyrryl ketones. H. FISCHER and F. SCHUBERT (Z. physiol. Chem., 1926, **155**, 99—112).—Both 2- and 3-pyrryl ketones can be obtained in good yields from substituted pyrroles and acyl chlorides by condensation in carbon disulphide solution in presence of aluminium chloride, the latter being preferably added last. In some cases, the expected ketones are accompanied by by-products of high m. p. Acetyl chloride and ethyl 2 : 4-dimethylpyrrole-3-carboxylate thus afford a blue-violet *product*, from the alcoholic solution of which only the colourless ethyl 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 139°, and a *substance*, m. p. 207°, could be isolated. Analogous preparations are described of ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate, m. p. 143°, *ethyl 5-acetyl-2-methylpyrrole-3-carboxylate*, m. p. 152°, ethyl 5-chloroacetyl-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 187°, ethyl 3-chloroacetyl-2 : 4-dimethylpyrrole-5-carboxylate, m. p. 162°, *ethyl 5-chloroacetyl-2-methylpyrrole-3-carboxylate*, m. p. 216° (also obtained from ethyl 2-methylpyrrole-3-carboxylate and chloroacetonitrile), and *ethyl 3-propionyl-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 140°. Hydrolysis of the last-named affords the corresponding *-5-carboxylic acid*, m. p. 213° (decomp.), which on distillation yields *3-propionyl-2 : 4-dimethylpyrrole*, m. p. 123°. Propionyl chloride and ethyl 2 : 4-dimethylpyrrole-3-carboxylate yield similarly ethyl 5-propionyl-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 151°, together with a *substance*, m. p. 233°, acidified alcoholic solutions of which are orange; butyryl chloride yields analogously *ethyl 5-butyryl-2 : 4-dimethylpyrrole-3-carboxylate*, m. p. 136°, together with a *substance*, m. p. 190°. *Ethyl 3-butyryl-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 116°, *ethyl 5-butyryl-2-methylpyrrole-3-carboxylate*, m. p. 131°, *ethyl 5-benzoyl-2-methylpyrrole-3-carboxylate*, m. p. 167°, *4-acetyl-2 : 3 : 5-trimethylpyrrole*, m. p. 209° [*by-product*, m. p. 259° (*hydrochloride*, red)], *4-propionyl-2 : 3 : 5-trimethylpyrrole*, m. p. 154°, *4-benzoyl-2 : 3 : 5-trimethylpyrrole*, m. p. 174°, *ethyl 5-benzoyl-2 : 4-dimethylpyrrole-3-carboxylate*, m. p. 108°, and *ethyl 3-benzoyl-2 : 4-dimethylpyrrole-5-carboxylate*, m. p. 118°, are described. The action of acetyl chloride on acetonepyrrole yields a red, amorphous *product*.

F. G. WILLSON.

Complex salts obtained by the action of α-picoline on alkali hexachloroiridites. M. GUILLOT (Compt. rend., 1926, **182**, 1090—1092).—Substitution of α-picoline for pyridine in reactions with alkali hexachloroiridites gives considerable difference in results (cf. Delépine, A., 1923, i, 89, 135, 243, 480). If the mixture is maintained at 100° for 0·5 hr., *trichlorotri-α-picolinoiridite*, $Ir(C_6H_7N)_3Cl_3$, is formed with *trichlorodi-α-picolinoaquoiridite*, $Ir(C_6H_7N)_2H_2OCl_3$, as an intermediate product. At lower temperatures, the reaction takes place very slowly, the products being resinous. When ammonium hexachloroiridite was used, ammonium α-picolinotetrachloroiridite, $(NH_4)_2Ir(C_6H_7N)Cl_5$, was obtained; this with excess of the former and in presence of ammonium chloride and α-picoline yields $(Ir,C_6H_7N,Cl_5)(C_6H_7N,H)_2,2(NH_4)_3IrCl_6,3NH_4Cl$, C_6H_7N,HCl. The potassium analogue of this substance was also obtained. The action of the calculated quantity of hydrochloric acid on trichlorodi-α-picolinoaquoiridite in presence of a large excess of α-picoline hydrochloride yields $(Ir,C_6H_7N,Cl_5)(C_6H_7N,H)_2$, from which the silver derivative was prepared. It was not found possible to obtain compounds containing more than 3 mols. of α-picoline. Oxidation of $(Ir,C_6H_7N,Cl_5)(C_6H_7N,H)_2$ by means of concentrated nitric acid yielded *α-picoline hydrogen α-picolinotetrachloroiridate*, whilst trichlorodi-α-picolinoaquoiridite is converted quantitatively by aqua regia into tetrachlorodi-α-picolinoiridate. H. J. EVANS.

Pharmaceutical products [quinolines]. J. CALLSEN.—See B., 1926, 464.

Triphenylmethyl. XXXV. Halogen-substituted acridyls. Reactivity of the halogen in them. M. GOMBERG and D. L. TABERN (J. Amer. Chem. Soc., 1926, **48**, 1345—1358; cf. A., 1925, i, 1266).—In extension of the "quinoidation" hypothesis previously formulated (Gomberg and Blicke, A., 1923, i, 913) to explain the lability of certain nuclear halogen atoms in derivatives of triphenylmethyl, a series of eight chlorine-substituted *C*-phenyl-*N*-phenylacridols has been prepared, from the salts of which, in all cases save one, the corresponding chloroacridyls have been obtained. The nuclear halogen atoms of each of these acridyls retain their benzenoid immobility in all cases except those in which it is in the *para*-position with respect to the aryl-substituted carbon atom of the acridyl nucleus, when the lability becomes equal to that obtaining in *para*-halogenated triarylmethyls and xanthenyls. This is interpreted as indicating that in the diphenylacridyls only the two benzenoid rings of the acridyl nucleus are capable of benzenoid–quinonoid tautomerisation, and it is concluded that in the acridyls, in common with other free radicals, selective absorption and quinonoid tautomerisation are concomitant phenomena.

10-*Phenyl*-5-p-*chlorophenyl*-5-*acridol*, m. p. 178—179° (*methyl ether*, m. p. 169°; *ethyl ether*, m. p. 157°), is obtained by the action of magnesium *p*-chlorophenyl bromide on *N*-phenyl acridone. When treated with acetyl chloride and hydrogen chloride in benzene–chloroform, it yields a *chloride-hydrochloride*, yellow, which is converted into the normal *chloride* when boiled in chloroform with calcium carbonate. The latter affords the corresponding free radical when treated with zinc dust in bromobenzene, and from the solution the *peroxide*, m. p. 183° (decomp.), and *iodide*, brick-red, were obtained. Reduction of the acridol affords the corresponding *acridan*, m. p. 147—148°, without removal of the nuclear halogen atom. 10-*Phenyl*-5-m-*chlorophenyl*-5-*acridol*, m. p. 177°, its *chloride-hydrochloride*, *chloride*, the corresponding *acridyl*, its *peroxide*, m. p. 192—193° (decomp.), and *iodide*, and the *acridan*, m. p. 147°, 10-*phenyl*-5-o-*chlorophenyl*-5-*acridol*, m. p. 178°, its *chlorides*, the corresponding *acridyl*, and its *peroxide*, m. p. 186—187° (decomp.), and *iodide*, dark red, and the *acridan*, m. p. 183—184°, are obtained similarly, the nuclear halogen being immobile in both series. Condensation of 4-chlorodiphenylamine-2-carboxylic acid (cf. Ullmann and Wagner, A., 1907, i, 846; 1910, i, 254) with iodobenzene in boiling nitrobenzene in presence of potassium iodide and copper-bronze affords 4-*chlorotriphenylamine*-2-*carboxylic acid*, m. p. 157—158°, which, when heated with phosphorus pentachloride and aluminium chloride in benzene, is converted into 3-*chloro*-10-*phenylacridone*, m. p. 229—230°. Condensation of the latter with magnesium phenyl bromide affords 3-*chloro*-5 : 10-*diphenyl*-5-*acridol*, m. p. about 202°, from which the *chloride-hydrochloride* and *chloride*, the *acridyl* and its *peroxide*, m. p. 218—219° (decomp.), and *iodide*, and the *acridan*, m. p. 197°, are obtained as above, the nuclear halogen not being removable. Similarly, 5-chlorodiphenylamine-2-carboxylic acid affords 5-*chlorotriphenylamine*-2-*carboxylic acid*, m. p. 138°, 2-*chloro*-10-*phenylacridone*, yellow, m. p. 288—289°, and 2-*chloro*-5 : 10-*diphenyl*-5-*acridol*, m. p. 155° (*chloride-hydrochloride*, hygroscopic, and *chloride*). When the last-named chloride is shaken with zinc dust, water, and carbon disulphide, 1·5 atomic equivalents of chlorine are removed, indicating that the formation of the acridyl radical is followed by the usual elimination of 0·5 atomic equivalent of halogen from a radical of the "second order" (cf. A., 1923, i, 913). The colour of the latter is about as intense as that of the free acridyl. Its *peroxide*, obtained by exposing the carbon disulphide solution to the atmosphere, has m. p. about 200°. The lability of the nuclear halogen atom is also indicated by the formation of the *chloride* of the corresponding 2-*anilino*-derivative, brick-red, when the above normal chloride is warmed with aniline. When boiled with anhydrous formic acid, the above acridol is reduced to the corresponding *acridan*, m. p. 146—147°, without removal of the nuclear halogen atom (cf. Guyot and Kovache, A., 1913, i, 647). The following compounds, prepared by reactions analogous to those above, are described: 4′ : 4″-*dichlorotriphenylamine*-2-*carboxylic acid*, m. p. 220—221°; 3-*chloro*-10-p-*chlorophenylacridone*, m. p. not below 270°; 2-*chloro*-5-*phenyl*-10-p-*chlorophenyl*-5-*acridol*, m. p. 169—170° (*chloride-hydrochloride* and *chloride*), the corresponding *acridyl* [*peroxide*, m. p. 223—224° (decomp.); *iodide*], and *acridan*, m. p. 163°; 2′ : 2″-*dichlorotriphenylamine*-2-*carboxylic acid*, m. p. 212—213°; 1-*chloro*-10-o-*chlorophenylacridone*, golden-yellow; 1-*chloro*-5-*phenyl*-10-o-*chlorophenylacridol*, m. p. 158—159° (*chloride-hydrochloride* and *chloride*), the corresponding *acridyl peroxide*, decomp. 197—198°, *iodide*, and *acridan*, m. p. 135°; 2′ : 5′-*dichlorodiphenylamine*-2-*carboxylic acid*, m. p. 235°; 2′ : 5′ : 2″ : 5″-*tetrachlorotriphenylamine*-2-*carboxylic acid*, m. p. 223—227°; 1 : 4-*dichloro*-10-(2 : 5-*dichlorophenyl*)*acridone*; and 1 : 4-*dichloro*-5-*phenyl*-10-(2 : 5-*dichlorophenyl*)*acridol*. The last-named yields the corresponding *acridan* when reduced with zinc dust and acetic acid, without loss of nuclear halogen.

F. G. WILLSON.

Pyrazolone series. Action of thiosemicarbazide and semicarbazide on ketonic esters. I. S. C. DE (J. Indian Chem. Soc., 1926, **3**, 30—40).—Ethyl acetoacetate reacts with semicarbazide and thiosemicarbazide to yield, initially, the corresponding semi- and thiosemi-carbazones. These, with ammonia, yield the corresponding pyrazolone derivatives with the elimination of alcohol. When heated alone or with alcohol or water, the semicarbazones yield methylpyrazolone, alcohol, water, and carbon dioxide being eliminated, whilst the thiosemicarbazone yields a thiocarbamide derivative of the pyrazolone, alcohol only being eliminated. In dilute sodium carbonate solution, the semi- and thiosemi-carbazones condense with a second mol. of ethyl acetoacetate. The following new compounds are obtained by these methods: 3-*methylpyrazolone*-1-*thiocarbamide*, m. p. 180° [4 : 4′-*dibromo*- and 4-*bromo*-derivatives, m. p.

250° and 220°, respectively; 4-*benzeneazo*-derivative, m. p. 217° (decomp.); 4-iso*nitroso*-derivative, m. p. 180° (*silver* salt)]; 2-*methyl*iso*pyrazolone*-1-*thiocarbamide hydrochloride*, m. p. 151°; *ethyl* 3-*methylpyrazolone*-1-*thiocarbonyl*-β-*aminocrotonate*, m. p. 145° (*silver* salt); 3-*methylpyrazolone*-1-*carbamide*, m. p. 192° [4 : 4'-*dibromo*-derivative, m. p. 225°; 4-*benzeneazo*-derivative, m. p. 235°; 4-iso*nitroso*-derivative, m. p. 210° (*silver* salt)]; 3-*methyl*iso*pyrazolone hydrochloride*; *ethyl* 3-*methylpyrazolone*-1-*carbonyl*-β-*aminocrotonate*, m. p. 175—176° (decomp.) (*silver* salt).

J. W. BAKER.

Manufacturing barbituric acid derivatives. L. THORP.—See B., 1926, 514.

Reaction of mesoxalic acid with carbamide. H. BILTZ and G. SCHLIEMANN (J. pr. Chem., 1926, [ii], **113**, 101—104).—Michael's synthesis of allantoin (A., 1884, 426) has been repeated, but his results were obtained only if the mesoxalic acid and carbamide were moist. If water was eliminated from the mixture before heating (to 110°), water, ammonia, and carbon mon- and di-oxide were evolved; the residue was chiefly ammonium oxalurate. J. M. GULLAND.

Compound of veronal with pyramidone. II. P. PFEIFFER and O. ANGERN (Z. physiol. Chem., 1926, **154**, 276—289; cf. A., 1925, i, 1318).—The mixed m.-p. curve method indicates that veronal, but not diethylveronal, forms molecular additive *compounds* with acetamidoantipyrine, m. p. 169—169·5°, antipyrine, and sarcosine anhydride, m. p. 151° after softening at 131°, but not with benzanilide or ketones; diphenylamine behaves similarly to veronal, but diphenylmethylamine forms no such compounds; the results indicate that the existence of these compounds depends on the presence of the imino-group in veronal and of a cyclic amino-group in the other component. The *compound* of diphenylamine with sarcosine anhydride has m. p. 92—93°.

C. R. HARINGTON.

Action of formaldehyde on methylthiouracil and its methyl ether. G. POETSCH and R. BEHREND (Annalen, 1926, **448**, 89—98; cf. Schmedes, A., 1925, i, 435).—4-Methylthiouracil reacts with formaldehyde in presence of dilute hydrochloric acid, yielding 4-*methyl*-5-*hydroxymethylthiouracil* (decomp. 280—290° without melting). This loses formaldehyde when kept or heated with solvents, regenerating methylthiouracil. It is reduced by tin and hydrochloric acid to 4 : 5-*dimethylthiouracil*, m. p. 274—275°, sintering at 267° (*sodium* salt), which with hydrochloric acid at 155—160° affords 4 : 5-dimethyluracil (Kircher, A., 1912, i, 53). With bromine water, it yields 4-bromo-5-hydroxy-4 : 5-dimethyldihydrouracil (cf. *ibid.*). In boiling concentrated hydrochloric acid, 4-methylthiouracil and formaldehyde give a *substance* (A), $C_{11}H_{16}O_4N_4S_2$ (decomp. 305° without melting), which affords, on bromination, the *compound* (B), $C_{11}H_{14}O_4N_4Br_2$, m. p. 232—234°, sintering at 230°. 4-*Methyl*-5-*hydroxymethyl*-2-*methylthioluracil*, m. p. 220—221°, prepared similarly from 4-methyl-2-methylthioluracil and formaldehyde, is also very unstable. On reduction, it yields the dimeric *substance*, $C_{12}H_{16}O_2N_4S_2$, decomp. 310—315°. The constitution of the latter and of compounds (A) and (B) is discussed. H. E. F. NOTTON.

Preparation and resolution of *dl*-*cis*-2 : 5-dimethylpiperazine. F. B. KIPPING and W. J. POPE (J.C.S., 1926, 1076—1079; cf. Pope and Read, *ibid.*, 1912, **101**, 2325; Stoehr, A., 1893, i, 486; 1897, i, 298).—Stoehr's β-2 : 5-dimethylpiperazine has been identified as the *cis*-isomeride by resolving it into its optically active components by means of *d*-hydroxymethylenecamphor. The reduction product of 2 : 5-dimethylpyrazine using sodium and alcohol contains about 5% of this isomeride, and about 95% of the α- or *trans*-2 : 5-dimethylpiperazine. *dl*-*cis*-2 : 5-Dimethylpiperazine forms a 1 : 4-*dibenzoyl* derivative, m. p. 145—146°, and a 1 : 4-*di*-p-*toluenesulphonyl* derivative, m. p. 146—147°, whilst the *trans*-compound forms a 1 : 4-*di*-p-*toluenesulphonyl* derivative, m. p. 225°. d-cis-2 : 5-*Dimethylpiperazine*-d-*bismethylenecamphor* has m. p. 210°, $[\alpha]^{20}_{5461}$ +747°; l-*isomeride*, slightly impure, m. p. 176—177°, $[\alpha]^{20}_{5461}$ +635°. These salts on treatment with bromine yield the *d*- and *l*-dimethylpiperazine hydrobromides, which after benzoylation furnished the corresponding *dibenzoyl* derivatives, d-*isomeride*, m. p. 164—165°, $[\alpha]_{5461}$ +247°, l-*isomeride*, impure, m. p. 140—142°, $[\alpha]_{5461}$ −146°. *cis*-2 : 5-Dimethylpiperazine was erroneously described by Pope and Read as *cis*-2 : 6-dimethylpiperazine. J. S. H. DAVIES.

Relative stability of cyclic bases. X. Piperazine ring. J. VON BRAUN, O. GOLL, and F. ZOBEL (Ber., 1926, **59**, [*B*], 936—945; cf. A., 1923, i, 838).—The piperazine ring is an extraordinarily unstable structure, less rigid than any other ring. The replacement of the 4-methylene group of piperidine by the imino-radical causes much greater weakness than its replacement by oxygen.

Further examination of the action of ammonia on piperazinedipiperidinium bromide (A., 1925, i, 1457) proves the absence from the products of di-ε-aminoamylpiperazine and β-aminoethyl-ε-aminoamylaminoethylpiperidine, $C_5H_{10}N\cdot[CH_2]_2\cdot N(CH_2\cdot CH_2\cdot NH_2)\cdot[CH_2]_5\cdot NH_2$, so that fission occurs exclusively in the piperazine ring. For purposes of comparison, *di*-ε-*benzamidoamylpiperazine*, m. p. 150° (*dihydrochloride tetrahydrate*, m. p. 130°, or, anhydrous, m. p. 239°), is prepared from ε-chloroamylbenzamide and piperazine and hydrolysed to *di*-ε-*aminoamylpiperazine*, m. p. 36—37°, b. p. 210—212°/11 mm. (*hydrochloride*, decomp. 262°; *picrate*, m. p. 157°). For similar reasons, 1-β-aminoethylpiperidine, obtained conveniently by reducing piperidinoacetonitrile with sodium and alcohol, is transformed by the successive action of bromoethylphthalimide and hydrochloric acid at 140° into β'-*aminoethyl*-β-*aminoethylpiperidine*, $C_5H_{10}N\cdot[CH_2]_2\cdot NH\cdot[CH_2]_2\cdot NH_2$, d^{19}_4 0·940 (*dipicrate*, m. p. 165°; *hydrochloride*, m. p. 202°); ε-chloroamylbenzamide is condensed with 1-β-aminoethylpiperidine to ε'-benzamidoamyl-β-aminoethylpiperidine (*picrate*, m. p. 197°), which is hydrolysed to 1-ε'-*aminoamyl*-β-*aminoethylpiperidine*, b. p. 169—170°/11 mm. (non-crystalline *picrate*; *hydrochloride*, m. p. 215°; diphenylthiocarbamide derivative, m. p. 122°). All

these amines are highly resistant to aqueous ammonia. αβ-Dipiperidinoethane and a *base*, $C_{11}H_{23}N_3$, b. p. 140°/11 mm., m. p. 32—34°, have been isolated from the products of the action of ammonia on piperazine-dipiperidinium bromide (cf. *loc. cit.*).

The piperazine ring behaves towards cyanogen bromide like other unstable nitrogenous ring systems, since its dimethyl derivative is thereby converted exclusively into *methylvinylcyanamide*, b. p. 77—80°/13 mm., m. p. 28—29°, and methyl-β-bromoethylcyanamide (isolated as the additive *product* with dimethylpiperazine). The superior stability of the dihydro-*iso*indole to the piperazine ring is established by the conversion of *piperazinebisdihydroisoindolium bromide*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>N<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4$, m. p. not below 300°, by the successive action of silver oxide and boiling water, into *αβ-bisdihydroisoindylethane*, m. p. 122°. Similarly, tetrahydro*iso*quinoline is transformed by ethylene bromide into *αβ-di-2-tetrahydroisoquinolylethane*, m. p. 97° (*hydrochloride*; *hydrobromide*), which with ethylene bromide affords *piperazineditetrahydroisoquinolinium bromide*; fission of the corresponding hydroxide yields αβ-di-2-tetrahydro*iso*quinolylethane and 2-β-hydroxyethyltetrahydro*iso*quinoline in addition to acetaldehyde and tetrahydro*iso*quinoline. The bromide is transformed by ammonia into the ethane derivative, 2-β-aminoethyltetrahydro*iso*quinoline, and tetrahydro*iso*quinoline. H. WREN.

Desmotropic forms of 2 : 5-diketopiperazines and polypeptides. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1926, **153**, 83—87).—Glycine anhydride is converted by aniline at 205—210° into an enolic form, which when hydrolysed and benzoylated yields a *benzoyl* derivative of glycylglycine, m. p. 213° (decomp.). This compound gives no ninhydrin reaction and is not identical with ordinary benzoylglycylglycine. The enolic form of glycine anhydride when boiled with benzoic anhydride yields a *monobenzoyl* derivative, m. p. 254° (decomp.). Similar enolic forms have been also obtained from the anhydrides of alanine and of sarcosine and from leucylglycine anhydride. They are considered to possess the grouping $-CH{:}C(OH)-$. W. O. KERMACK.

Transformations of peptide substances. IX. Isomeric diketopiperazines : *iso*-2 : 5-diketo-6-*iso*butyl-3-methylenepiperazine. M. BERGMANN and F. STATHER (Annalen, 1926, **448**, 32—37).—Dileucyl-*l*-cystine (Fischer and Suzuki, A., 1905, i, 30) is converted by hydrogen chloride in methyl-alcoholic solution into its *dianhydride*, $C_{18}H_{30}O_4N_4S_2$ (no m. p.; darkens above 275°). The latter is desulphurised by warm sodium hydroxide, yielding, on acidification, iso-2 : 5-*diketo*-6-iso*butyl*-3-*methylenepiperazine*, $(C_9H_{14}O_2N_2)_x$, (yellow *sodium* salt; *diacetyl* derivative, m. p. 99°). Cryoscopic measurements show that this compound and *iso*-2 : 5-diketo-6-methyl-3-methylenepiperazine (A., 1925, i, 1474) are broken up in phenol solution into unit molecules (x=1), but these are not identical with the simple unassociated diketopiperazine, since, on removing the solvent, the original high-molecular compound is recovered. H. E. F. NOTTON.

Transformations of peptide substances. X. Isomeric diketopiperazines : *allo*-2 : 5-diketo-3-methylenepiperazine and *allo*-2 : 5-diketo-6-methyl-3-methylenepiperazine. M. BERGMANN and H. ENSSLIN (Annalen, 1926, **448**, 38—48; cf. preceding abstract).—A second type of crystalline high-molecular compounds, polymeric with the diketopiperazines, has now been prepared. The new *allo*-form differs from the corresponding *iso*-compound (cf. A., 1925, i, 1474) in being much more sparingly soluble in the common solvents and in phenol. It does not yield an acetyl derivative and its solution in aqueous sodium hydroxide is colourless. Like the *iso*-form, it is completely depolymerised in melting resorcinol, from which, however, it can be recovered unchanged. Since depolymerisation does not effect an interconversion of the two forms, they must differ, not only in their degree of association, but also in the structure of the associating units themselves. allo-2 : 5-*Diketo*-3-*methylenepiperazine*, $(C_5H_6O_2N_2)_x$ (darkens above 250° without melting), is obtained when glycylserine anhydride is heated with acetic anhydride and sodium acetate at 120—130°. It is hydrolysed by fuming hydrochloric acid to the tetrapeptide hydrochloride, $C_{10}H_{16}O_5N_4Cl_2$, previously obtained from the corresponding *iso*-form (*loc. cit.*). No tetrapeptide is obtained from glycylserine anhydride under these conditions. Alanylserine anhydride is converted by acetic anhydride and sodium acetate into allo-2 : 5-*diketo*-6-*methyl*-3-*methylenepiperazine*, $(C_6H_8O_2N_2)_x$. Unlike the *iso*-compound, this cannot be hydrogenated in the presence of palladium-black, but both forms are hydrolysed to the same tetrapeptide hydrochloride (decomp. 255—258°). H. E. F. NOTTON.

Preparation of di- and poly-piperidyls. K. RÜLKE and F. CLOTOFSKI.—See B., 1926, 464.

New isomerism in the isatin series. VII. G. HELLER and H. LAUTH (J. pr. Chem., 1926, [ii], **112**, 331—338; cf. Heller and Baumgarten, A., 1918, i, 235).—The correctness of Hantzsch's view (A., 1923, i, 1226), that the so-called "dimethylisatin II" is bimolecular, *i.e.*, α-tetramethylisatoid, is admitted. The existence of β-tetramethylisatoid ("dimethylisatin III"), however, is reaffirmed, and "dimethylisatin IV" is shown to be formed from tetramethylisatoid, not by loss of water, to give an anhydride (Hantzsch, *loc. cit.*), but by loss of CO_2 (*i.e.*, $-CO-H_2O+H_2$) to give anhydrodimethylindoxyl-α-dimethylanthranilide, $Me_2C_6H_2<\begin{matrix}CO\cdot CH\cdot NH\\N-CO\end{matrix}>C_6H_2Me_2$, m. p. 315°, which is readily oxidised by chromic acid to *anhydrodimethylisatin-α-dimethylanthranilide*, $Me_2C_6H_2<\begin{matrix}CO\cdot C=N\\N\cdot CO\end{matrix}>C_6H_2Me_2$, m. p. 244°. This last compound is synthesised from 5 : 7-dimethylisatin *O*-methyl ether and 3 : 5-dimethylanthranilic acid, an intermediately formed *acid*, m. p. 175°, being isolated.

In the preparation of α-tetramethylisatoid by

Hantzsch's method there is also obtained *N*-benzoyldimethylisatin, m. p. 180—181°.

C. HOLLINS.

Isomeric relationships in the pyrazole series. VIII. 5(3)-Phenyl-3(5)-methylpyrazole. K. VON AUWERS and H. STUHLMANN (Ber., 1926, 59, [*B*], 1043—1055).—The action of hydrazine hydrate on benzoylacetone affords 5(3)-phenyl-3(5)-methylpyrazole, b. p. 191—193°/14 mm., m. p. 127° (*picrate*, m. p. 159°; *benzoyl* derivative, m. p. 83—84°; 4-*chloro*-5(3)-*phenyl*-3(5)-*methylpyrazole*, m. p. 108—110°, and its *hydrochloride*, m. p. 196°). Treatment of the base with methyl iodide or methyl iodide, sodium methoxide, and methyl alcohol gives a mixture of 3-*phenylpyrazole*-1 : 5-*dimethyl*-, b. p. 162°/12 mm., m. p. 36°, d_4^{20} 1·074, n_{He}^{20} 1·594 (*picrate*, m. p. 184°), and 5-*phenyl*-1 : 3-*dimethyl-pyrazole*, b. p. 146°/12 mm., m. p. 21—22°, d_4^{20} 1·061, n_{He}^{20} 1·578 (*picrate*, m. p. 127°). The mixed isomerides are also obtained from methylhydrazine and benzoylacetone or γ-ethoxy-α-phenyl-Δ^{β}-buten-α-one, but not from alcoholic methylamine and phenylmethylpyrazole. Acetylphenylacetylene and methylhydrazine give both isomerides, whereas the additive compound of the former with dipropylamine affords exclusively 5-phenyl-1 : 3-dimethylpyrazole, the constitution of which is thereby established. Ethylation of 5(3)-phenyl-3(5)-methylpyrazole yields 5-*phenyl*-3-*methyl*-1-*ethylpyrazole*, b. p. 145°/14 mm., d_4^{20} 1·034, n_{He}^{20} 1·562 (*picrate*, m. p. 116°), and 3-*phenyl*-5-*methyl*-1-*ethylpyrazole*, b. p. 170°/14 mm., d_4^{20} 1·048, n_{He}^{20} 1·582 (*picrate*, m. p. 196°), in the ratio 9 : 1. The greater tendency to the formation of 1 : 5-dialkyl derivatives is shown by the production of phenyl-1 : 5- and -1 : 3-dimethylpyrazoles in the ratio 2 : 1 by fission of 3-phenyl-1 : 2 : 5-trimethylpyrazolium iodide. The influence of the nature of the alkyl radical is shown by the quantitative conversion of 3-*phenyl*-2 : 5-*dimethyl*-1-*ethylpyrazolium iodide*, m. p. 120—121°, into 3-phenyl-5-methyl-1-ethylpyrazole. *Methyl* 5(3)-*phenyl*-3(5)-*methylpyrazolecarboxylate*, m. p. 61·5—62°, and the corresponding *ethyl* ester, m. p. 73·5—74·5°, yield mixtures of phenyldialkylpyrazoles in which the 1 : 5-derivatives preponderate. Carbonyl chloride and 5(3)-phenyl-3(5)-methylpyrazole in ethereal solution at −12° afford the *compound* $CO(N_2C_3HMePh)_2$, m. p. 136°, and 5(3)-*phenyl*-3(5)-*methylpyrazolecarboxyl chloride*, m. p. 94° (corresponding *amide*, m. p. 157—158°). Attempts to synthesise 5-phenyl-3-methylpyrazole-1-carboxylamide from acetylphenylacetylene and semicarbazide gave only *acetylphenylacetylenesemicarbazone*, m. p. 127—128°.

The action of phenylhydrazine on benzoylacetone or γ-ethoxy-α-phenyl-Δ^{β}-buten-α-one gives an intermediate product, m. p. 153° (possibly a phenylhydrazone), which is immediately converted by the acid of laboratory air into 1 : 5-diphenyl-3-methylpyrazole; it is transformed by benzoyl chloride and pyridine into labile 3-methyl-1 : 5-diphenylpyrazole, m. p. 63°. γ-Ethoxy-α-phenyl-Δ^{β}-buten-α-one and *as*-phenylmethylhydrazine give a mixture of *compounds*, $C_{17}H_{18}ON_2$, m. p. 78—79°, and 107°, respectively, from which *p*-nitrophenylhydrazine replaces the hydrazine group, giving a *N*-*p*-nitrophenyl *derivative* of phenylmethylpyrazole, m. p. 100—101°, whereas hydroxylamine causes the formation of 5-phenyl-3-methyl*iso*oxazole, and benzoyl chloride in the presence of pyridine yields a *substance*, $C_{24}H_{22}O_2N_2$, m. p. 185—186°. H. WREN.

Formation and nitration of alkyloxypyrazoles. H. J. BACKER and W. MEIJER (Rec. trav. chim., 1926, 45, 428—432; cf. this vol., 305).—The yield of the alkyloxypyrazoles found by Wolff (A., 1904, i, 722) as by-products in the preparation of pyrazolones is increased to 20—30% by using a concentrated solution of hydrazine hydrochloride in methyl or ethyl alcohol for condensation with the ketonic ester. The reaction is explained by the assumption that the hydrazone first produced passes into an intermediate 5-hydroxy-5-alkyloxydihydropyrazole, which then loses a molecule of alcohol on the one hand to yield the pyrazolone, and water on the other with production of the alkyloxypyrazole. 5-*Methoxy*-3-*methylpyrazole*, m. p. 49—50°, from methyl acetoacetate, is converted by nitric acid into 4-*nitro*-5-*methoxy*-3-*methylpyrazole*, m. p. 167° (yellow solution in alkali carbonates). 4-*Nitro*-5-*ethoxy*-3-*methylpyrazole*, m. p. 126° (*monohydrate*, m. p. 103·5°; *silver* salt described), results from the nitration of the corresponding ethoxypyrazole. The following pyrazoles, being already substituted in position 4, cannot be nitrated: 5-*methoxy*-3 : 4-*dimethylpyrazole*, m. p. 85°, from methyl methylacetoacetate; 5-*methoxy*-3-*methyl*-4-*ethylpyrazole*, m. p. 106—107°, from methyl ethylacetoacetate; 5-ethoxy-3 : 4-dimethylpyrazole, m. p. 98° (Wolff gives 93°); 5-*ethoxy*-3-*methyl*-4-*ethylpyrazole*, m. p. 86°, from ethyl ethylacetoacetate; 5-*ethoxy*-3-*methyl*-4-*propylpyrazole*, m. p. 80·5°, from ethyl propylacetoacetate (b. p. 212—215°), together with 3-*methyl*-4-*propyl*-5-*pyrazolone*, m. p. 209—210°.

G. M. BENNETT.

Acetyl-*o*-phenylenediamine [*o*-aminoacetanilide] and acetyl-1 : 2 : 3-benztriazole. F. BELL and J. KENYON (J.C.S., 1926, 954).—*o*-Nitroacetanilide is reduced with aluminium amalgam in moist ether, and acetyl-*o*-phenylenediamine, m. p. 132°, is extracted with benzene from the precipitate produced. Addition of sodium nitrite to a solution of the product in hydrochloric acid gives a precipitate of acetyl-1 : 2 : 3-benztriazole, m. p. 51°, very easily hydrolysed to 1 : 2 : 3-benztriazole, m. p. 98°.

C. HOLLINS.

Mechanism of the oxidation of uric acid. H. BILTZ and G. SCHIEMANN (J. pr. Chem., 1926, [ii], **113**, 77—100).—Behrend (A., 1904, i, 950) explained the oxidation of uric acid in alkaline solution (giving potassium uroxanate or allantoin) as occurring via the hypothetical hydroxyacetylenediureinecarboxylic acid. Biltz and his collaborators (A., 1920, i, 884, 885; 1924, i, 569) have obtained, in addition, potassium hydrogen oxonate and potassium oxalurate, explaining this by the assumption of the above intermediate. Much of the present communication is a general account of experiments designed to isolate derivatives of the acid, of which the details are given elsewhere (Schiemann, Diss., Breslau, 1925).

Reduction of the hypothetical acid in acid solution or in alkaline solution, followed by acidification,

should afford acetylenediureine. Reduction of the alkaline, oxidised solution with zinc dust at the ordinary temperature gave a 68% yield of allantoin, which could also be obtained from the same solution without treatment with zinc. Reduction at 70° gave either potassium acetate or carbonate, according to the method of working up. Reduction with sodium amalgam produced similar results. On the other hand, acidification to eliminate the carbon dioxide of the carboxyl group, followed by sodium amalgam reduction in alkaline medium, led to the expected acetylenediureine, and a 19% yield was obtained with sodium amalgam in acetic acid, although only allantoin was produced by reduction in sulphuric acid. When allantoin is reduced under exactly similar conditions in sulphuric acid, it gives an almost theoretical yield of acetylenediureine, in which change reduction is believed to precede ring-formation, and this difference in behaviour is used to support the monocyclic formula for allantoin (cf. A., 1921, i, 894) as opposed to the dicyclic hydroxyacetylenediureine formula.

By treating the oxidation liquid with ammoniacal copper sulphate, about 33% of the theoretical yield of a *salt*, $C_{10}H_{20}O_{14}N_{10}Cu_3$, was obtained as an olive-green powder, from which one fifth of the total nitrogen could be eliminated as ammonia by sodium hydroxide. The salt is regarded as the dihydrate of a basic copper ammonium salt of hydroxyacetylenediureinecarboxylic acid. Attempts to isolate the organic constituent led only to oxalic acid, but comparison of the salt with precipitates prepared by treating possible oxidation products of uric acid with ammoniacal copper sulphate showed that in no case was there any similarity.

The authors' views of the mechanism of the oxidation are supported but not established by the above experiments, and oxidation of acetylenediureine was carried out in the hope of producing the hypothetical acid. Hydrogen peroxide gave allantoin in poor yield, together with some cyanuric acid, which was obtained alone at the expense of the allantoin at higher temperatures and concentrations (compare A., 1918, i, 409). The importance of this reaction lies in the fact that the intermediate stage must be the hypothetical hydroxyacetylenediureine. On two occasions a strong *acid*, $(CHON)_x$ (double-pyramids, decomp. 255°), was isolated (*sodium* salt described). No decomposition to cyanic acid took place on heating.

The mechanism of the oxidation involves the spontaneous loss of carbon dioxide from hydroxyacetylenediureinecarboxylic acid in acid solution and this assumption receives support by a comparison with acetylenediureinedicarboxylic acid (A., 1899, i, 574). This, at 185°, or in boiling aqueous solution, is quantitatively converted into carbon dioxide and acetylenediureine. *Dimethyl acetylenediureinedicarboxylate*, decomp. 322°, was prepared.

The unlikely possibility was considered that 5-hydroxy-ψ-uric acid, the intermediate product in the acid oxidation of uric acid to alloxan (A., 1924, i, 569), might also be an intermediate in alkaline oxidation. 5-Hydroxy-ψ-uric acid (A., 1917, i, 286) and alkali give ammonia, but no potassium uroxanate or allantoin. Alkaline permanganate oxidation afforded only oxalic acid (50% yield) and no carbamide or oxaluric acid, whilst acid oxidation led to potassium oxalurate (47%) and carbamide (1 mol.). The authors conclude therefore that 5-hydroxy-ψ-uric acid is not produced intermediately in the alkaline oxidation of uric acid. J. M. GULLAND.

Electrochemical oxidation in the purine group. F. FICHTER and W. KERN (Helv. Chim. Acta, 1926, 9, 429—441).—Anodic oxidation of uric acid in lithium carbonate solution at 40—60°, using current equivalent to 1 atom of oxygen, gives allantoin (max. yield 68·5%). Using current equivalent to 3 atoms of oxygen, carbonylcarbamide is obtained (max. yield 13·8%), together with carbamide, formed by further degradation. The same products are obtained by oxidation of allantoin, which is therefore postulated as an intermediate product in the oxidation of uric acid to carbonylcarbamide (cf. Venable, A., 1918, i, 104, 409). Oxidation in 75% sulphuric acid solution, using current equivalent to 2 atoms of oxygen gives carbamide (62·9% yield) and small quantities of alloxan and parabanic acid. Oxidation of a partial suspension of theobromine in 4*N*-sulphuric acid at 20—30° and current equivalent to 4 farads per mol. gives methylalloxan (60% yield). When less current is used, 4 : 5-dihydroxy-3 : 7-dimethyluric acid is also formed. When more current is passed, further oxidation to methylparabanic acid (20—30% yield) takes place. Carbamide, ammonia, methylamine, and formic acid were identified. Oxidation of deoxytheobromine in *N*-sulphuric acid solution, using current equivalent to 8 farads per mol., gives methylparabanic acid (51·6% yield). Methylamine, ammonia, and formic acid are also identified. Oxidation of caffeine in 2*N*-sulphuric acid solution without a diaphragm (current equivalent to 8 farads per mol.) gives 1 : 3 : 1′ : 3′-tetramethylalloxantin (max. yield 80%), produced by reduction at the cathode of the dimethylalloxan formed, together with methylamine, ammonia, and formic acid, at the anode. Using a platinum gauze anode instead of one of lead dioxide, the yield of tetramethylalloxantin (12%) is very much reduced, and small quantities of dimethylalloxan (6—7%) and *apo*caffeine (5—6%) are obtained. Prolonged electrolysis gives dimethylparabanic acid. When a diaphragm is used, dimethylalloxan is formed without reduction to 1 : 3 : 1′ : 3′-tetramethylalloxantin. When oxidation is carried out in acetic acid solution, the last-named compound is converted by the ammonia formed in the reaction into ammonium tetramethylpurpurate. Addition of a little ammonium acetate has a stabilising action on the salt, which is rapidly decomposed by mineral acid, although less readily by organic acids, and the yield is thereby improved. The *sodium*, *potassium*, and *barium* salts of tetramethylpurpuric acid are obtained by addition of the appropriate metallic acetate instead of by ammonium acetate. Addition of calcium or lead acetate gives, respectively, the double *salts*:

$C_{12}H_{12}O_6N_5 \cdot CaO_2C \cdot CH_3, 2H_2O$;

$C_{12}H_{12}O_6N_5 \cdot PbO_2C \cdot CH_3$. The *lead* salt is obtained from the ammonium salt by double decomposition. Oxidation of deoxycaffeine in *N*-sulphuric acid

solution using a diaphragm, a lead dioxide anode, and an amount of current equivalent to 10 farads per mol. gives dimethylparabanic acid (11·6% yield).
M. CLARK.

o-Aminophenylhydrazine and some heterocyclic compounds derived from it. II. Synthesis of azoles, azines, heptazines, and octazines. P. C. GUHA and M. K. DE (J. Indian Chem. Soc., 1926, **3**, 41—58).—*o*-Aminophenylhydrazine (cf. Guha and Ray, A., 1925, i, 1461) has been condensed with a large number of *o*-diketones and their monoximes, diamines, esters and chlorides of dicarboxylic acids, and thiosemicarbazide to produce heterocyclic compounds, and thus are obtained: 5 : 6-*diphenyl*-1 : 4 : 7-*benzheptatriazine*, m. p. 114°; *benzheptatriazine* compounds from alloxan and isatin, both not melting below 300°; 5 : 6-*acenaphtha*-1 : 4 : 7-*benzheptatriazine*, m. p. 181°; 5 : 6-*phenanthra*-1 : 4 : 7-*benzheptatriazine*, m. p. 220°, *phenanthra*-o-*phenylenedihydrazone*, m. p. 160°; *isatin*-o-*phenylenedihydrazone*, m. p. 270°; 2 : 3 : 6 : 7-*dibenzo*-4 : 5-*dihydro*-1 : 4 : 5-*heptatriazine*, m. p. about 300°; 2 : 3-*benzo*-6 : 7-*methylbenzo*-4 : 5-*dihydro*-1 : 4 : 5-*heptatriazine*, m. p. above 300°; 2 : 3-*benzo*-6 : 7-*naphtho*-4 : 5-*dihydro*-1 : 4 : 5-*heptatriazine*, m. p. 146—148°; o-*phenyleneoxamazide*, m. p. above 300°; o-*phenylenesemimalonamazide*, m. p. above 300°; o-*phenylenethiocarbohydrazide*, m. p. above 300° (yielding a *disulphide*, m. p. 125°, when treated with iodine and sodium hydroxide). *o*-Nitrophenylhydrazine condenses with aldehydes and ketones to yield open-chain hydrazones which on reduction pass into ring compounds, and thus are obtained: p-*nitrophenylhydrazones* of acetaldehyde, m. p. 101°; o-nitrobenzaldehyde, m. p. 223°, salicylaldehyde, m. p. 192°, acenaphthenequinone, m. p. 244°, anthraquinone (mono), m. p. 206—207°, naphthaquinone (mono), m. p. 170°, phenanthraqunione, m. p. 245°. These on reduction yield respectively: μ-*methylbenziminazole* (*hydrochloride*, m. p. 173°); 2 : 3 : 7 : 8-*dibenzo*-1 : 5 : 6-*octatriazine* [*hydrochloride*, m. p. 145° (decomp.)]; 2 : 3-benzo-5 : 6-acenaphtha-1 : 4 : 7-triazine (above). The following are also obtained: *benzil*-o-*nitrophenyldihydrazone*, m. p. 136°, which readily oxidises to *diphenyldinitrodiphenylosotriazine*(?), m. p. 200° (decomp.); *diacetylmonoxime*-o-*nitrophenylhydrazone*, m. p. 221—222°; 1-*nitrophenyl*-3 : 4-*dimethyl*-1 : 2 : 5-*osotriazole*, m. p. 285° (decomp.); *oxalo*-o-*nitrophenylhydrazide*, m. p. 265°; oo′-*nitroaminohydrazobenzene*, m. p. above 300°.
J. W. BAKER.

3 : 3-Dibromopyriminazol-2-one [3 : 3-dibromo-2-keto-2 : 3-dihydropyriminazole] and attempts to prepare 2 : 3-diketo-2 : 3-dihydropyriminazole. F. REINDEL and F. ROSENDAHL (Ber., 1926, **59**, [*B*], 1064—1068; cf. A., 1924, i, 1235; 1925, i, 438; Tschitschibabin, A., 1925, i, 158).—Pyriminazol-2-one is converted by bromine (2 mols.) in glacial acetic acid solution into (?)3-*bromopyriminazol*-2-*one hydrobromide* and by the halogen (10 mols.) into 3 : 3-*dibromopyriminazolone perbromide hydrobromide*, $C_7H_5ON_2Br_5$, decomp. 150—152°, from which 3 : 3-*dibromopyriminazol*-2-*one*, decomp. 135° (also prepared by bromination of 3-nitrosopyriminazolone), is derived. Alkaline hydrolysis gives ill-defined products, whereas ammonia yields the *compound*, $C_{14}H_8O_2N_5Br$. 3 : 3-*Dianilinopyriminazol*-2-*one*, m. p. 167—168°, and (?) 3-p-*dimethylanilo*-2-*keto*-2 : 3-*dihydropyriminazole* are described. Oxalyl chloride and 2-aminopyridine give 2-pyridyloxamide, whereas with ethoxalyl chloride *ethyl* 2-*pyridyloxamate*, m. p. 77°, is obtained, with which ring closure could not be effected.
H. WREN.

Transformations of peptide substances. VIII. Dehydrogenation of amino-acids. M. BERGMANN and F. STERN (Annalen, 1926, **448**, 20—32).—Certain acyl derivatives of amino-acids are readily dehydrogenated, yielding derivatives of α-aminoacrylic acid (cf. A., 1925, i, 1134). When α-chloroacetamido-β-phenylpropionic acid (Leuchs, A., 1904, i, 867) is warmed with acetic anhydride, the primary product, 2-chloromethyl-4-benzyloxazolin-5-one, loses 1 mol. of hydrogen chloride, forming 2-methyl-4-benzylideneoxazolin-5-one (Erlenmeyer's lactimide of α-acetamidocinnamic acid, A., 1895, i, 281), which is readily hydrolysed to α-acetamidocinnamic acid. Similarly, α-chloroacetamido-β-(*p*-hydroxyphenyl)propionic acid (Fischer, *ibid.*, 1904, i, 652) yields 2-*methyl*-4-p-*hydroxybenzylideneoxazolin*-5-*one*, m. p. 131—132°, which is also obtained by heating a mixture of glycine and *p*-hydroxybenzaldehyde with acetic anhydride and sodium acetate at 115°. It is readily hydrolysed to α-*acetamido*-p-*hydroxycinnamic acid*, m. p. (+1H$_2$O) 148° (anhydrous) 203°. α-(α-Bromopropionamido)-propionic acid (*idem*, *ibid.*, 1907, i, 18), when heated with sodium acetate and acetic or benzoic anhydride, yields 2-*ethyl*-4-*methyleneoxazolin*-5-*one*, b. p. 76—77°, which changes on keeping into a colourless, vitreous solid, whilst it is converted by water into pyruvic acid.
H. E. F. NOTTON.

Derivatives of 2-keto-1 : 2-dihydrobenz*iso*thiazole ("2-thiobenzimide"). E. W. MCCLELLAND and A. J. GAIT (J.C.S., 1926, 921—925; cf. McClelland and Longwell, *ibid.*, 1923, **123**, 3310).—2 : 2′-Dithiobenzoyl chloride, treated with chlorine in carbon tetrachloride, gives a solution which probably contains the compound, ClS·C_6H_4·COCl. The solution reacts with ammonia and primary amines to give 2-keto-1 : 2-dihydrobenz*iso*thiazoles $C_6H_4<\begin{matrix}S\\CO\end{matrix}>NR$, where R=H (m. p. 155—156°), *Ph* (m. p. 140°), o-C_6H_4Me (m. p. 122—123°), *Me* (m. p. 51—52°; *hydrochloride*, m. p. 124—127°), *Pr* (oily). Oxidation of the *N*-substituted products gives the expected "saccharins" (*N*-alkyl- or -aryl-*o*-benzoicsulphinides); N-n-*propyl*-o-*benzoicsulphinide* has m. p. 73—75°. Hydrogen sulphide reduces the benz*iso*thiazoles, a dithiobenzoalkyl-(or aryl-)amide being formed.
C. HOLLINS.

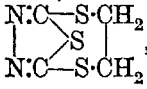
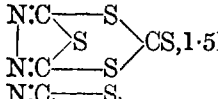
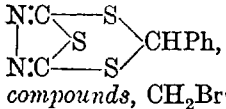
Thiazoles. XI. Synthesis of 2-*p*-aminophenyl-5-methylbenzthiazole and incidental compounds: isomerides of dehydrothio-*p*-toluidine and of chloramine-yellow. M. T. BOGERT and R. W. ALLEN (Ind. Eng. Chem., 1926, **18**, 532—533).—4-Iodo-3-nitrotoluene and alcoholic sodium disulphide give 3 : 3′-*dinitrodi*-p-*tolyl disulphide*, m. p.

175·5°. This with zinc dust and acetic acid gives the *zinc* salt of 3-*aminothio*-p-*cresol*. This with *p*-nitrobenzyl chloride forms 2-p-*nitrophenyl*-5-*methylbenzthiazole*, m. p. 182·5°, which with tin and hydrochloric acid yields 2-p-*aminophenyl*-5-*methylbenzthiazole*, m. p. 218°. The sulphonic acid of this compound is oxidised by sodium hypochlorite to a yellow dye similar in properties to chloramine-yellow NN.

A. DAVIDSON.

1-*m*-Toluidino-4-methylbenzthiazole hexabromide. R. F. HUNTER (Rec. trav. chim., 1926, **45**, 417—420; cf. J.C.S., 1925, **127**, 2023, 2270).—Bromine in chloroform solution converts *s*-di-*m*-tolylthiocarbamide into 1-m-*toluidino*-4-*methylbenzthiazole hexabromide*, m. p. 106° (decomp. 181—183°), to which the constitution $C_6H_3Me\langle^{SBr_4}_{NBr_2}\rangle C{\cdot}NH{\cdot}C_7H_7$ is assigned. It liberates iodine from a solution of potassium iodide in acetic acid only if water is present, and it is reduced by sulphurous acid to the parent toluidinomethylbenzthiazole of m. p. 185—186°.

G. M. BENNETT.

Synthesis of condensed heterocyclic systems. Interaction between 2 : 5-dithiol-1 : 3 : 4-thiodiazole and organic dihalides. P. C. RÂY and B. C. GUHA (J. Indian Chem. Soc., 1926, **8**, 23—29; cf. Rây, Guha, and Das, J.C.S., 1919, **115**, 1308).—Condensation of the dipotassium salt of 2 : 5-dithiol-1 : 3 : 4-thiodiazole with ethylene dibromide, thiocarbonyl chloride, and benzylidene chloride yields, in each case, (1) a fused heterocyclic ring compound, (2) a thiol-compound; and thus are obtained (1) the *compounds*  , m. p. 132—133°;  CS,1·5EtOH, m. p. 110—112°;  CHPh, m. p. 195—196°, and (2) the *thiol-compounds*, $CH_2Br{\cdot}CH_2{\cdot}SC_2N_2{\cdot}S{\cdot}SH$; $CS(SC_2N_2S{\cdot}SH)_2$; $CHPh(SC_2N_2S{\cdot}SH)_2$ (*lead* salts described).

J. W. BAKER.

Alipine hydrochloride. J. SEVILLA (Anal. Asoc. Quím. Argentina, 1925, **13**, 282—291; 357—374).—Alipine hydrochloride, $NMe_2{\cdot}CH_2{\cdot}CEt(OBz){\cdot}CH_2{\cdot}NMe_2HCl$, has m. p. 168—169°, d^{15} 1·0687, n^{20} 1·5224. Its principal chemical and pharmacological properties are described.

G. W. ROBINSON.

Preparation of pure α-sparteine methiodide. E. MERCK etc.—See B., 1926, 464.

Alkaloid of *Julocroton montevidensis*. C. ANASTASI (Anal. Asoc. Quím. Argentina, 1925, **13**, 348—356).—A white, crystalline alkaloid, *yulocrotine*, $C_{19}H_{26}O_3N_2$, has been obtained from the roots of *Julocroton montevidensis*.

G. W. ROBINSON.

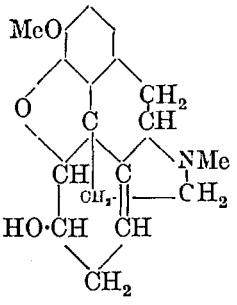
***Lobelia* alkaloids. III.** C. SCHOPF and E. BOETTCHER (Annalen, 1926, **448**, 1—19).—Further light has been thrown on the constitution of lobelan, $C_{22}H_{29}N$ (A., 1925, i, 1088), by the synthesis of its isomerides, *cis*- and *trans*-1-benzyl-2-(β-phenylethylmethylamino)*cyclo*hexane. Their methohydroxides, unlike that of lobelan, undergo the Hofmann degradation in the normal manner, yielding styrene, water, and *cis*- and *trans*-1-benzyl-2-dimethylamino*cyclo*hexane, respectively. Since a 2-benzyl group does not affect the course of the reaction, it is still more unlikely that one in the 3- or 4-position would do so; consequently lobelan cannot be a benzyl-(β-phenylethyl-methylamino)*cyclo*hexane. 1-*Benzyl*cyclo*hexanone*-2-*oxime*, m. p. 126—127°, reduced with sodium and alcohol, yields mainly trans-1-*benzyl*-2-*amino*cyclo*hexane*, which, after purification through the *benzoyl* derivative, m. p. 162—163°, has b. p. 148°/10 mm. (*dibenzoyl* derivative, m. p. 134—135°; *hydrochloride*, m. p. 236—237°; *hydrobromide*, m. p. 217—218°; *picrate*, m. p. 157—158°; *acetate*, m. p. 164°). trans-1-*Benzyl*-2-*dimethylamino*cyclo*hexane methiodide* has m. p. 205° (decomp.). Reduction of the oxime with sodium amalgam and glacial acetic acid yields the impure cis-*amino*-derivative, b. p. 150—154°/12 mm., from which the pure *benzoyl* derivative, m. p. 155°; *acetate*, m. p. 170—171°; *hydrochloride*, m. p. 223—224°; *hydrobromide*, m. p. 226—227°; and *methiodide*, m. p. 215—216°, are prepared. When the trans-*amino*-derivative is heated with β-phenylethyl bromide, trans-1-*benzyl*-2-(β-*phenylethylamino*)cyclo*hexane hydrobromide*, m. p. 167—168°, is formed. The free *base*, b. p. 170°/1 mm. (*hydrochloride*, m. p. 177°; *hydriodide*, m. p. 185°; *benzoyl* derivative, m. p. 102°), is converted by methyl iodide and sodium hydroxide into trans-1-*benzyl*-2-(β-*phenylethyl-methylamino*)cyclo*hexane*, b. p. 186°/1 mm. (*hydrochloride*, m. p. 180—181°). The latter yields a *methiodide*, m. p. 178—179°, and a crystalline *ammonium base*. cis-1-*Benzyl*-2-(β-*phenylethylamino*)cyclo*hexane*, b. p. 195°/1 mm. (*hydrobromide*, m. p. 214—215°; *benzoyl* derivative, m. p. 103—104°), and cis-1-*benzyl*-2-(β-*phenylethyl-methylamino*)cyclo*hexane methiodide*, m. p. 178°, are prepared similarly. The unstable *dibromide* of 1-benzyl-Δ^1-*cyclo*hexene (Auwers, A., 1915, i, 789) affords, on heating with 3·5 mols. of methylamine at 115—120°, a mixture of bases, b. p. 142—148°/10 mm. (dimethylamine gives a similar *product*, b. p. 137—139°/10 mm.), from which pure 1-*benzyl*-2-*methylamino*-Δ^6-cyclo*hexene hydrobromide*, m. p. 136—137°, can be isolated. Catalytic hydrogenation converts the latter into impure trans-1-*benzyl*-2-*methylamino*cyclo*hexane*, b. p. 149°/10·5 mm. (*hydrobromide*, m. p. 162—163°, shrinking at 145°), from which are obtained, by means of methyl iodide and β-phenylethyl bromide, *trans*-1-benzyl-2-dimethylammo*cyclo*hexane methiodide and *trans*-1-benzyl-2-(β-phenylethyl-methylamino)*cyclo*hexane, respectively. The constitution of these compounds is thus substantiated.

H. E. F. NOTTON.

Preparation of "herapathite." A. ZIMMERN (Compt. rend., 1926, **182**, 1082—1083; cf. Jörgensen, A., 1877, i, 210).—Larger crystals of "herapathite" (quinine sulphatoperiodide) than those hitherto obtained may be prepared by the action of iodine vapour on a solution of quinine sulphate in the presence of caffeine or quinol. In using two of these

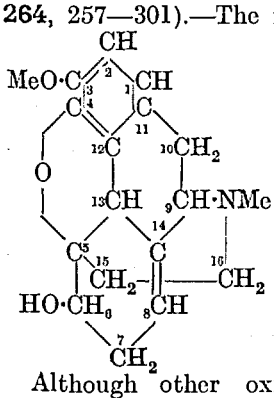
crystals as polariser and analyser, respectively, the colour in the position of extinction is sometimes olive green and sometimes bright red. H. J. EVANS.

Morphine group. III. Constitution of neopine. C. F. VAN DUIN, R. ROBINSON, and J. C. SMITH (J.C.S., 1926, 903—908).—Neopine hydrobromide, $C_{19}H_{22}O_3NBr$, m. p. 282—283° (decomp.), $[\alpha]_D^{23}$ +17·32° (cf. Dobbie and Lauder, *ibid.*, 1911, **99**, 34), on treatment with potassium hydroxide and extraction with benzene, yields neopine, $C_{18}H_{21}O_3N$, m. p. 127·5° (corr.), which is optically inactive in aqueous solution, but in chloroform has $[\alpha]_D^{23}$ −28·10°. *Acetylneopine* forms a *methiodide*, m. p. 256—257° (decomp.; corr.). By hydrogenation in dilute acetic acid in the presence of colloidal palladium, neopine is converted into dihydrocodeine, m. p. 55° ($+2H_2O$) or 112—113° (anhyd.). The *methosulphate* of neopine reacts with hot potassium hydroxide solution to give neopinemethine, m. p. 135°, identical with pure β-methylmorphimethine. Neopinemethine methiodide has m. p. 291° (decomp.) and $[\alpha]_D^{21}$ +241·1° in methyl alcohol or +262·0° in ethyl alcohol. Neopine thus bears the same relation to codeine as β-methylmorphimethine to the α-isomeride, and is best represented by the annexed formula, which differs from that of codeine (Gulland and Robinson, this vol., 83) in the removal of the double linking to a more protected position. In accordance with this view, neopine is more stable than codeine towards reagents for the ethylene linking. C. HOLLINS.



Morphine group. IV. New oxidation product of codeine. R. S. CAHN and R. ROBINSON (J.C.S., 1926, 908—912).—An ice-cooled 0·5% solution of codeine is oxidised by 1% aqueous permanganate to *dihydroxydihydrocodeine* (addition of 2OH at the double linking in Gulland and Robinson's formula for codeine, this vol., 83). *Triacetyldihydroxydihydrocodeine*, m. p. 200°, forms a *perchlorate*, m. p. 281° (slight decomp.). Wieland and Kotake's formula for codeine (A., 1925, i, 1090) is discussed. C. HOLLINS.

Oxidation of codeine with mercuric acetate. H. DIETERLE and P. DICKENS (Arch. Pharm., 1926, **264**, 257—301).—The results obtained in the work described below are interpreted with the help of the annexed formula of Knorr (A., 1907, i, 789) and Pschorr (*ibid.*, 547, 635); they appear to agree better with this than with any of the alternatives more recently proposed, but particular attention is paid to the considerations put forward by Gadamer (A., 1914, i, 1088; Z. angew. Chem., 1913, **26**, 625).



Although other oxidising agents (cf. Wieland and Kappelmeier, A., 1911, i, 743) give unsatisfactory results, Gadamer's reagent, viz., mercuric acetate, oxidises codeine smoothly. In cold aqueous solution the oxidation continues for about 6 months, and ceases when the mercuric acetate consumed is equivalent to one molecular proportion of oxygen. In a hot solution, the attack is much more rapid (0·5 hr.). During the oxidation (in the cold) the specific rotation of the solution rises to a maximum and then falls again; this indicates that the attack is at, or in the neighbourhood of, an asymmetric carbon atom, probably No. 9. The product, isolated by evaporating the solution to dryness, freed from excess of mercuric acetate, is a shellac-like mass containing about 57% of combined mercury (together with the equivalent of 21% of acetic acid and 20% of alkaloid, determined by titration with potassium permanganate). It is impossible to remove the combined mercury in such a way as to set free the oxidised codeine (27 different methods were tried). When attempts are made to separate the mercury eventually as sulphide, the mercury sulphide precipitate contains also all the alkaloidal material, no matter how drastic the previous treatment has been. When the product (from either hot or cold oxidation) is heated with formic acid, the combined mercury is removed, but reduction also takes place, and there is regenerated 80% of the original codeine, together with an unstable *base* (representing the remaining 20%), only isolated in a crystalline condition as the l-*hydrogen tartrate*, m. p. 186°. Reduction with zinc and concentrated hydrochloric acid or acetic acid gives the same results as the treatment with formic acid. A milder reduction, viz., with hydrogen and palladised charcoal, is fruitless, but when sodium amalgam is used, again 80% of the original codeine is regenerated, but the remaining 20% now reappears as dihydrocodeine. It is suggested that when the codeine is oxidised by mercuric acetate, the nitrogen becomes quinquevalent, a double linking being formed between the nitrogen atom and carbon No. 16. The subsequent reduction may then proceed in one of two directions.

The ethylenic linking between carbon atoms 8 and 14 being saturated in dihydrocodeine—which was obtained by reduction with hydrogen and palladised charcoal as described by Mannich and Löwenheim (A., 1921, i, 124), their form of m. p. 111—112° not being observed—it also was subjected to mercuric acetate oxidation. This proceeds only in a hot solution. The $[\alpha]_D$ changes from −100° to +100°, but when the combined mercury is removed by hot formic acid, the product is again lævorotatory. This *base* is an amorphous mass (decomp. 118—132°, $[\alpha]_D$ −125°). It neither acetylates nor yields a methiodide; this confirms the supposition that oxidation takes place at the nitrogen atom. When the product is reduced, it regenerates dihydrocodeine.

If the oxidation takes place as suggested, the acetyl derivatives also should be attacked, but the methiodides, in which the nitrogen atom is already quinquevalent, should be unaffected. This is so: acetylcodeine is rapidly oxidised (to the same extent) in a hot solution; again, the change in specific rotation does not run parallel with the separation of mercurous acetate. The product eventually isolated is an

amorphous *base* (*hydrochloride*, m. p. 137—139°, $[\alpha]_D$ +40°), which is still under examination. *Acetyldihydrocodeine*, m. p. 117—118°, $[\alpha]_D$ −120°, is oxidised in a similar way, and also yields an amorphous *base*, decomp. 94—112°. Codeine methiodide, dihydrocodeine methiodide, acetylcodeine methiodide, and *acetyldihydrocodeine methiodide* (m. p. 235—236°, $[\alpha]_D$ −30°) all resist both oxidation and mercuration. These later results suggest that when mercuration takes place it does not precede, but follows oxidation, and so takes place in the same ring, probably at tertiary carbon atoms (cf. Gadamer and von der Brück, Arch. Pharm., 1923, **261**, 117). This reasoning again suggests the formation of an unsaturated linking between the nitrogen atom and carbon atom 16. W. A. Silvester.

Alkali xanthates as reagents for alkaloids. E. Navarro (Anal. Fís. Quím., 1926, **24**, 125—149).—The author has examined the reactions of potassium methylxanthate, potassium ethylxanthate, potassium propylxanthate, potassium *iso*butylxanthate, and potassium *iso*amylxanthate, respectively, with the principal alkaloids and alkaloid salts, in neutral and acid solutions. In the case of the so-called strong bases, crystalline precipitates or turbidities are produced which appear to be true salts. The xanthates may be used for the detection of alkaloids and, conversely, with certain alkaloids, for the detection of methyl, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols. Photomicrographs are given of the crystalline precipitates obtained.

G. W. Robinson.

Organic derivatives of phosphoric acid. III. Determination of iron. I. F. Zetzsche and M. Nachmann.—See this vol., 705.

Trypanocidal action and chemical constitution. IV. Arylamides of aminohydroxyphenylarsinic acids. L. F. Hewitt and H. King (J.C.S., 1926, 817—831; cf. King and Murch, A., 1925, i, 319; this vol., 186).—The introduction of *N*-*m*-aminobenzoyl groups into 3-amino-4-hydroxy- and 4-amino-2-hydroxy-phenylarsinic acids does not enhance the trypanocidal activity. The arseno-derivative of 3′-amino-4′-hydroxybenzoyl-4-amino-2-hydroxyarsenobenzene is superior to its parent acid, being permanently curative on one fourth of the tolerated dose.

o-Aminophenol, prepared by reduction of *o*-nitrophenol with faintly alkaline sodium hyposulphite below 30°, is converted by acetic anhydride into 2-methylbenzoxazole, which, on nitration with mixed acid and hydrolysis with hydrochloric acid, yields 5-nitro-2-aminophenol and the 4-nitro-compound in the ratio 4 : 1. The 5-nitro-derivative is obtained in orange needles, m. p. 203—204°, or green plates, m. p. 170° (with immediate conversion into the higher-melting variety), and forms an N-*monoacetyl* derivative, m. p. 271—272°, an ON-*diacetyl* derivative, m. p. 193—194°, and a *triacetyl* derivative, m. p. 138—139°. From 4-nitro-2-aminophenol an N-*monoacetyl* derivative, m. p. 279—280°, and an *ON*-diacetyl derivative, m. p. 187—188°, are obtained. Nitration of carbonyl-*o*-aminophenol gives, after hydrolysis, 5-nitro-2-aminophenol; 2-acetamidophenol gives only 4 : 6-dinitro-2-acetamidophenol, which is the main product when triacetyl-2-aminophenol is nitrated.

4-Amino-2-hydroxyphenylarsinic acid (*hydrochloride*, *nitrate*, and *sulphate* described), prepared from 5-nitro-2-aminophenol, is converted into 4-m-*nitrobenzamido*-2-*hydroxyphenylarsinic acid* (*sodium* salt described), and by subsequent reduction into 4-m-*aminobenzamido*-2-*hydroxyphenylarsinic acid* (*sodium* and *ammonium* salts, *hydrochloride*, *nitrate*, *sulphate*, and corresponding *arseno*-compound described). On nitration of the nitrobenzamido-acid, there is formed 3′ : 5-*dinitro*-4-*benzamido*-2-*hydroxyphenylarsinic acid*, which is hydrolysed to 5-*nitro*-4-*amino*-2-*hydroxyphenylarsinic acid*, or is reduced by ferrous hydroxide to 3′ : 5-*diamino*-4-*benzamido*-2-*hydroxyphenylarsinic acid* (*hydrochloride*, *sulphate*, and *nitrate* described). 4 : 5-*Diamino*-2-*hydroxyphenylarsinic acid*, obtained by reduction of the nitroamino-acid with sodium hyposulphite, gives with nitrous acid a *diazoimine*.

3′-*Nitroanisoyl*-4-*amino*-2-*hydroxyphenylarsinic acid* (*sodium* and *ammonium* salts described) is reduced by ferrous hydroxide to 3′-*aminoanisoyl*-4-*amino*-2-*hydroxyphenylarsinic acid* (*sodium* salt, *hydrochloride*, *sulphate*, *nitrate*, and *arseno*-compound described). From 4-amino-2-hydroxyphenylarsinic acid and 3-nitro-4′-ethylcarbonatobenzoyl chloride there is prepared 3′-*nitro*-4′-*ethylcarbonatobenzoyl*-4-*amino*-2-*hydroxyphenylarsinic acid*. This is hydrolysed by cold *N*-sodium hydroxide to 4-m-*nitro*-p-*hydroxybenzamido*-2-*hydroxyphenylarsinic acid*, which is reduced to the corresponding *amine* (*hydrochloride*, *nitrate*, *sulphate*, *diazo-oxide*, and *arseno*-compound described).

3-m-*Nitrobenzamido*-4-*hydroxyphenylarsinic acid* (*ammonium* salt described) is reduced to 3-m-*aminobenzamido*-4-*hydroxyphenylarsinic acid* (*hydrochloride*, *sulphate*, *nitrate*, and *arseno*-compound described); 3′-*nitroanisoyl*-3-*amino*-4-*hydroxyphenylarsinic acid* (*sodium* salt) to 3′-*aminoanisoyl*-3-*amino*-4-*hydroxyphenylarsinic acid* (*hydrochloride*, *sulphate*, *nitrate*, and *arseno*-compound described). Hydrolysis of 3′-*nitro*-4′-*ethylcarbonatobenzoyl*-3-*amino*-4-*hydroxyphenylarsinic acid* gives the 3′-*nitro*-4′-*hydroxybenzoyl* derivative, which is reduced to 3-m-*amino*-p-*hydroxybenzamido*-4-*hydroxyphenylarsinic acid* (*hydrochloride*, *sulphate*, *nitrate*, *diazo-oxide*, *arseno*-compound, and the *diazo-oxide* of the arseno-compound described), together with a little of the corresponding *azoxy*-derivative (insoluble *magnesium* salt). C. Hollins.

Action of alkyl chloroformates on hydroxyarylarsinic acids. C. S. Hamilton and F. W. Johnson (J. Amer. Chem. Soc., 1926, **48**, 1405—1408; cf. A., 1925, i, 600).—The following carbalkoxyhydroxyarylarsinic acids (alkyl arsinoaryl carbonates) were prepared by the action of alkyl chloroformates on arylarsinic acids in alkaline solution: p-*arsinophenyl methyl*, p-*arsinophenyl ethyl*, p-*arsinophenyl propyl*, p-*arsinophenyl* iso*propyl*, p-*arsinophenyl butyl*, p-*arsinophenyl* iso*butyl*, and 2-*nitro*-4-*arsinophenyl methyl carbonates*, all having m. p. above 250°; 2-*nitro*-4-*arsinophenyl ethyl*, m. p.

154°; 2-*nitro*-4-*arsinophenyl propyl*, m. p. 133°; 2-*nitro*-4-*arsinophenyl* iso*propyl*, m. p. 168°; 2-*nitro*-4-*arsinophenyl butyl*, m. p. 137°; 2-*nitro*-4-*arsinophenyl* iso*butyl*, m. p. 141°; m-*arsinophenyl methyl*, m. p. 143°; m-*arsinophenyl ethyl*, m. p. 128°; m-*arsinophenyl propyl*, m. p. 115·5°; m-*arsinophenyl* iso*propyl*, m. p. 154°; m-*arsinophenyl butyl*, m. p. 87°; and m-*arsinophenyl* iso*butyl carbonate*, m. p. 100°. All the above compounds decompose at the m. p.

F. G. WILLSON.

Production of unsymmetrical arsenobenzene compounds. DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORM. ROESSLER and A. ALBERT. —See B., 1926, 462.

Production of derivatives of organic arseno-compounds. DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORM. ROESSLER and A. ALBERT. —See B., 1926, 462.

Reaction of some polyhydric phenols with sodium antimonyl tartrate. [Diantimonyl derivatives of di-2 : 3 : 4-trihydroxybenzylidene-3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene.] W. G. CHRISTIANSEN.—See this vol., 722.

Production of heterocyclic compounds containing arsenic or antimony. A. BINZ and C. RÄTH.—See B., 1926, 512.

Manufacture of aromatic stibinic acids. CHEM. FABR. VON HEYDEN.—See B., 1926, 514.

Tellurium tetrachloride and aryl alkyl ethers. G. T. MORGAN and R. E. KELLETT (J.C.S., 1926, 1080—1088; cf. this vol., 83; Rust, A., 1898, 137; Rohebaech, *ibid.*, 1901, i, 273; Lederer, *ibid.*, 1916, i, 647; 1920, i, 40, 482).—Tellurium tetrachloride reacts quantitatively with anisole in the presence or absence of chloroform to yield p-*anisyltelluritrichloride*, m. p. 190° (Rust's " dichlorotellurobisanisole "), which is yellow, and after solution in sodium hydroxide and precipitation with acetic acid furnishes a hydrated oxide, which yields 2 : 4-dinitrophenol and a *compound*, m. p. 190—210°, on treatment with warm dilute nitric acid. *Bis*-p-*anisylditelluride* (Rohebaech and Lederer's " *p*-telluroanisole "), obtained almost quantitatively by reducing the trichloride with potassium metabisulphite, is readily oxidised by hydrogen peroxide, and the product regenerates the trichloride with chlorine and the tribromide, m. p. 187·5°, with bromine. The colourless *di*-p-*anisyltelluridichloride*, m. p. 181—182°, obtained by heating excess of anisole with tellurium tetrachloride for 24 hrs. at 150—180°, is resistant to the action of metabisulphite, and is attacked only with difficulty by zinc dust, when colourless *bis*-p-*anisyltelluride*, m. p. 53—54°, is formed, which yields a dibromide, m. p. 190°. The preparation of 2-*methoxytolyl*-5-*telluritrichloride*, m. p. 232—233°, *bis*-2-*methoxy*-m-*tolyl ditelluride*, m. p. 77—78°, 4-*methoxytolyl*-3-*telluritrichloride*, m. p. 135°, and 3-*methoxytolyl*-(4 or 6)-*telluritrichloride*, m. p. 154°, according to the same general methods is described. Uncrystallisable products were obtained from the ethers of β-naphthol, resorcinol, and quinol. *Trichlorotelluripropionic acid*, m. p. 145—150°, obtained from tellurium tetrachloride and propionic anhydride, when reduced with aqueous metabisulphite, yields *ditellurodipropionic acid*, m. p. 75° (*silver*, *copper*, and *potassium* salts described), which with bromine in chloroform yields *tribromotelluripropionic acid*, m. p. 139—141°. The behaviour of *n*-butyric anhydride and *iso*valeric anhydride with tellurium tetrachloride shows that the tendency to undergo this condensation diminishes rapidly on ascending the series.

J. S. H. DAVIES.

Structure of the compounds produced by the addition of mercuric salts to olefines. L. T. SANDBORN and C. S. MARVEL (J. Amer. Chem. Soc., 1926, **48**, 1409—1413).—Treatment of *l*-menthyl cinnamate with mercuric acetate in methyl-alcoholic solution in presence of acetic acid affords l-*menthyl* β-*methoxy*-α-*acetoximercuri*-β-*phenylpropionate*, m. p. 95—105°, $[\alpha]_D^{21}$ −23·1° in chloroform (cf. Schrauth, Schoeller, and Struensee, A., 1910, i, 347; 1911, i, 595). Treatment of the latter with methyl-alcoholic sodium bromide yields l-*menthyl* β-*methoxy*-α-*bromomercuri*-β-*phenylpropionate*, m. p. 145—146°, $[\alpha]_D^{25}$ −48·6°, together with an optical *isomeride*, m. p. 134—135°, $[\alpha]_D^{25}$ +61·9°. l-*Menthyl* β-*methoxy*-α-*iodomercuri*-β-*phenylpropionate* is also obtained similarly as a mixture of the two *isomerides*, m. p. 126—128°, $[\alpha]_D^{25}$ +65·89°, and m. p. 102—103°, $[\alpha]_D^{25}$ −24·27°, respectively, but the corresponding α-*chloromercuri*-derivative, m. p. 150—152°, $[\alpha]_D^{25}$ −45·08°, could not be obtained in an isomeric form. The existence of these compounds in optically isomeric forms indicates that the compounds formed by the addition of mercuric salts to olefines have the structure :C(OH)·C(HgX): (cf. Adams, Roman, and Sperry, A., 1922, i, 946).

F. G. WILLSON.

Action of mercuric acetate on *o*-toluidine. L. VECCHIOTTI (Gazzetta, 1926, **56**, 155—160).—The interaction of aqueous mercuric acetate (1 mol.) and *o*-toluidine (1 mol.) yields an *o-toluidinedimercuriacetate*, m. p. 208°, isomeric with the compound, m. p. 228°, obtained when the reaction takes place in methyl-alcoholic solution (cf. Schrauth and Schoeller, A., 1912, i, 930). The position of the two mercuric acetate residues has not been determined, but they are not the 4 and 6 or the 3 and 5 positions. The corresponding *hydroxide*, m. p. 235°; *chloride*, decomp. without melting at 221°; *bromide*, decomp. without melting at 232°; *acetotoluidide*, softening at 214°, m. p. 219°, are described. Treatment of the last compound with sodium chloride and chlorine yields a new *dichloro-o-toluidine*, m. p. 162—163°, the structure of which remains to be established.

T. H. POPE.

Action of mercuric acetate on 2 : 4-dichloroaniline. L. VECCHIOTTI and N. CARANI (Gazzetta, 1926, **56**, 147—152; cf. A., 1924, i, 957; 1925, i, 1058).—The interaction of mercuric acetate and 2 : 4-dichloroaniline in aqueous alcoholic solution yields 2 : 4-*dichloroaniline*-6-*mercuriacetate*, m. p. 170—171°. The corresponding *hydroxide*, m. p. 230°; the *chloride*,

m. p. 193°; the *acetyl* derivative, blackening at 260°, m. p. 283°; and 6-*mercuribis*-2 : 4-*dichloroaniline*, m. p. 168°, obtained by treating the acetate with sodium hydrogen sulphate, are described. Treatment of the acetyl derivative with calcium chloride and chlorine gives 2 : 4 : 6-trichloroacetanilide.

T. H. POPE.

Organic derivatives of tin. C. OECHSLIN etc. —See B., 1926, 465.

Structure of the compound $C_{14}H_{18}O_4N_2$ obtained from caseinogen by enzymic digestion. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1926, **153**, 16—53).—The compound (I), $C_{14}H_{18}O_4N_2$, m. p. 147°, $[\alpha]_D$ −22·75°, previously described as being obtained from the hydrolysis of caseinogen and yielding tyrosine and proline on acid hydrolysis, loses water in a desiccator over phosphorus pentoxide, to form an *anhydride* (I), $C_{14}H_{16}O_3N_2,H_2O$, m. p. 187°, after previous sintering at 83°, $[\alpha]_D^{17}$ −102·50° in alcohol. It forms no copper salt and is neutral to litmus. When anhydride (I) is treated with *N*-barium hydroxide solution for 60 hrs., there is obtained a *compound* (II), $C_{14}H_{18}O_4N_2,H_2O$, which sinters at 120°, becomes at 127° a frothy liquid, which again solidifies at 180°, and finally melts at 206°; it has $[\alpha]_D^{20}$ −141·9° in water. When kept over phosphorus pentoxide in a vacuum, an *anhydride* (II) is formed, needles, m. p. 226—228°, $[\alpha]_D^{17}$ +67·1° in alcohol. Compound (I) is resistant to trypsin and pepsin. By the action of diazomethane on a suspension in ether of an aqueous solution of the compound (I), there is obtained a *tetramethyl* derivative, m. p. 198—199° (decomp.). When anhydride (I) is methylated under similar conditions, a *monomethyl* derivative, $C_{15}H_{18}O_3N_2$, is obtained, m. p. 156—157°. Methylation of *dl*-leucylglycine gives a *trimethyl-leucylglycine*, leaflets, m. p. 237° after previous sintering. When it reacts with α-bromo-γ-methylvaleryl chloride, the compound (I) yields an *α-bromo-γ-methylvaleryl* derivative, $C_{20}H_{27}O_5N_2Br$, m. p. 102° after previous sintering at 71° (characteristic decomp. point at 144°). Aqueous ammonia converts this compound into the leucyl derivative of compound (I), $C_{20}H_{29}O_5N_3,H_2O$, m. p. 217° after previous sintering. When boiled with formic acid, compound (I) yields a *diformyl* derivative, $C_{16}H_{18}O_6N_2$, m. p. 72° after previous sintering (on further heating froths and decomp. 85°; at 170°, again becomes a pale yellow liquid, decomp. 285°). Benzenesulphonyl chloride yields a *derivative*, $C_{26}H_{26}O_8N_2S_2$, m. p. 105° after previous sintering. The following salts have also been obtained: *silver* salt, $C_{14}H_{17}O_4N_2Ag,H_2O$, decomp. 202°, *hydrochloride*, m. p. 115° after previous sintering, and *copper* salt, $C_{28}H_{34}O_8N_4Cu$. From the interaction of prolyl chloride hydrochloride and tyrosine ethyl ester, there has been isolated a *compound*, $C_{14}H_{18}O_4N_2,NaCl$, m. p. 250° (approx.) after previous sintering. When *dl*-tyrosine ethyl ester and *dl*-proline ethyl ester are heated together at 130—140°, a little *tyrosylproline anhydride*, m. p. 226° (decomp.), results. If *l*-tyrosine and *l*-proline are similarly heated together, an optically active *anhydride* is obtained in even poorer yield, m. p. 226—228°, $[\alpha]_D^{16}$ +15·35° (in alcohol). This compound, although of lower optical rotation than anhydride (II), shows very close agreement with it in all its other properties. Both compounds separate from water in plates, $C_{14}H_{16}O_3N_2,3H_2O$ (sinter at 80°, again become solid, and remelt at 222°). Barium hydroxide converts this synthetic anhydride into an inactive compound, $C_{14}H_{18}O_4N_2$, m. p. 232° after previous sintering, and this product yields a microcrystalline *tetramethyl* derivative, decomp. 182°, similar to the tetramethyl derivatives of compounds (I) and (II). dl-*Bromo-γ-methylvaleryl*-(N)dl-*α-amino-δ-hydroxyvaleric acid*, m. p. 129—130°, obtained by the condensation of *dl*-α-γ-methylvaleryl chloride and *dl*-α-amino-δ-hydroxyvaleric acid, is converted by aqueous ammonia into N-dl-*leucyl*-dl-*α-amino-δ-hydroxyvaleric acid*, m. p. 212—214°. This dipeptide is hydrolysed by sulphuric acid or by enzymes, and when heated at 180° in a vacuum over phosphorus pentoxide, is converted into a *compound*, $C_{22}H_{38}O_5N_4$, m. p. 224°, and does not give rise to leucylproline.

W. O. KERMACK.

Porphyrins. X. Hæmatoporphyrin monomethyl ether. W. KÜSTER and A. MÜLLER (Z. physiol. Chem., 1926, **155**, 113—121).—The hydrolysis of hæmatoporphyrin dimethyl ether with alkalis could not be controlled to yield a homogeneous product. Hydrolysis with glacial acetic acid at 90° yields the homogeneous monomethyl ether; from this the crystalline hydrochloride could not be obtained (cf. Küster and Deihle, A., 1913, i, 1004). The hydrolysis also proceeds readily during the preparation of the complex zinc salt of the dimethyl ether. The monomethyl ether is converted by diazomethane into a *trimethyl* derivative, m. p. 151—152°, and by chromic acid into hæmatinic acid and the imide, $C_8H_{11}O_3N$, m. p. 59°, which are also obtained similarly from the dimethyl ether. Hydrolysis of the imide with barium hydroxide affords the anhydride, $C_8H_{10}O_4$, b. p. 210—211°; b. p. 115—116°/18 mm., which, with zinc dust and acetic acid, yields two *substances*, m. p. 141° and 101—102°, respectively. The dimethyl ether is reduced (in alkaline solution with sodium amalgam) to a *porphyrinogen*, which yields, on aëration of the solution, a *porphyrin*, which with chromic acid mixture yields the above imide and hæmatinic acid.

F. G. WILLSON.

Porphyrins. IX. Dichlorohæmatoporphyrin dimethyl ether, a di- and a tri-chlorometaporphyrin dimethyl ether. W. KÜSTER and W. ZIMMERMANN (Z. physiol. Chem., 1926, **153**, 125—137).—Dichlorodimethyl(chloro)hæmin when treated with acetic acid–hydrochloric acid solution is converted into *dichlorohæmatoporphyrin dimethyl ether*, $C_{36}H_{40}O_6N_4Cl_2$, red needles. When dimethyl(chloro)-hæmin is treated with excess of chlorine, a *pentachlorodimethyl(chloro)hæmin* is obtained, and this compound on treatment with acetic acid–hydrochloric acid solution yields amorphous trichlorometaporphyrin dimethyl ether, $C_{36}H_{37}O_6N_4Cl_3$, and *dichlorometaporphyrin dimethyl ether*, $C_{36}H_{36}O_6N_4Cl_2$.

W. O. KERMACK.

Basic character of hæmin. W. KÜSTER (Z. physiol. Chem., 1926, **153**, 119—124).—From the mother-liquors from the recrystallisation of dimethyl-(chloro)hæmin a compound, $C_{37}H_{37}O_4N_4Cl_2Fe$, has been obtained (rhombs), which is considered to be a *dimethyl(chloro)hæminium methochloride*. It is stable to aqueous sodium hydroxide, but is converted by alcoholic potassium hydroxide into dimethyl(chloro)-hæmin, $C_{36}H_{34}O_4N_4ClFe$, and by aqueous ammonia into a *compound*, $C_{37}H_{36}O_4N_4ClFe$.

W. O. KERMACK.

Isolation of some hitherto undescribed products of hydrolysis of proteins. II. S. B. SCHRYVER and H. W. BUSTON (Proc. Roy. Soc., 1926, **B**, **99**, 476—487).—After hydrolysis of oat protein with sulphuric acid, the amino-acids were fractionated by the authors' carbamate process. By fractional crystallisation of the zinc salts of the monoamino-acid fraction, there was obtained a mixture of zinc salts soluble in cold water and alcohol, which yielded two *copper* salts, one of which was insoluble in methyl alcohol. The insoluble salt yielded a *hydroxyamino-butyric acid*, $C_4H_9O_3N$, giving *dibenzoyl* and *phenyl-carbimide* derivatives, m.p. 112° and 143°, respectively. The soluble copper salt gave a *hydroxyvaline*, $C_5H_{11}O_3N$, *dibenzoyl* derivative, m. p. 117°, *phenyl-carbimide* derivative, m. p. 145°. The position of the substituent groups has not been determined. (Cf. A., 1922, i, 182.) H. J. CHANNON.

Horn-dissolving action of alkali sulphides. R. WEISS (Z. physiol. Chem., 1926, **153**, 166).—A claim for priority against Pulevska (cf. A., 1925, i, 1341). W. O. KERMACK.

Fission products of cerebrone. E. KLENK (Z. physiol. Chem., 1926, **153**, 74—82).—Barium hydroxide converts cerebrone, by hydrolysis of the fatty acid, into a base, *psychosine*, isolated as its *sulphate*, $C_{23}H_{45}O_7N,0{\cdot}5H_2SO_4$, m. p. 225° (decomp.) after sintering at 170°. Cerebrone is hydrolysed by acetic–sulphuric acid, to give galactose and *cerebronyl*-N-*sphingosine*, $C_{24}H_{49}O{\cdot}CO{\cdot}NH{\cdot}C_{17}H_{33}O_2$, m. p. 86—87°. It forms a *tri*-m-*nitrobenzoyl* derivative, m. p. 96—97°. W. O. KERMACK.

Determination of the empirical formula of naturally occurring substances of high mol. wt. O. DISCHENDORFER (J. pr. Chem., 1926, [ii], **113**, 1—8).—The minute changes in percentage composition for small differences in the empirical formulæ of substances of high mol. wt. may often be made appreciable by introducing heavy atoms into the molecule so as to increase the non-carbon–hydrogen content. Graphs are given showing that the difference in percentage of carbon and hydrogen made by a CH_2 more or less in the empirical formula of a hydrocarbon rises to a maximum and then falls as the weight of such addendum is increased. In the case of a substance already containing atoms other than carbon and hydrogen (*e.g.*, in the carbohydrate, $C_{30}H_{52}O_{26}$), it may happen that the optimum has already been passed, and no advantage results from further addenda. Examples of the application of the method are given. C. HOLLINS.

Micro-method for determining carbon in organic compounds. H. L. LOCHTE (J. Amer. Chem. Soc., 1926, **48**, 1301—1305; cf. A., 1925, ii, 600).—The bomb combustion method previously described can be adapted to the determination of carbon in 10—30 mg. samples of non-halogenated substances by employing a Monel-metal bomb, 180 by 30 mm., into which is fitted a close-fitting lining cut from a Pyrex glass test-tube. Absorption of the carbon dioxide in the saturated barium hydroxide solution is effected by rotating the bomb in an inclined position at about 100 r.p.m. for 30 min., subsequent titration of the carbonate being preferably effected by Lindner's procedure (A., 1922, ii, 657). Nitrogen and sulphur do not interfere with the method, but chlorine compounds cause excessive corrosion of the bomb. Liquids of b. p. above about 100° can be analysed by being weighed on to a weighed pellet of an ignitor such as benzoic acid, but no satisfactory method of dealing with liquids of lower b. p. has been devised. F. G. WILLSON.

Rapid, dry method for the determination of carbon and hydrogen. E. BERL and H. BURKHARDT (Ber., 1926, **59**, [*B*], 890—896).—An intimate mixture of the substance (containing 10—15 mg. of carbon) and lead chromate free from organic matter is heated to dull redness between layers of ignited quartz sand in a narrow hard glass or silica tube. Water is determined by absorption in concentrated sulphuric acid, carbon dioxide gravimetrically or volumetrically. The presence of nitrogen in the substance does not cause complications; if halogen is present, the front portion of the lead chromate is heated only to 170—180°. H. WREN.

Rapid, semi-micro-method for the determination of nitrogen. E. BERL and H. BURKHARDT (Ber., 1926, **59**, [*B*], 897—900).—A modification of Dumas' process is described by which nitrogen may be rapidly determined in organic substances (amount required equivalent to 3—6 mg. of nitrogen) with small use of gas. Combustion is effected in a vacuum or at normal pressure if the compound is readily volatile. H. WREN.

Refractometric determination of alcohols and esters in aqueous and in cotton-seed oil solutions. J. C. MUNCH (J. Amer. Chem. Soc., 1926, **48**, 994—1003).—Refractive indices of aqueous and cotton-seed oil solutions of methyl, ethyl, *n*- and *iso*-propyl, *n*-, *iso*-, *sec*.-, and *tert*.-butyl, *iso*-, *sec*.-, and *tert*.-amyl alcohols, and most of their formates, acetates, propionates, butyrates, and *iso*valerates, have been measured. The relation between concentration of the solution and refractive index was found to be approximately linear in all cases, and the refractive index can be used to measure concentrations of these solutions. Treated mathematically, a significant correlation was found to exist between the "refractive increment" (=change in refractive index per unit increase in concentration) of aqueous solutions and that of oil solutions, enabling the one to be calculated from the other. The original should be consulted for the numerical data.

F. G. WILLSON.

Bromometric examination of fats. H. P. KAUFMANN.—See B., 1926, 447.

Use of thiocyanogen in fat analysis. H. P. KAUFMANN.—See B., 1926, 447.

Ether. III. Determination of aldehyde as a contaminant. E. P. PHELPS and A. W. ROWE.—See B., 1926, 461.

Test for xanthine. G. SCHWEIZER (Chem.-Ztg., 1926, **50**, 430).—When a trace of xanthine is warmed with a crystal of potassium chlorate and a few c.c. of hydrochloric acid and evaporated to dryness, carbamide and alloxan are formed, and on further heating on a water-bath, the alloxan is gradually converted into the red form. On adding a few drops of potassium hydroxide solution to the red residue, an intense ultramarine-blue colour appears, due to the formation of potassium *iso*alloxanate. The sodium salt of this acid is also blue, the barium salt is violet, and the silver salt dark red.

C. T. GIMINGHAM.

Electrometric determination of alkaloids without the use of the hydrogen electrode. S. POPOV and M. J. MCHENRY (J. Amer. Pharm. Assoc., 1925, **14**, 473—476).—Saturated calomel and a plain platinum wire, cleaned with dichromate, are employed as electrodes. A convenient form of titration vessel is described. The alkaloid or its salt is dissolved in anhydrous or aqueous alcohol, and carbon dioxide is removed from the apparatus. Excess of 0·1*N*-hydrochloric acid is added to the free alkaloid, and then titration is carried out with potassium hydroxide. Three breaks represent the conversion of the alkaloid into the hydrochloride, the excess of acid added, and the conversion of the salt into the alkaloid.

CHEMICAL ABSTRACTS.

Biochemistry.

Hæmoglobin. J. BARCROFT (J.C.S., 1926, 1146—1170).—A lecture delivered before the Chemical Society on Feb. 11, 1926.

Adsorption of nitrogen by hæmoglobin. J. B. CONANT and N. D. SCOTT (J. Biol. Chem., 1926, **68**, 107—121).—Measurements of the amounts of nitrogen taken up by aqueous solutions of hæmoglobin, when equilibrated with known gas mixtures, indicate that the amount taken up, in excess of that which can be dissolved, is proportional to the concentration of hæmoglobin; the relationships observed agree with the adsorption equation of Freundlich, viz., amount adsorbed$=aP^b$, the value of b varying from 0·1 to 0·4 for different samples and conditions; the statement of Bohr (A., 1905, ii, 729) that, in the absence of oxygen, no excess nitrogen is taken up by solutions of hæmoglobin could not be confirmed. On the assumption that oxygen and carbon monoxide are adsorbed by hæmoglobin in an analogous manner, a hypothesis is developed which relates the exponent n of the equation of Hill (A., 1913, i, 1250) to the exponent b of the adsorption equation, thus offering a possible explanation of the reason why the n of Hill's equation is not an integer and is smaller than that predicted from the number of molecules of oxygen involved. C. R. HARINGTON.

Oxygen content of methæmoglobin. M. NICLOUX and J. ROCHE (Bull. Soc. Chim. biol., 1926, **8**, 71—97).—The reduction of methæmoglobin to hæmoglobin, and the oxidation of hæmoglobin indicate that methæmoglobin contains one atom of oxygen less than oxyhæmoglobin and one atom more than hæmoglobin. C. P. STEWART.

Formation of methæmoglobin: action of hydroxylamine on hæmoglobin. J. ROCHE (Bull. Soc. Chim. biol., 1926, **8**, 98—112).—An empirical equation is derived for the conversion of oxyhæmoglobin into methæmoglobin by the action of hydroxylamine hydrochloride. C. P. STEWART.

Fixation of hydrogen sulphide in the blood. A. DESGREZ, H. BIERRY, and L. LESCŒUR (Compt. rend., 1926, **182**, 1112—1116).—It is suggested that the facts regarding the absorption of hydrogen sulphide by the blood may be explained on the assumption that the hydrogen sulphide is united solely to the inorganic bases in the blood. The index of acidity of a solution containing sulphides (or carbonates) is defined as the ratio between the alkali equivalent of the total amount of hydrogen sulphide or carbon dioxide present to the amount of acid required to render the solution neutral to methyl-red. At p_H 7·6 sulphides exist in solution in the form of 1 mol. of acid sulphide and 0·15 mol. of hydrogen sulphide, and carbonates as 1 mol. of hydrogen carbonate with 0·04 mol. of carbon dioxide. When hydrogen sulphide is absorbed by the blood, some carbon dioxide is liberated, the ratio of hydrogen sulphide absorbed to carbon dioxide liberated being the ratio of their indices of acidity (*i.e.*, 2·30 : 2·08 at p_H 7·6).

L. F. HEWITT.

Hæmatoporphyrin. I. Optical properties and determination in Harder's gland in the white rat. II. Photo-sensitisation of red corpuscles by hæmatoporphyrin. R. FABRE and H. SIMONNET (Bull. Soc. Chim. biol., 1926, **8**, 56—66).—I. Spectrophotometrically the fluorescence of hæmatoporphyrin shows a maximum intensity at λ 3650 Å. The intensity varies with dilution, being greatest at 1 : 8000. Comparison of the intensity of fluorescence between known solutions of hæmatoporphyrin and extracts from physiological material affords a method of determination. Application of this method shows the hæmatoporphyrin content of Harder's gland in the white rat to be 1·25—1·50 $\times$ 10^{-5} g. per pair of glands of mean weight 0·18 g.

II. The rate of the photo-sensitising action of hæmatoporphyrin on red cells of the horse depends on the concentration of hæmatoporphyrin, and the action is exerted solely by the radiation of the yellow

region of the spectrum. The difference between this result and that of Hausmann, who, working with *paramœcia*, found the activity to be in the green region of the solar spectrum, may be due to the presence of hæmoglobin. C. P. STEWART.

Fractionation of serum proteins. I. Electrodialysis. G. ETTISCH and W. BECK (Biochem. Z., 1926, **171**, 443—453).—By means of a series of curves relating conductivity with p_H and protein content, it is shown that electrodialysis of serum proteins occurs in three stages, involving, first, separation of electrolytes along with continuous precipitation of protein; secondly, a sudden fall together in both p_H and conductivity at a point near p_H 7, but differing for different samples of serum; thirdly, no further changes in p_H, protein content, or conductivity. P. W. CLUTTERBUCK.

Fractionation of serum proteins. II. Theory of electrodialysis. G. ETTISCH (Biochem. Z., 1926, **171**, 454—466).—A theoretical discussion of the course of electrodialysis using Ruppel's arrangement, together with a comparison of the different combinations of membranes. P. W. CLUTTERBUCK.

Coagulation of proteins in drops. VIII. Differences in the coagulation of pure serum and serum from hæmolysed blood of the horse, ox, pig, and dog. S. REINER, F. PLUHAŘ, and B. HÁNÝS (Biochem. Z., 1926, **171**, 156—168).—The characteristics of the coagulation of horse's, ox', pig's, and dog's serum by 23 protein precipitants in 0·1*M*-concentration are given in detail. In the case of the horse, ox, and pig, especially the last, the rate of coagulation increases with the age of the animal when mercuric chloride, cadmium nitrate, copper sulphate, lactic acid, and, irregularly, tannic acid, are used. With phosphotungstic acid, sulphosalicylic acid, pyrogallol, and ferrous and ferric salts, marked differences between the rate of coagulation of pure serum and that of serum from hæmolysed blood are observed. Phenol, ethyl alcohol, and nitric acid in 0·1*M*-concentration have no precipitant action, acetaldehyde, chloral, and resorcinol in isolated instances only. The concentration of chlorides in the serum is of little influence. The p_H of the serum is of importance in the cases of methyl alcohol and tannic acid only. E. C. SMITH.

Inhibition and acceleration of hæmolysis. E. PONDER (Proc. Roy. Soc., 1926, **B**, **99**, 461—476).—A quantitative study of the inhibition of hæmolysis by sucrose, sodium hydroxide, and arginine, and its acceleration by acetic, aspartic, and glutamic acids, histidine hydrochloride, and potassium chloride. H. J. CHANNON.

Chemical constitution of living matter. W. W. LEPESCHKIN (Biochem. Z., 1926, **171**, 126—145).—Living protoplasm is distinguished from dead by the chemical combination of the lipin with the protein constituents, the severing of which combination constitutes the death of the tissue. E. C. SMITH.

Spermine. IV. F. WREDE (Z. physiol. Chem., 1926, **153**, 291—313).—Spermine is found, not only in semen, but also in many tissues—muscle, brain, spleen, liver, pancreas, and testicles. It occurs in the female as well as in the male pancreas (cattle). The semen contains 50—100 times as much spermine as the testicles, and it appears that spermine is either secreted into the semen elsewhere in the seminal tract or develops from some precursor. Spermine is very stable towards acids and alkalis. It rapidly decolorises alkaline permanganate, and after heating with zinc dust, either spermine or its salts give the pyrrole (pine-splinter) reaction. Analyses of the hydrochloride and the picrate agree with the formula $C_{10}H_{26}N_4$ for the free base. Three of the nitrogen atoms appear to be primary (Van Slyke) and the other is probably secondary. By passing air through a solution of spermine in which finely-powdered copper is suspended, the molecule is broken up, and, together with ammonia, two bases of the formulæ $C_7H_{14}N_2$ and $C_4H_{12}N_2$ are obtained. The former takes up two atoms of hydrogen on reduction with hydrogen and platinum-black, and has one primary amino-group. It appears to be a cyclic compound. The latter base, $C_4H_{12}N_2$, contains two primary amino-groups and is not identical with putrescine.

Physiologically, spermine has similar effects to choline. It is not very toxic. Small doses increase the blood pressure somewhat in rabbits, whilst larger doses cause a fall. A diminution in respiration rate and in heart rate also occurs. H. D. KAY.

Physiological ontogeny. A. Chicken embryos. IX. Iodine reaction for the determination of glutathione in the tissues as a function of age. H. A. MURRAY (J. Gen. Physiol., 1926, 9, 621—624).—Iodine titration of the sulphydryl group in tissue according to the method of Tunnicliffe (A., 1925, i, 752) shows that the percentage concentration of this group in the dried substance of chicken embryos decreases with age, particularly during the third quarter of the incubation period. W. O. KERMACK.

Naturally occurring porphyrins and porphyratins. O. SCHUMM (Z. physiol. Chem., 1926, **153**, 225—249).—The ether-soluble porphyrin which occurs in small quantities in the blood of normal adults is coproporphyrin. The spectroscopic reactions of this pigment are described in detail. No other ether-soluble porphyrin is present. The ether-soluble porphyrin in human (fistula) bile, as in human meconium, appears to be coproporphyrin. In lead poisoning, there is an increase in the amount of ether-soluble porphyrin in the urine. This is again almost entirely coproporphyrin, although traces of uroporphyrin may also be present in the ether-soluble fraction. On the other hand, the pigment in the urine in cases of sulphonal poisoning and in a case of hæmatoporphyrinuria of unknown origin is mainly uroporphyrin. After the ingestion of cooked blood, or α-hæmatin, the following pigments are found in the fæces in varying quantities: α-hæmatin, copratin, Papendieck's chloroform-soluble porphyrin, coproporphyrin, and copratoporphyrin. The properties and spectroscopic reactions of copratin and copratoporphyrin are described. The iron compound of coproporphyrin obtained by Zaleski's method behaves spectroscopically like the pigment produced by boiling

an ammoniacal solution of coproporphyrin with Stoke's reagent. H. D. KAY.

Unsaturated fatty acids in tissues. I. Ox heart-muscle. W. R. BLOOR (J. Biol. Chem., 1926, **68**, 33—56).—The total fatty material was extracted from ox heart and separated into phospholipin (kephalin and lecithin) and fat fractions. With respect to unsaturated fatty acids, the following average results were obtained: of the fatty acids of the kephalin fraction, 61% were unsaturated, consisting of 6% of arachidonic acid and the rest mainly linoleic acid; in the lecithin fraction, the unsaturated acids amounted to 53%, comprising 5·6% of arachidonic acid, 45% of linoleic acid, and the rest oleic acid; in the fat, 42% of the acids were unsaturated, there being less than 2% of arachidonic acid, 15% of linoleic acid, and the remainder oleic acid. In all fractions, about 25% of the acids could not be classified. Cholesterol was found in the fat fractions, but no cholesterol esters. The differences both in the total weights of the phospholipin fractions and in the composition of the fractions obtained from different samples of tissue were so great as to indicate that these substances are to be regarded partly as mobile reserve material concerned in fat metabolism. C. R. HARINGTON.

Adipocere. G. STRASSMANN and FANTL (Deut. Z. ges. gerichtl. Med., 1925, **6**, 168—174; from Chem. Zentr., 1926, I, 143).—From a mass of adipocere from a corpse which had remained many years in water, 80% was soluble in ether; 20% consisted of soaps, tissue residues, etc. The ether-soluble portion consisted of free fatty acids of high mol. wt., together with small quantities of neutral fat and cholesterol. The low iodine value indicated saturation of the fatty acids. The adipocere is considered to originate from the body fats, since the mol. wts. of the fatty acids would have been lower had they originated from the putrefactive decomposition of proteins. G. W. ROBINSON.

Chlorides of the blood in different conditions of the gastric secretion. A. KASSIRSKY (Bull. Univ. Asie Central [Tachkent], 1926, **10**, 71—76).—In the majority of cases the blood chloride is low about 1½ hrs. after breakfast, but in an important number of cases it is unaltered or high. The blood chloride before and after breakfast is independent of the state of gastric secretion. The blood chloride alters during secretion, but there is no parallelism between it and the hydrochloric acid of the gastric juice. It is probable that the latter is derived, not solely from the blood chloride, but from the sodium chloride deposits in the tissues, the blood acting largely as a carrier. C. P. STEWART.

Effect of the so-called carnosine fraction of meat extract on the secretion of the gastric glands. R. KRIMBERG and S. A. KOMAROV (Biochem. Z., 1926, **171**, 169—176).—The carnosine fraction prepared from fresh meat has a much stronger excitatory action on gastric secretion than the similar fraction from commercial meat extract. An amount of the carnosine fraction corresponding with 112 g. of moist muscle-tissue evoked the secretion of 23 c.c. of gastric juice in a 9-kg. dog. E. C. SMITH.

Excretion of fat in urine. E. FAERBER (Z. physiol. Chem., 1926, **154**, 302—309).—The urine of healthy children is completely free from fat, whereas, according to previous workers, that of adults contains small amounts of fat; normal dog's urine contains fat in appreciable amount. C. R. HARINGTON.

Detection of bilirubin. M. STERNBERG (Biochem. Z., 1926, **171**, 217).—The bilirubin (in urine) is oxidised by carefully warming with hydrogen peroxide in the presence of phosphoric acid and 50% alcohol. The green colour of biliverdin develops and intensifies on cooling. E. C. SMITH.

Phenol in normal and pathological blood. E. BECHER, S. LITZNER, and W. TÄGLICH (Münch. med. Woch., 1925, **72**, 1676—1677; from Chem. Zentr., 1926, I, 427).—Phenol can be detected and determined quantitatively in normal blood by means of Millon's reagent. Whilst in normal blood phenol occurs only in the combined state, in pernicious anæmia small amounts of free phenol are also present. G. W. ROBINSON.

Refractometric investigation of the breakdown of the protein of fœtal organs. O. KANNER (Biochem. Z., 1926, **171**, 191—197).—Neither carcinomatous nor non-carcinomatous serum has any proteolytic action on embryonic kidney, mammary, stomach, or liver-tissue, unless the subject is cachectic, in which case the liver-tissue only is attacked, no difference, however, being observed between carcinomatous and non-carcinomatous cachexia. E. C. SMITH.

Enzymes of the hydatid cyst. G. R. CAMERON (Australian J. Exp. Biol., 1926, **3**, 11—14).—The enzymes of the hydatid cyst are confined to the cyst wall, and although diastatic enzymes are especially prominent, lipase and certain proteolytic enzymes are present. C. P. STEWART.

Hexosephosphoric acid in normal and diabetic blood and its behaviour towards adrenaline and insulin. H. LAWACZECK (Klin. Woch., 1925, **4**, 1858—1861; from Chem. Zentr., 1926, I, 151).—When the blood-sugar content in diabetes falls on account of diet, the hexosephosphoric acid content of the blood falls or remains unaltered. When the blood-sugar content is only slightly lowered, but the diabetic symptoms are improved, there is a marked increase in the hexosephosphoric acid content. It is decreased by injection of adrenaline and increased by injection of insulin. G. W. ROBINSON.

Influence of phosphate ions on the blood and urine sugar of the normal and diabetic organism. K. FRIEDLÄNDER and W. G. ROSENTHAL (Arch. exp. Path. Pharm., 1926, **112**, 65—81).—Intravenous injection of isotonic or slightly hypertonic, alkaline, or neutral phosphate solutions shows no effect on the blood- and urine-sugar of normal men and dogs nor on that of depancreatised dogs when insulin is completely absent. On the other hand, diabetics show a distinct fall in the blood-sugar, the minimum being reached 2½—4 hrs. after the injection, and the

urine-sugar is similarly decreased. In general, the effect is more pronounced in severe than in slight cases of diabetes. Since the effect is observed equally with alkaline and neutral solutions of phosphate, it must be due to the phosphate ion.

C. P. STEWART.

Behaviour of the urinary quotient C : N in adrenaline glycosuria. H. WADA (Biochem. Z., 1926, **171**, 204—209).—In adrenaline glycosuria there is no increase in the excretion of dysoxidisable carbon compared with that of nitrogen, such as occurs in diabetes and many cases of phloridzin glycosuria.

E. C. SMITH.

Changes in the C : N quotient in alkaline urine containing sugar as a result of decomposition. H. WADA (Biochem. Z., 1926, **171**, 210—216).—On keeping alkaline urine containing sugar for 24 hrs. at the ordinary temperature, the sugar is partly converted into non-reducing substances, thus raising the ratio of dysoxidisable carbon to nitrogen. Acid urine remains unchanged. This error can be avoided by immediate freezing of the urine. E. C. SMITH.

Lipolytic power and the cholesterol content of the blood-serum of luetics. H. VON WEISS and M. DÖRLE (Biochem. Z., 1926, **171**, 225—230).—Of 23 seronegative cases of lues, 21 cases showed a diminution in, or total absence of, lipolytic activity, and 18 an increased cholesterol content of the serum. Of 56 seropositive cases, 53 cases showed a diminution in, or total absence of, lipolytic activity, and 42 cases increased serum-cholesterol. The decrease in lipolytic power is therefore more constant and more pronounced than the increase in cholesterol.

E. C. SMITH.

Higher hydrolytic products of proteins in the blood. Residual nitrogen. H. STRAUSS (Vox Medica, 1925, **5**, 295—305, 359—368, 413—418; from Chem. Zentr., 1926, I, 428).—The amino-nitrogen in blood varies from 7 to 11 mg. %. Normal blood does not contain higher hydrolytic products of proteins. In kidney disease with hypertension and puerperal eclampsia, peptones occur in the blood in relationship with the blood pressure. Higher hydrolytic products of proteins do not occur in the blood in essential hypertonia or in renal disease without increase in blood pressure. The results obtained agree with the biological effect of sera on blood pressure. G. W. ROBINSON.

Determination of sodium thiosulphate in urine with reference to kidney function. S. A. HOLBØLL (Klin. Woch., 1925, **4**, 1636—1640; from Chem. Zentr., 1926, I, 453).—Nijiri's method (Wiener klin. Woch., 1922, **35**, 582) for the determination of thiosulphate in urine is only applicable, when the titration is made in acid reaction, if the animal charcoal used does not adsorb thiosulphate and if the urine is fresh and free from pathological constituents, including *Bacillus coli* and leucocytes. The thiosulphate test is not specific for renal function, since the amount excreted depends, not only on the activity of the kidneys, but also on oxidation in the organism, which is greater in individuals with higher basal metabolism. G. W. ROBINSON.

Tetany. P. DRUCKER and F. FABER (J. Biol. Chem., 1926, **68**, 57—68).—The hypocalcæmia observed during tetany in children is not due to alkalinity of the blood, since neither the p_H nor the hydrogen carbonate shows significant variations from the normal. During tetany, whether or not ammonium chloride is being administered, the concentration of ionised calcium as calculated from the equation of Rona and Takahashi (A., 1913, i, 544) may be greater than the concentration of total calcium actually observed; this indicates that the blood, under these conditions, is not saturated with calcium and that the above-mentioned equation is not applicable. Administration of calcium chloride causes a greater increase in the calcium of the blood than either ammonium chloride or calcium lactate, since it promotes acidosis at the same time that it acts as a source of supply of calcium. Irradiation of tetanic patients with ultra-violet light raises the calcium of the blood to the normal level; moreover, after such treatment the calcium-ion concentration, calculated by the above equation, is normal, so that it is assumed that the blood has become saturated with calcium. C. R. HARINGTON.

Excretion of intravenously injected calcium. J. DADLEZ (Biochem. Z., 1926, **171**, 146—155).—Calcium injected intravenously as the chloride is excreted in the urine to the extent of about 50% in 3 hrs. by normal rabbits and both normal and tuberculous men, and is completely excreted in the urine and fæces in 3 days. It is impossible to bring about the retention of calcium in tuberculous patients even by a series of injections at short intervals.

E. C. SMITH.

Respiration and carbohydrate exchange of animal tissues. I. Formation of lactic acid in, and its disappearance from, animal tissues. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1926, **171**, 381—402).—Methods are described for the manometric measurement of the consumption of lactic acid by tissues of warm-blooded animals, and for the determination of carbohydrate in a few mg. of sliced tissue. Addition of lactate to Ringer solution containing starved rat's liver causes an increase in respiration of 50—100%, together with a disappearance of lactic acid, which, if withdrawn by oxidation, would correspond with about half the total respiration. In the simultaneous presence of sugar and sodium lactate, " aërobic glycolysis " is inhibited. The observed greatly increased respiration of liver, when placed in serum, together with the reduced R.Q., may be explained in part by the action of the lactic acid in the serum. In the kidney, by means of lactate, the respiration increases, compared with that of Ringer solution containing sugar, by about 30—40%, and disappearance of lactic acid is also accelerated. On the other hand, respiration of the grey matter of rat's brain is not generally more strongly increased than by sugar. Addition of lactic acid causes increased " aërobic " and decreased " anaërobic " glycolysis. Attack on sugar by smooth muscle differs from that of striated muscle, but corresponds with that of the other tissues. With smooth muscle dextrose is preferentially, glycogen and starch faintly,

and lævulose still less attacked, whereas with skeletal muscle the utilisation of glycogen exceeds that of both dextrose and lævulose, which themselves are attacked about equally. Glyceraldehyde and dihydroxyacetone form less lactic acid than dextrose in all the tissues tested, and di- and tri-hexosan, the substances forming glycogen and amylose, which are chiefly converted into lactic acid by muscle extract, are inactive with glycolysing tissues.

P. W. CLUTTERBUCK.

Respiration and carbohydrate exchange of animal tissue. II. Respiration and carbohydrate exchange in the liver and muscle of warm-blooded animals. R. TAKANE (Biochem. Z., 1926, **171**, 403—420).—When the diaphragm of a starved rat is allowed to respire for several hours in Ringer's solution, the disappearance of carbohydrate accounts for only half the oxygen used, whilst lactic acid disappearance accounts for only 15% of the respiration. The rest of the oxidation must involve protein and fat. In presence of lactate, lactic acid disappeared, but carbohydrate utilisation was not greatly affected. During respiration of the diaphragm in serum, carbohydrate utilisation increased, but the lactic acid decrease was small in proportion. If the concentration of lactic acid in serum is increased, carbohydrate utilisation decreases, and removal of sugar by dialysis may result in carbohydrate synthesis. The R.Q., the total respiration, and the carbohydrate utilisation increase in serum on addition of insulin, the disappearance of carbohydrate corresponding with the increased oxygen utilisation. In slices of liver of starved rats, lactic acid was built up into carbohydrate with increased total respiration, whereas without lactate, carbohydrate utilisation occurred corresponding with 50% or more of the oxygen utilisation. In serum, similar behaviour is obtained. Without addition of lactate to serum, sugar utilisation amounted to 50—100% of the oxidation. Increase of lactate generally caused synthesis of carbohydrate.

P. W. CLUTTERBUCK.

Respiration and carbohydrate exchange of animal tissue. III. Difference of *d*- and *l*-lactic acids in regard to respiration and carbohydrate synthesis in the organism. O. MEYERHOF and K. LOHMANN (Biochem. Z., 1926, **171**, 421—435).—*d*-Lactic acid is utilised very readily by the tissues of warm-blooded animals, *l*-lactic acid scarcely at all. This difference is much less marked in the case of frog's muscle and is very small in the case of yeast.

P. W. CLUTTERBUCK.

Biochemical behaviour of glutose. E. M. BENEDICT, H. D. DAKIN, and R. WEST (J. Biol. Chem., 1926, **68**, 1—14).—Glutose (cf. Lobry de Bruyn and van Ekenstein, A., 1898, i, 227) was prepared by heating invert-sugar with calcium hydroxide and removing fermentable carbohydrates from the resulting solution by means of yeast. For the quantitative investigation of a solution (*e.g.*, urine) containing both dextrose and glutose, the former was first determined polarimetrically and then removed by yeast fermentation; the glutose was then determined by heating with excess of Fehling's solution and weighing the cuprous oxide formed, assuming the reducing power of glutose to be one half of that of dextrose. When administered to normal persons in doses of about 40 g., diarrhœa was produced, and the glutose was, for the most part, excreted unchanged; no effect on the respiratory quotient was observed. In diabetic patients, glutose was mostly excreted unchanged, the rate of excretion of dextrose not being affected; phloridzinised dogs excreted glutose entirely unchanged. No constant results were observed after administration of glutose to patients with ketosis. The symptoms of insulin shock were not relieved by glutose.

On warming with phenylhydrazine and sodium carbonate, glutose yielded methylglyoxalbisphenylhydrazone; with zinc ammonium hydroxide it gave methyliminazole; on warming for 3 days at 60° with 5% sodium hydroxide, it gave about 30% of *dl*-lactic acid, 10% of unidentified hydroxy-acids, traces of volatile acids, succinic acid, and of lactones, but no saccharic acid.

C. R. HARINGTON.

Carbohydrate nutrition of the cells and changes in the nucleus and plastids. A. MAIGE (Cellule, 1925, **35**, 325—340; from Chem. Zentr., 1926, I, 412).—In experiments with bean embryos from which starch had been removed, sucrose, maltose, lactose, dextrose, lævulose, galactose, mannose, and glycerol were found to act as nutrients. Mannitol was not utilised. The nuclei of starved cells increase on being transferred to sugar solutions. No increase takes place in mannitol or glycerol solutions.

G. W. ROBINSON.

Does addition of sodium chloride increase the value of a maize diet for growing animals? H. H. MITCHELL and G. G. CARMAN (J. Biol. Chem., 1926, **68**, 165—181).—Addition of 1% of sodium chloride to a basal diet consisting of 86% of maize meal, 10% of caseinogen, 2% of cod-liver oil, and 1% of calcium carbonate caused a definite increase in the rate of growth of young rats and chickens. The addition of sodium chloride was also followed by increased retention of both sodium and chlorine; maize appears to be more deficient in sodium than in chlorine.

C. R. HARINGTON.

Biological value of nitrogen of mixtures of white flour and animal foods. H. H. MITCHELL and G. G. CARMAN (J. Biol. Chem., 1926, **68**, 183—215).—In experiments on young rats the following figures were obtained for the biological values (calculated as percentage of the total food nitrogen which is retained) of various foodstuffs: white flour 52, whole egg 94, egg-albumin 83, milk 85, veal 62, and beef 69. The biological value of mixtures of the above foods is greater than that calculated from their individual values; this effect is probably due to the supplementing by one protein of the particular amino-acid, the deficiency of which limits the biological value of the other protein. The rats used in these experiments excreted 20—30 mg. of creatinine per kg. body-weight per day.

C. R. HARINGTON.

Alleged interchangeability of arginine and histidine in metabolism. W. C. ROSE and G. J. COX (J. Biol. Chem., 1926, **68**, 217—223).—Further data are presented in confirmation of the authors'

previous conclusion (A., 1924, i, 1370) that arginine cannot replace histidine in metabolism. The failure of Stewart (this vol., 198) to reach a definite conclusion on this point is ascribed to the paucity of his experimental data. C. R. HARINGTON.

Minimum endogenous nitrogen metabolism. M. SMITH (J. Biol. Chem., 1926, **68**, 15—31).—By feeding a normal subject for 24 days on an approximately nitrogen-free diet which was in excess of his energy requirements, the daily excretion of nitrogen was reduced to 0·0242 g. per kg. body-weight; no ill effects were observed, although the nitrogen balance was negative throughout the experiment. The total exogenous (urea+ammonia) nitrogen excretion was greater than the intake of nitrogen by an amount approximately equal to one third of the creatinine nitrogen; it is suggested that this difference may be due to the loss of one nitrogen atom from arginine in its conversion into creatinine.

C. R. HARINGTON.

Influence of muscle work on metabolism in varying conditions of diet. E. P. CATHCART and W. A. BURNETT (Proc. Roy. Soc., 1926, **B**, **99**, 405—426).—Muscular work causes a small rise in the output of nitrogen and sulphur and small changes in urinary nitrogen distribution. Definite differences in the oxygen demand during work on meat-containing and meat-free diets were obtained; on an exclusively carbohydrate diet the oxygen demand appears to be slightly lowered. H. J. CHANNON.

Ultra-violet radiation and metabolism with a new method of determining metabolism. J. A. CAMPBELL (Proc. Roy. Soc., 1926, **B**, **99**, 451—461).—Neither radiation by the total rays from the mercury-vapour lamp (223—770 μμ) nor by groups of its rays (290—436, 400—770, 400—436 μμ) has any effect on the metabolism of men, rats, and mice.

H. J. CHANNON.

Activation of starfish eggs by acid. R. S. LILLIE (J. Gen. Physiol., 1926, **8**, 339—367).—Exposure of unfertilised starfish eggs for a suitable time to dilute solutions of weak acids in isotonic balanced salt solutions causes complete activation. For each acid the rate of activation (reciprocal of optimum exposure) varies with the temperature and concentration; for a given temperature it is proportional to concentration within a considerable range. Solutions (of different acids) which activate at the same rate have approximately equal C_H, a result which seems to show that the rate of activation is determined by the C_H at the site of activation within the egg. C. P. STEWART.

Pharmacology of changes of concentration. IV. Action of anions. L. JENDRASSIK and L. ANTAL (Biochem. Z., 1926, **171**, 296—306).—Addition or increase of the concentration of the sodium salts yielding bromide, iodide, sulphate, nitrite, nitrate, thiocyanate, fluoride, citrate, oxalate, hydrogen carbonate, carbonate, or phosphate causes temporary stimulation of the isolated rabbit's small intestine, and decrease of their concentration causes temporary inhibition. Sodium chloride is best replaceable by nitrite or nitrate. With 50—100% substitution of sodium chloride in Tyrode solution by bromide, iodide, or sulphate, the spontaneous movement of the intestine disappears, fluoride and calcium-precipitating salts having the same action in much smaller concentration. Neither the change in the concentration of sodium or chlorine ions, nor the decrease of calcium ions is sufficient to explain the action of the salts, and a specific anion effect is postulated (cf. this vol., 91). P. W. CLUTTERBUCK.

Effect of iodides on the nitrogen partition. G. P. GRABFIELD and A. M. PRENTISS (J. Pharm. Exp. Ther., 1926, **27**, 231—234).—Administration of iodides to normal human subjects causes no change in the nitrogen partition of blood or urine.

C. P. STEWART.

Preparation and chemical composition of the active substances of *Digitalis* leaves, their pharmacological and therapeutic properties. M. CLOETTA (Arch. exp. Path. Pharm., 1926, **112**, 261—342; cf. *ibid.*, 1920, **88**, 113).—Three active substances are present in the leaves of *Digitalis*, digitoxin, $C_{44}H_{70}O_{14}$, gitalin, $C_{17}H_{28}O_6$, m. p. 245°, optically inactive, and *bigitalin*, $C_{40}H_{64}O_{14}$, m. p. 282°, optically inactive. Bigitalin dissolved in 60% alcohol is hydrolysed by hydrochloric acid, yielding 1 mol. of bigitaligenin, $C_{22}H_{34}O_5$, m. p. 232°, $[\alpha]_D$ +33·62° (in alcohol) (*monoacetyl* derivative, m. p. 170°; *diacetyl* derivative, m. p. 240°; *dibenzoyl* derivative, m. p. 278°), and 3 mols. of digitoxose, $C_6H_{12}O_4$, m. p. 110°. Further, a small quantity of an oily substance, apparently a methyl- or ethyl-glucoside, may also be isolated. When heated in a high vacuum, bigitalin yields an anhydro-sugar, $C_6H_{10}O_3$, m. p. 116°, identical with that previously obtained from digitoxin and apparently anhydrodigitoxose. Bigitalin yields a *hexa-acetyl* derivative, $C_{52}H_{76}O_{20}$, m. p. 134°, and a *hexabenzoyl* derivative, m. p. 155°. By the action of concentrated hydrochloric acid, bigitaligenin is converted into *dianhydrobigitaligenin*, $C_{22}H_{30}O_3$, m. p. 211°, $[\alpha]_D^{20}$ +576° (*acetyl* derivative, m. p. 213°). Reduction of bigitaligenin leads to the formation of *dihydrobigitaligenin*, m. p. 212°, $[\alpha]_D^{20}$ −10·3°, and *tetrahydrobigitaligenin*, m. p. 246°, $[\alpha]_D^{20}$ −24·34°. Similarly, dianhydrobigitaligenin forms a *tetrahydro*-derivative, m. p. 181°. Gitalin (*diacetyl* derivative, m. p. 127°) when hydrolysed by dilute hydrochloric acid yields 1 mol. of gitaligenin, $C_{11}H_{18}O_3$, m. p. 222°, $[\alpha]_D^{22}$ +31·23°, and 1 mol. of digitoxose. When gitaligenin is treated with concentrated hydrochloric acid a simple anhydride is not formed, but further condensation occurs so as to yield dianhydrobigitaligenin. Similarly, when gitaligenin is acetylated under conditions which cause the removal of water, diacetylbigitaligenin is obtained, and benzoylation or reduction of gitaligenin leads to the formation of dibenzoylbigitaligenin or tetrahydrobigitaligenin, respectively. It appears that gitaligenin exists in *Digitalis* leaves, as does also the oily substance, apparently a methyl- or ethyl-glucoside. In addition, a *compound* of probable formula $C_{24}H_{40}O_4$, m. p. 279°, $[\alpha]_D^{20}$ −60·50°, and another *substance*, m. p. 238°, $[\alpha]_D^{20}$ −30·65°, have also been isolated. Pharmacologically gitalin and bigitalin are similar to digitoxin, but are less active. The pharmacological actions of many

of the compounds mentioned above are discussed in considerable detail from a theoretical and practical point of view. W. O. KERMACK.

Nephropathic action of dicarboxylic acids and their derivatives. V. Alkyl-, hydroxy-, and keto-acids. R. C. CORLEY and W. C. ROSE (J. Pharm. Exp. Ther., 1926, **27**, 165—180).—Glutaric acid has a marked toxic action on the kidney, but neither its isomerides dimethylmalonic, ethylmalonic, and pyrotartaric acids, nor methylmalonic acid, nor the α-hydroxy- and keto-derivatives of glutaric acid are toxic. H. J. CHANNON.

Ethyl*iso*amylbarbituric acid (amytal); its use as an intravenous anæsthetic. I. H. PAGE and P. CORYLLOS (J. Pharm. Exp. Ther., 1926, **27**, 189—200).—Methods are described for preparing solutions, suitable for intravenous injection, of the sodium salt of ethyl*iso*amylbarbituric acid. Given intravenously (dosage 45—60 mg. for dogs) it is a useful anæsthetic for animal experimentation; the blood-pressure fall is not great, and recovery is rapid, whilst the circulation and respiration are well maintained. Attention is directed to ethylene glycol as a useful solvent in physiological experimentation. C. P. STEWART.

Action of *o*-, *m*-, and *p*-chlorophenol. T. KURODA (Arch. exp. Path. Pharm., 1926, **112**, 60—64).—Tested on *Bacillus coli*, *m*-chlorophenol showed the strongest antiseptic action; *p*-chlorophenol was weaker, and *o*-chlorophenol the weakest. On *Staphylococcus aureus*, the actions of the *p*- and *m*-compounds were roughly equal, both being stronger than the *o*-compound. In frogs, the lethal doses were 40, 25, 15 mg. per 100 g. of the *o*-, *m*-, and *p*-compound, respectively, and in rabbits, 120, 65, 65 mg. per kg. C. P. STEWART.

Antiseptic properties of crotonaldehyde. A. BERTHELOT and G. AMOUREUX (Bull. Soc. Chim. biol., 1926, **8**, 209—210).—Crotonaldehyde is even less active than acraldehyde. It prevents all growth of *Bacillus coli* only when present to the extent of 5%; of *B. subtilis* and of *Staphylococcus aureus* in 4% solution. C. P. STEWART.

Acute aniline poisoning. A. G. YOUNG, C. W. MUEHLBERGER, and W. J. MEEK (J. Pharm. Exp. Ther., 1926, **27**, 101—123).—In acute aniline poisoning death is due to heart failure; aniline does not give rise to the formation of methæmoglobin. H. J. CHANNON.

Hæmatological studies of aniline poisoning. A. G. YOUNG (J. Pharm. Exp. Ther., 1926, **27**, 125—131).—There is a relative increase in erythrocytes, hæmoglobin, and oxygen capacity, with a very low blood pressure in acute aniline poisoning; chronic poisoning causes anæmia. The brown colour of the blood and urine is due to the presence of *p*-aminophenol. H. J. CHANNON.

Acetanilide poisoning. A. G. YOUNG and J. A. WILSON (J. Pharm. Exp. Ther., 1926, **27**, 133—147).—The action of acetanilide on the heart, blood, and respiration is similar to that of aniline; it forms *p*-aminophenol in the blood and urine, and does not give rise to methæmoglobin. H. J. CHANNON.

Glycogen content of the liver and muscles in cases of arsenic poisoning. C. PADERI (Arch. Farm. sper. Sci. aff., 1926, **41**, 47—56).—The results of experiments on rabbits show that poisoning by means of arsenic is accompanied by increase in the sugar content of the blood at the expense of the glycogen of the liver. A portion of the glycogen which disappears does not, however, undergo this change and may constitute the source of the lactic acid which appears in appreciable proportion in the blood in cases of arsenic poisoning. The glycogen of the muscles is more resistant than that of the liver under the above conditions. T. H. POPE.

Effect of homologous alcohols on sugar formation in the frog's liver. III. E. J. LESSER (Biochem. Z., 1926, **171**, 83—88).—Perfusion of the livers of winter frogs with Barkan, Broemser, and Hahn's solution (*ibid.*, 1921, **119**, 116) containing propyl alcohol, results in a 2- to 6-fold increase in the production of sugar, which returns to normal after removal of the propyl alcohol. E. C. SMITH.

Non-existence of certain enzymes. S. KOSTYTSCHEV (Z. physiol. Chem., 1926, **154**, 262—275).—A critical discussion, bringing forward reasons for doubting the existence of various enzymes which have been described in the literature. C. R. HARINGTON.

Specificity of enzymes. M. BRIDEL (Bull. Soc. Chim. biol., 1926, **8**, 170—174; and J. Pharm. Chim., 1926, [viii], **3**, 401—406).—Since rhamnodiastase hydrolyses the primeverosides rapidly and β-glucosides slowly, whilst the reverse is true of emulsin, and since similar differences in the rate of hydrolysis are found when, *e.g.*, emulsin acts on different β-glucosides such as salicoside (salicin) and arbutoside (arbutin), the author concludes that it is unnecessary to postulate a specific primeverosidase, and that the primeverosides are β-glucosides, the dextrose and xylose of primeverose being joined through the reducing group of the latter and a hydroxyl group of the former. C. P. STEWART.

Applicability of law of mass action to action of enzymes. S. G. HEDIN (Z. physiol. Chem., 1926, **154**, 252—261).—A theoretical discussion in confirmation of the author's previous argument (A., 1925, i, 1212) that the relationship between the concentrations of enzyme, substrate, and the enzyme–substrate complex cannot be expressed by an equation according to the law of mass action; further, arguments based on the results of previous workers are advanced to prove that the concentration of enzyme–substrate complex may be of the order of 0·01—0·03*N*, and that therefore the modified mass law equation proposed by Josephson (*ibid.*, i, 1359), in which this quantity is treated as negligible, cannot be accepted. C. R. HARINGTON.

Catalase and its relationship to biological oxidations. Liver catalase. II. S. HENNICHS (Biochem. Z., 1926, **171**, 314—371).—The "activity" of catalase (see A., 1924, i, 697) was determined with

smaller concentrations of substrate (< 0·015*N*-hydrogen peroxide). A direct oxidative destruction of the enzyme was established, but no proportionality between the number of molecules of hydrogen peroxide decomposed and the loss of activity of the enzymes could be ascertained. An attempt was made to prepare from horse-liver the pure enzyme by means of Willstätter's method, the p_H of adsorption and elution being studied, with kaolin and alumina as adsorption media. A preparation was obtained of *C. F.* 20,000—25,000, the activity of which was 300—400 times that of the liver substance, the ash content varying between 11·3 and 12·8%, the iron content between 3·3 and 4·1%. The affinity constant of the system catalase–substrate is $K_M = 22$, *i.e.*, of the same order of magnitude as with other enzymes. The dependence of heat inactivation on time supports the view that the enzyme is composed of a number of enzyme homologues of varying stability. The inactivation constant K_c lies between 0·0534 and 0·0020. Activation of liver catalase by means of protoplasmic poisons, *e.g.*, toluene and alcohol, gives completely parallel results with those of Euler working with yeast- and blood-catalase (A., 1919, i 425, 614; 1920, i, 580), and is shown to be dependent on the presence of cells. Determination of the iron content in catalase of different degrees of purity did not indicate any relationship between the iron content and enzymic activity. The activity of the purest catalase preparations, calculated on the iron content (c.mm.O_2/mg.Fe/hr.), lies between 10^7 and 10^8. The behaviour of highly active catalase preparations with hydrogen cyanide does not support Warburg's assumption that cyanide acts specifically on the iron content. P. W. Clutterbuck.

Methods for measuring rate of hydrolysis of starch and dextrin by taka-diastase. Effect of p_H on starch-liquefying power of taka-diastase. Effect of p_H on dextrin-liquefying power of taka-diastase. H. L. Maslow and W. C. Davison (J. Biol. Chem., 1926, **68**, 75—81, 83—93, 95—99).—The course of hydrolysis of starch by taka-diastase was observed polarimetrically, iodometrically, by measuring the copper-reducing power, and by measuring the viscosity; all methods gave similar curves, and the last-mentioned is recommended as being the simplest. In an unbuffered solution, taka-diastase can hydrolyse starch over the range p_H 2—9, the optimum being at p_H 3; in presence of a 0·5*N*-concentration of "universal buffer" the lower limit is p_H 3, and the optimum p_H 4; outside these limits of p_H, in both cases, the enzyme is irreversibly inactivated. The dextrin-liquefying enzyme of taka-diastase is active over the range p_H 2—9, the optimum being at p_H 4, in an unbuffered solution.

C. R. Harington.

Enzymes and light. IX. Diastase. IV. L. Pincussen (Biochem. Z., 1926, **171**, 1—6; cf. A., 1923, i, 405),—Diastase which has been rendered almost inactive by exposure to ultra-violet light is partly reactivated by the addition of a small quantity of non-irradiated diastase. This effect is brought about by the colloidal accompanying substances.

E. C. Smith.

Enzyme action. XXXIV. Actions of esterases at different temperatures. H. M. Noyes, I. Lorberblatt, and K. G. Falk (J. Biol. Chem., 1926, **68**, 135—150).—The effect of temperature was observed on the rate of hydrolysis of various esters by esterases extracted from the tissues and eggs of trout and eels and from castor-oil beans. Considerable variations were found, according to the nature of the substrate, the age of the fish, and the length of the experiment, but in certain cases (especially with phenyl acetate as substrate) the rate of hydrolysis was definitely greater at 16—18° than at 37°; the results indicate that the rate of hydrolysis is determined by the balance between the increasing rate of action and increasing rate of inactivation of the enzyme which accompanies rise in temperature. The differences observed between the effects of temperature on the rates of hydrolysis of different esters by the same enzyme preparation, suggested the presence of more than one esterase in these preparations. C. R. Harington.

Enzyme action. XXXV. Lipase actions of extracts of tissues of rabbits at different ages. H. M. Noyes, K. G. Falk, and E. J. Baumann (J. Gen. Physiol., 1926, **9**, 651—675).—The lipase activity of extracts of particular tissues, including kidney, liver, lung, skin, leg-muscle, heart-muscle, brain, spleen, stomach, and small intestine from rabbits of various ages, have been measured, using as substrates glyceryl triacetate, methyl butyrate, phenyl, benzyl, methyl, ethyl, and *iso*butyl acetates, methyl and ethyl butyrates, methyl and ethyl benzoate. The results indicate, in certain of the tissues, a tendency with advanced age to revert to a more embryonic type (cf. A., 1925, i, 1360).

W. O. Kermack.

Phosphatase and the preparation of acid esters of pyrophosphoric acid. C. Neuberg and J. Wagner (Biochem. Z., 1926, **171**, 485—500).—Aromatic and aliphatic monoesters of phosphoric acid are hydrolysed by both animal and plant phosphatase. The diphenyl ester is also attacked, but the triphenyl derivative has not as yet been hydrolysed by phosphatase of fungi. *Dipotassium diphenyl pyrophosphate* was prepared by the action of potassium hydroxide on the reaction product of phenol and phosphorus oxychloride in pyridine solution; it can be heated to 300° without decomposition and is hydrolysed rapidly and almost quantitatively by both animal and vegetable phosphatase.

P. W. Clutterbuck.

Mode of action of proteolytic enzymes. P. Girard (Bull. Soc. Chim. biol., 1926, **8**, 30—34).—Comments on the paper of Hugounenq and Loiseleur (A., 1925, i, 1507) on the same subject, and a claim for priority (Bull. Soc. Chim. biol., 1925, **7**, 75—96).

C. P. Stewart.

Proteolytic enzymes of the placenta. B. Arinstein (Biochem. Z., 1926, **171**, 15—21).—No evidence could be obtained for or against the existence of a specific trypsin in the placenta. E. C. Smith.

Inactivation of pepsin by heat. L. Kraus (Biochem. Z., 1926, **171**, 307—313).—Since pepsin

after inactivation shows an increase in dry weight, in hydrogen content, and in hydroxyl (benzoylatable) groups, the assumption that absorption of water occurs during inactivation appears justified.

P. W. CLUTTERBUCK.

Is cyanic acid an intermediate product of the action of urease on carbamide? J. B. SUMNER (J. Biol. Chem., 1926, **68**, 101—105).—Using urease prepared from the jack bean, the author has been unable to repeat the experiments of Fearon (A., 1924, i, 351) indicating the formation of cyanic acid during the action of urease on carbamide; he further regards the theory of Fearon as being *a priori* improbable owing to the stability of the cyanates at the reaction which is the optimum for the action of urease.

C. R. HARINGTON.

Preparation of yeast glycogen. T. YOKOYAMA (Beitr. Physiol., 1925, **3**, 95—110; from Chem. Zentr., 1926, I, 141—142).—Dry yeast is digested with 50% potassium hydroxide solution at 100° for 30 hrs. The solution separated by centrifuging is precipitated with 96% alcohol and the precipitate is washed with 60% alcohol until free from alkali. It is then dissolved in water and freed from gum by precipitation with Fehling's solution (containing no sodium salts). Proteins are removed by means of Brücke's reagent and the glycogen is precipitated by 60% alcohol. It is further purified by dissolving in hydrochloric acid and reprecipitating with alcohol. The glycogen has α_D +192°.

G. W. ROBINSON.

Synthesis of coproporphyrin by yeast. IV. H. FISCHER and H. HILMER (Z. physiol. Chem., 1926, **153**, 167—214).—Ordinary yeast contains hæmin, Kammerer's porphyrin, and coproporphyrin. It has been confirmed that a pure strain of such yeast, grown in a porphyrin-free medium to which iron salts have been added, will produce a yeast which gives a hæmochromogen spectrum and contains relatively large amounts of coproporphyrin. Hæmin is probably directly synthesised by yeast. From experiment on *Saccharomyces anamensis* it is thought that coproporphyrin is also directly synthesised. In artificial media this organism produces coproporphyrin almost exclusively, although if it is grown on beer wort (free from porphyrins) hæmochromogen is readily observed. Cytochrome is a possible precursor of coproporphyrin in yeast. Coproporphyrin is greatly increased after autolysis.

The effect of diet on the excretion of porphyrins has been followed. The blood pigments are apparently not the cause of the increase of porphyrin when flesh food is added to the diet, since serum alone brings about an increase.

H. D. KAY.

Porphyratin from yeast and seeds. Does yeast contain blood pigment? O. SCHUMM (Z. physiol. Chem., 1926, **154**, 171—197, 314—317).—From yeast, oats, wheat, rye, malt, almonds, and cacao-beans there was obtained, by treatment with acetic acid and chloroform or acetic acid and ether, the same porphyratin (the cytochrome of Keilin, A., 1925, i, 1112); this substance contained iron, gave the benzidine reaction, and had an absorption spectrum closely similar to that of hæmatin; on treatment with hydrazine hydrate and acetic acid, it gave a porphyrin which corresponded, in its spectroscopic properties, with the α-porphyroidin previously described (*ibid.*, 88). Careful experiments with fresh yeast failed to reveal the presence of perceptible amounts of blood pigment; the above-described porphyratin originated from the yeast itself and not from any contamination by insects (cf. Fischer and Hilger, A., 1924, i, 1131; Fischer and Fink, *ibid.*, 1925, i, 105).

C. R. HARINGTON.

Formation of acetaldehyde and acetylmethylcarbinol during the fermentation and respiration of yeast. L. ELION (Biochem. Z., 1926, **171**, 40—44).—During the fermentation of sugar by yeast, acetaldehyde occurs both as a primary product and as a secondary product by oxidation of ethyl alcohol. Acetylmethylcarbinol is formed by aëration of a suspension of yeast in aqueous ethyl alcohol or acetaldehyde, its formation during the fermentation of sugar being therefore secondary to the fermentation process.

E. C. SMITH.

Behaviour of *p*-xyloquinone towards yeast. C. NEUBERG and E. SIMON (Biochem. Z., 1926, **171**, 256—260).—After the addition of *p*-xyloquinone, which is known to arise very readily from diacetyl by condensation, to sucrose undergoing fermentation by yeast, neither diacetyl nor acetylmethylcarbinol is found, but the yield of acetaldehyde is increased, arising from alcohol by oxidation with simultaneous reduction of the *p*-xyloquinone to *p*-xyloquinol.

E. C. SMITH.

Action of drugs and irradiation on yeast. I. Basis of the Arndt-Schulz law. H. ZELLER (Biochem. Z., 1926, **171**, 45—75).—The results obtained by Schulz (A., 1889, 181) are criticised. Of the substances classified by him as cell-stimulants, only sodium chloride, potassium iodide, and phosphorus are truly stimulant, the effect being increased in the presence of glycogen. Barium chloride and potassium dichromate are poisonous. The remaining substances, of the type of mercuric chloride and copper sulphate, are inhibitory. The greater the glycogen content of the cell the greater is the concentration of the poison that can be withstood and the more rapidly the cell recovers. The cell contains no glycogen at the beginning and at the end of fermentation. Administration of glycogen to the yeast causes an increase in the output of carbon dioxide. Irradiation with *X*-rays causes increased output, but sunlight, after temporary slight stimulation, inhibits.

E. C. SMITH.

Nitrogenous equilibrium in the yeast cell and augmentation of the invertase action. H. VON EULER, K. JOSEPHSON, and H. FINK (Z. physiol. Chem., 1926, **154**, 310—313).—Yeast, of which the activity with respect to invertase had been increased by preliminary treatment with fermentable sugar (cf. Willstätter and others, A., 1925, i, 1214), showed a slight decrease in the total nitrogen and no significant change in the amino-nitrogen; there was therefore no evidence of a synthesis of peptides such as might be expected if the process of activation consisted of an actual formation of fresh enzyme.

C. R. HARINGTON.

Yeast amylase and the fermentation of polysaccharides. A. GOTTSCHALK (Z. physiol. Chem., 1926, **153**, 215—224).—The substrate during the autofermentation of yeast is mainly glycogen. Erythrocellulose of yeast is fermentable to a slight extent, " yeast gum " is hardly attacked at all. The labile modification of dextrose produced during the enzymic hydrolysis of glycogen is esterified by acetone yeast in presence of acid potassium phosphate. The co-enzyme of zymase is active in the esterification process, not in the process of activation of the dextrose. The wash water from acetone yeast contains only small quantities of amylase, but larger amounts of maltase. Washed acetone yeast (both bottom and top yeast) still contains, however, both amylase and maltase—it is not possible to separate the two enzymes in this way. Relative to maltase, yeast amylase is present in very limited amounts in the organism. Addition of glycogen to yeast juice from washed bottom yeast causes an increase in the amount of free sugar, which is much less than that produced by an addition of the corresponding amount of maltose. H. D. KAY.

Plant proteases. VI. Proteases of yeast. R. WILLSTÄTTER and W. GRASSMANN (Z. physiol. Chem., 1926, **153**, 250—282).—Yeast proteases may be separated by specific adsorption on alumina into two distinct components, a trypsin-like enzyme and one similar to erepsin. The former enzyme is more readily adsorbed than the latter. Their adsorption reactions are different from those of animal trypsin and erepsin. The tryptic component of yeast protease has an optimum p_H of 5—6. It hydrolyses gelatin and denatured albumin. It does not attack unchanged egg-albumin or dipeptides. The erepsin, on the other hand, decomposes dipeptides, but does not attack gelatin. The two proteases differ in stability. On keeping a yeast autolysate, the erepsin is decomposed, whilst the trypsin remains unchanged. H. D. KAY.

Gas formation in the upper layers of sugar-agar. E. KLIENEBERGER (Zentr. Bakt. Parasitenk., I, 1925, **96**, 181—213; from Chem. Zentr., 1926, I, 419—420).—The conditions governing the formation of gas by the action of bacteria in the upper layers of sugar-agar are discussed from the point of view of its use for the study of the fermentation of carbohydrates and the systematic classification of bacteria. G. W. ROBINSON.

Effect of thorium-*X* on ammoniacal fermentation. A. MAUBERT (Compt. rend., 1926, **182**, 1182—1185; cf. A., 1923, i, 262).—Thorium-*X* increases the formation of ammonia in urine by *Micrococcus ureæ* in doses above 0·5 γ per c.c. of liquid, the maximum effect being obtained with a dose of 1·0 γ per c.c., then falling to a constant value at higher doses. L. F. HEWITT.

Forms of lactic acid produced by pure and mixed cultures of bacteria. C. S. PEDERSON, W. H. PETERSON, and E. B. FRED (J. Biol. Chem., 1926, **68**, 151—164).—An organism which, in pure culture, produces a preponderance of one of the optical isomerides of lactic acid, may, when grown in mixed culture with an organism which does not form lactic acid, produce a preponderance of the other isomeride. In mixed cultures of lactic acid-forming organisms, the form of lactic acid produced in greatest amount is determined by the temperature, which will favour the growth of one organism more than another. Solubility curves are given for zinc *dl*-, *d*-, and *l*-lactate, from which it appears that separation of the *d*- and *l*- forms from the *dl*-form, by fractional crystallisation, is best effected at 35°. C. R. HARINGTON.

Nature of diphtheria toxin. K. G. DERNBY (J. Gen. Physiol., 1926, **8**, 311—315; cf. Biochem. Z., 1921, **123**, 245; 1922, **132**, 412; **134**, 1; 1923, **138**, 505; Compt. rend. Soc. Biol., 1921, **85**, 1177; 1923, **88**, 109; J. Path. Bact., 1921, **24**, 150).—From data previously published, the hypothesis is advanced that diphtheria toxin is, for the greater part, neither secreted by the living cells nor extracted from the dead bacilli. During the life, and after death and autolysis of the bacilli, specific proteolytic enzymes are liberated which attack the proteins both of the autolysing bacilli and the broth (or infected tissue). Some of the primary split products are the toxic substances which, by further action of the same enzymes, are rendered non-toxic. C. P. STEWART.

Biochemical decomposition of carbon monoxide. C. WEHMER (Ber., 1926, **59**, [*B*], 887—890).—Carbon monoxide is comparatively readily oxidised to carbon dioxide in the presence of air by bacteria of the soil. Under anaërobic conditions, carbon monoxide is also oxidised by a different race of bacteria; the necessary oxygen is obtained from the sulphates of the soil with consequent formation of hydrogen sulphide and iron sulphide. Anaërobic oxidation of methane or hydrogen could not be satisfactorily established. H. WREN.

Cell physiology. I. Action of the chlorides of sodium, potassium, calcium, and magnesium, on the protoplasm of *Amœba proteus*. R. CHAMBERS and P. REZNIKOFF (J. Gen. Physiol., 1926, **8**, 369—401).—By means of micro-dissection and injection, the authors have studied the effect on *Amœba proteus* of the chlorides of sodium, potassium, calcium, and magnesium, alone, in combination, and with variations of p_H. Sodium and potassium chlorides readily penetrate the amœba from the exterior and are more toxic to the exterior of the cell than to the interior. The reverse is true of calcium chloride and magnesium chloride. The toxic effects of sodium and potassium chlorides on the exterior of the cell can be antagonised by calcium chloride, and this antagonism occurs at the surface. In presence of calcium chloride, sodium chloride penetrates more slowly than when present alone. The prevention of repair of a torn membrane by toxic solutions of sodium and potassium chlorides can be antagonised by calcium chloride. Sodium chloride and hydrogen chloride are mutually antagonistic in the interior of the amœba, but no antagonism between the salts and hydrogen chloride was found on the exterior. C. P. STEWART.

Photolysis of the luminescent granules of *Eucharis multicornis*. A. R. MOORE (J. Gen. Physiol., 1926, **8**, 303—310).—The photolytic action of light on the luminescent granules of *Eucharis multicornis* conforms to the Bunsen–Roscoe law, proceeds as a first-order reaction, and is not accelerated by a rise in temperature. C. P. STEWART.

Latent period in the action of copper on respiration. S. F. COOK (J. Gen. Physiol., 1926, **9**, 631—650).—When cells of *Aspergillus niger* or of *Nitella* are immersed in a solution of copper chloride, the respiration as measured by the production of carbon dioxide remains constant for an interval ("latent period") and then rapidly falls. It is considered that the copper is activated within the cell by a reversible reaction, and the experimental curves show agreement with calculated curves, in which appropriate velocity constants have been used.
W. O. KERMACK.

Mechanism of insulin action. A. I. VIRTANEN (Biochem. Z., 1926, **171**, 76—78).—Theoretical.
E. C. SMITH.

Mechanism of insulin action. E. F. MUELLER, H. J. WIENER, and R. VON E. WIENER (Arch. Int. Med., 1926, **37**, 512—540).—A deposit of insulin in the body acts as a nerve stimulation, which increases the glycogen-forming function of the liver. The effect continues as long as the insulin deposit exists as such, and is particularly strong if the deposit is made in the skin. The nerve effect is weaker after deposition of the insulin in organs in which absorption takes place rapidly—*e.g.*, the subdermal tissues—and is lacking after intravenous administration. The hormone effect in the circulation and in the body-tissues is relative to the dose, but the neural effect of insulin is independent of the dose. Simultaneously with the beginning of absorption of insulin from the deposit into the circulation, the hormone effect is manifested, and as the deposit diminishes the nerve effect progressively decreases. C. P. STEWART.

Effect of insulin on the urinary quotient C : N in normal rabbits. H. WADA (Biochem. Z., 1926, **171**, 218—224).—The dysoxidisable carbon of the urine of normal rabbits is not affected by treatment with insulin, but in conditions in which oxidation of carbohydrate is affected, and the dysoxidisable carbon is increased, insulin brings about a return to the normal value. The urinary nitrogen may be considerably increased or decreased by insulin, hence the ratio of dysoxidisable carbon to nitrogen is correspondingly affected. E. C. SMITH.

Storage of vitamin-*A*. H. C. SHERMAN and M. L. CAMMACK (J. Biol. Chem., 1926, **68**, 69—74).—The survival period of growing rats, when placed on a diet lacking vitamin-*A*, is dependent on their previous diet, increasing with the vitamin-*A* content of the latter up to a maximum. There is, however, no quantitative relationship between the concentration of vitamin in the diet and the amount stored, and the process of storage appears to be a slow one; the maximum possible storage varies somewhat at different ages, being greatest at six months.
C. R. HARINGTON.

Accessory growth factors. VII. H. VON EULER and M. RYDBOM (Z. physiol. Chem., 1926, **153**, 283—290).—Defibrinated blood of rats, cattle, and guinea-pigs contains a factor which is capable of causing normal growth in rats on a diet defective in fat-soluble vitamins. If the blood is subjected to irradiation, its potency is slightly increased. Oxyhæmoglobin, hæmatin, and hæmatoporphyrin are not active. The relation of the potency to the cholesterol content of the blood is not yet established.

The average weight of the young at birth, in a standard breed of rats inbred for two years and fed on a standardised diet to which all the known vitamins have been added, has been found to have fallen from 20 to 10 g. If put on a diet deficient in vitamin-*A*, this "degenerate" race is found to require much more cod-liver oil per day than formerly (20—40 mg. as against 3) to maintain normal growth.
H. D. KAY.

Influence of vitamin-*A* on the absorption of a foreign fat. W. NAKAHARA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 161—166).—Vitamin-*A* (biosterin) appears to facilitate the assimilation of a foreign fat (olive oil) in the animal body.
C. P. STEWART.

Concentration of the growth-promoting principle obtained from yeast (vitamin-*B*). P. A. LEVENE and B. J. C. VAN DER HOEVEN (Science, 1925, **62**, 594; see this vol., 98).—The fraction of yeast extract prepared by Osborne and Wakeman's method is adjusted to p_H 4, and active material is precipitated from the supernatant liquid with alcohol. The solution of this material is treated with nitrous acid, yielding a substance containing C 38·2, H 6·0, N 10·3, P 7·6, S (chiefly ·SH) 1·46; amino-N, 0. The active material is extracted with silica gel. Extraction of the gel at p_H 9·5 affords a material containing 4% S, and active to the rat in daily doses of 0·00008 g. A. A. ELDRIDGE.

Surface activity and the action of vitamins. I. The vitaminoid state. II. Surface activity and vitamin content of foods. F.-V. VON HAHN (Pflüger's Archiv, 1925, **208**, 732—744; 745—760; from Chem. Zentr., 1926, I, 156).—I. Vitamin activity, particularly in the cases of the vitamins-*B* and -*C*, is correlated with high surface activity. Vitamins are not chemically defined substances, and it would be better to speak of a "vitaminoid state." The action of vitamins is considered to be an activation of the membrane of the digestive tract, whereby it becomes permeable to colloids.

II. The surface activity of a number of extracts, as shown by their effect in lowering surface tension, was found to be well correlated with their vitamin contents. G. W. ROBINSON.

Molecular structure of plant fibres determined by *X*-rays. O. L. SPONSLER (J. Gen. Physiol., 1926, **9**, 677—695).—*X*-Ray analysis of the plant fibre suggests that its wall has a lattice structure in which the unit cell has the dimensions 6·10×5·40×

10·30 Å. and contains two $C_6H_{10}O_5$ groups. Four of these unit cells apparently constitute the crystallographic unit cell. The $C_6H_{10}O_5$ groups are arranged in parallel chains in which the odd-numbered groups have a different orientation from the even-numbered. The chains are spaced 6·10 Å. in one direction and 5·40 Å. in the perpendicular direction, and in these two directions also the odd-numbered chains have a different orientation from the even-numbered. The fibre as a whole is considered as being built up of a series of concentric layers of unit cells.

W. O. KERMACK.

Structure of cell-membranes and their behaviour during disintegration. J. KÖNIG (Biochem. Z., 1926, **171**, 261—276).—The cellulose, lignin, and cutin fractions of fir wood, wheat straw, bran, grass, apple and potato skins, and flax are separated, and, since the lignin and cutin always have the same structure as both the cellulose and the original membranes, it is concluded that they are not present in combination with cellulose, but merely in close structural association with it. Whereas lignin contains methyl or methoxy-groups and is oxidised readily by hydrogen peroxide and ammonia, cutin is not at all, and the hexosans and pentosans are only slightly, attacked. Cutin (from rye bran) can be hydrolysed, the physical properties and analysis of the products corresponding with a mixture of cetyl nonoate and octadecyl decoate. The solubility of the pentosans, hexosans, and lignin also varies with the kind and age of the plant, a gradual transition along with an alteration in the degree of polymerisation and condensation being assumed. A comparison of the percentage of the above constituents in young grass and in grass before and after flowering supports the view that the cell-membrane, first formed, consists of pure orthocellulose, on or in which carbohydrate anhydride complexes (pentosans, hexosans, etc.) and their methoxy-derivatives are laid, from which, by ring closure, the lignins are formed. From similar determinations, an attempt is made to explain the formation of humus from organic material of the soil.

P. W. CLUTTERBUCK.

Mechanism of the formation of lactic acid in Phanerogams. C. NEUBERG and G. GORR (Biochem. Z., 1926, **171**, 475—484).—Pea seeds, acetone-dried seeds, peas which after slight germination have been treated with mercuric chloride, aqueous extracts of ground peas, and the alcohol-ether precipitate of such aqueous extracts (in presence of toluene) can convert 1—2% solutions of methylglyoxal in the absence of air almost quantitatively into racemic lactic acid (yield 70—80%). Similar preparations from beans and lupins also can attack methyl- and phenyl-glyoxals.

P. W. CLUTTERBUCK.

Nitrogen metabolism in etiolated corn [maize] seedlings. S. L. JODIDI (J. Agric. Res., 1925, **31**, 1149—1164).—During the first eight days of germination in the absence of light, 48% of the protein present in the seed is converted into water-soluble substances by the action of pre-existing proteolytic enzymes. During the same period there is an increase in amino-acid nitrogen, a decrease in peptide nitrogen, and an increase in acid amide nitrogen and a decrease in humin nitrogen.

C. P. STEWART.

Migration of nitrogenous substances in the beech during the autumnal fading of the leaves. R. COMBES (Compt. rend., 1926, **182**, 1169—1171; cf. this vol., 647).—During the fading of the leaves in autumn, nitrogenous (and other) substances migrate from the leaves to the stems and roots, the process occupying some 2 months.

L. F. HEWITT.

Isolation of a new glucoside, polydatoside, hydrolysable by rhamnodiastase, from the fresh roots of *Polygonum cuspidatum*, Sieb. and Zucc. M. BRIDEL and C. BEGUIN (Bull. Soc. Chim. biol., 1926, **8**, 136—143).—See this vol., 440.

Mineral composition of sunflowers grown for silage. R. E. NEIDIG (J. Agric. Res., 1925, **31**, 1165—1171).—The author gives the composition of the ash of sunflowers for different systems of planting and at various stages of growth, and a comparison of the minerals removed from the soil by sunflowers and maize. Sunflowers draw more heavily than maize on certain soil elements, especially potassium and calcium.

C. P. STEWART.

Proteins of green forage plants. I. Proteins of some leguminous plants. II. Proteins of the mangold root. Comparison with proteins of mangold seed. W. L. DAVIES (J. Agric. Sci., 1926, **16**, 280—292; 293—301).—I. Proteins have been prepared from lucerne, sainfoin, vetch, broad red clover, and crimson clover, cut at the flowering stage, and the distributions of nitrogen in the preparations was investigated, using both the Hausmann and Van Slyke methods. The percentages of amide-, monoamino-, and diamino-nitrogen are closely similar in proteins from the different plants, but the content of the diamino-acids varies considerably. There is much mineral matter in the extracts from lucerne, vetch, and sainfoin, but little in those from the two clovers.

II. Three samples of protein, isolated from the mangold root by different methods, show close agreement with each other in regard to the distribution of nitrogen. Two globulins were obtained from mangold seed, differing in elementary composition, in physical properties, and in content of arginine and histidine. A small amount of an albumin was also isolated. The root and seed proteins are similar, differing mainly in the higher lysine content of the former.

C. T. GIMINGHAM.

Fatty substances of the plant growing point. E. RHODES and R. M. WOODMAN (Proc. Leeds Phil. Lit. Soc. [Sci.], 1925, **1**, [1], 27—36).—Fats have been determined at the seat of growth (root and shoot tips) and in the various parts remote from this zone (main body of root and stem) at various stages of life between germination and maturity. *Vicia faba*, L., and *Pisum sativum*, L., were chosen because they contain practically no fats as food reserves in the seed, and such fats therefore as do appear result from synthetic activity. The root growing point contains an oil which has a relatively high iodine number (133)

and appears to contain chiefly glycerides of oleic and linoleic acids together with substances of a lipin nature. Further quantities of fatty acids of the nature of hydroxy- and saturated acids are removable by subsequent saponification with alcoholic potassium hydroxide. As growth proceeds, the parts of the plant more remote from this synthetic zone are found to contain more saturated fats. Oils have been left behind by the moving growing point, have migrated to the surface, and suffered partial drying. Figures are also given for the amounts of fatty substances in root tips entirely removed from the seed and in this state caused to grow in sterile culture solutions. During such growth, a large increase is shown in the amounts of all substances soluble in fat solvents. The fatty materials released by subsequent saponification also increase rapidly in amount and are of the nature of hydroxy- and relatively saturated acids.

J. S. CARTER.

Nutritive value of various layers of the wheat and corn [maize] kernel. A. KLEIN, B. HARROW, L. PINE, and C. FUNK (Amer. J. Physiol., 1926, **76**, 237—246).—Feeding tests and chemical fractionation of the proteins of various milling fractions of wheat and maize combine to show that those fractions which contain the peripheral layers possess proteins of higher biological value than those which contain the endosperm. The outer layers are richer in globulins and glutelins and poorer in gliadin (or zein). It is difficult to define the respective parts played by vitamins and proteins in the enhanced nutritive value of the peripheral layers, since there is some evidence that these two factors are interrelated.

R. K. CANNAN.

Biological value of bread protein. M. HINDHEDE (Biochem. J., 1926, **20**, 330—334).—The author maintains that the protein of bread is of full nutritional value. The reason why Martin and Robison (*ibid.*, 1922, **16**, 407) found that it was only 30—35% as efficient as animal protein is considered to be due to the fact that the duration of their experiment was not long enough and that their diet did not contain a low enough quantity of digestible nitrogen.

S. S. ZILVA.

Phosphates in vegetation experiments. M. DOMONTOVICH (Contrib. Sci. Inst. Fertilisers Leningrad, Bull., 1924, **12**, 141—175).—A review of work on the utilisation capacity of various phosphates by different plants; the reactions involved in respect of the effect of other ions on the solubility of phosphates are discussed. The following constants are derived: $[Ca^{\cdot\cdot}]^3[PO_4'']^2 = K$; $[H^{\cdot}][PO_4'']/[HPO_4''] = K_3$; $[H^{\cdot}][HPO_4'']/[H_2PO_4'] = K_2$. Assuming complete dissociation of all dissolved phosphates, the total concentration of phosphates in a saturated solution, $Z = [PO_4'''] + [HPO_4''] + [H_2PO_4'] = \sqrt{K/[Ca^{\cdot}]^3}\{1 + ([H^{\cdot}]/K_3) + [H^{\cdot}]^2/K_2K_3)\}$. The influence of the reaction on the assimilation of phosphate, the effect of calcium on the utilisation of raw phosphates, the rôle of root excretions, root absorption, and the reaction of root sap are discussed.

CHEMICAL ABSTRACTS.

Effect of leaf-roll disease in potatoes on the composition of the tuber and "mother tuber." W. MCLEAN (J. Agric. Sci., 1926, **16**, 318—324).—Tubers from plants showing the symptoms of leaf-roll disease are characterised by a lower percentage of dry matter and a higher percentage of nitrogen in the dry matter as compared with tubers from healthy plants. The contents of "mother tubers" from plants with leaf-roll are utilised by the young plants much more slowly than is the case with tubers from healthy plants.

C. T. GIMINGHAM.

Electrodialysis in biochemistry. C. DHÉRÉ (Bull. Soc. Chim. biol., 1926, **8**, 144—159).—A review, with bibliography, of the application of electrodialysis to the purification of proteins, enzymes, carbohydrates, hormones, etc.

C. P. STEWART.

Determination of the electrical conductivity of biological fluids. BRIGAUDET and G. CARPENTIER (Bull. Soc. Chim. biol., 1926, **8**, 311—313).—The current momentarily flowing through the special conductivity cell from a known source of *E.M.F.* is measured directly in a milliammeter.

R. K. CANNAN.

Complete precipitation of proteins by the hydroxides of tervalent metals. I. Use of common alum. II. Chrome and ferric alums. H. WUNSCHENDORFF (Bull. Soc. Chim. biol., 1926, **8**, 184—191, 192—198).—A colloidal solution of aluminium hydroxide effects only a partial precipitation of protein from horse serum. When, however, alum is added in sufficient quantity and aluminium hydroxide is formed *in situ* by addition of alkali, the precipitation of protein is complete. The amount of alkali added may vary within wide limits, but it is convenient to add sufficient to form a neutral solution. Chrome alum and ferric alum act similarly, but are more efficient.

C. P. STEWART.

Deproteinising by means of alum. L. C. MAILLARD and H. WUNSCHENDORFF (Bull. Soc. Chim. biol., 1926, **8**, 251—263).—Previous observations (this vol., 189 and preceding abstract) on the precipitation of proteins by the hydroxides of aluminium, chromium, and iron are now reduced to a general method for the removal of proteins from solutions. As devised for serum, the technique involves the addition to the serum of a solution of potassium alum and neutralisation with alkali to bromothymol-blue. The filtrate is colourless, approximately neutral, and almost free from aluminium. Ammonium salts, carbamide, and uric acid added to serum may be recovered quantitatively from the protein-free filtrate.

R. K. CANNAN.

Determination of the total quantity of blood. G. PETRÁNYI (Magyar Orvosi Archiv., 1925, **26**, 346—359).—Methods are described which involve determination of hæmoglobin, the percentage of carbon monoxide–hæmoglobin after inhalation of carbon monoxide, or the changes in concentration following the injection of sodium chloride or other solutions.

CHEMICAL ABSTRACTS.

Determination of calcium in blood-serum. J. W. TREVAN and H. W. BAINBRIDGE (Biochem. J., 1926, **20**, 423—426).—The calcium in the serum is

precipitated as oxalate, washed with a saturated solution of ammonium oxalate to avoid loss through the solubility of the calcium salt in water, and then converted into carbonate by heating the centrifuge tube in which it is separated and washed. The calcium carbonate is titrated with acid, the end-point being more distinct than that obtained in a permanganate titration. The determination can be carried out on 1 c.c. of serum and reasonably accurate results can be obtained with smaller quantities down to 0·1 c.c. S. S. ZILVA.

Colorimetric determination of calcium in blood. J. H. ROE and B. S. KAHN (J. Biol. Chem., 1926, **67**, 585—591).—Proteins are removed from blood-serum by means of trichloroacetic acid, the filtrate is made just alkaline to phenolphthalein, and the calcium precipitated as phosphate; the precipitate is separated on the centrifuge and the phosphate determined by a modification (cf. following abstract) of the method of Bell and Doisy. The method requires 2 c.c. of serum and the error is ±2%. C. R. HARINGTON.

Molybdic oxide colorimetric method for determination of phosphorus in blood. J. H. ROE, O. J. IRISH, and J. I. BOYD (J. Biol. Chem., 1926, **67**, 579—584).—The accuracy of the colorimetric method of Bell and Doisy (A., 1920, ii, 769) and of its subsequent modifications (Briggs, A., 1922, ii, 718) for the determination of phosphorus depends on the selection of such relative concentrations of molybdic acid and quinol as will ensure the maximum difference between the rates of reduction of the phosphomolybdic acid formed and the excess of molybdic acid present; further, it is advantageous to adjust the reaction to a point between 0·9 and 1·9*N* acidity, over which range change in reaction has no effect on colour development. In order to achieve these objects, modifications are suggested in the reagents for determination of phosphorus in blood, after incineration of the organic matter with sulphuric and nitric acids and hydrogen peroxide. C. R. HARINGTON.

Macallum's test for calcium. M. M. SAMPSON (Science, 1925, **62**, 400—401).—A criticism of the purpurin test for calcium in plant and animal cells (Grandis and Mainini, A., 1900, ii, 625; Macallum, Ergeb. Physiol., 1908, **7**, 611). The test is satisfactory if the medium from which the cells are transferred or in which they are killed is alkaline in reaction. A. A. ELDRIDGE.

Purpurin method of localising calcium. A. B MACALLUM (Science, 1925, **62**, 511; cf. preceding abstract).—The purpurin test for calcium is sometimes indecisive, since the reagent is not sensitive to calcium present in concentrations of less than 1 in 800. A. A. ELDRIDGE.

Determination of carbamide in blood. E. P. CLARK and J. B. COLLIP (J. Biol. Chem., 1926, **67**, 621—627).—Proteins are removed from the blood by the method of Folin and Wu (A., 1919, ii, 308), the filtrate is heated at 150° for 10 min. in an autoclave with dilute hydrochloric acid, and the ammonia determined in a modified form of Pregl's micro-Kjeldahl apparatus. The error of the method is less than ±2%. C. R. HARINGTON.

Determination of carbamide in blood. L. PÉCHON (Bull. Soc. Chim. biol., 1926, **8**, 314—316).—The observation of Pagel (A., 1924, ii, 575) is confirmed that successive samples of blood drawn from the same individual may show considerable differences in carbamide concentration. This fact may cause important errors in the determination of the constant of Ambard. R. K. CANNAN.

Volumetric micro-determination of phosphoric acid [in serum]. K. SAMSON (Deut. med. Woch., 1925, **51**, 1571—1572; from Chem. Zentr., 1926, I, 186).—After removal of proteins, the inorganic phosphoric acid is precipitated from hot solutions by ammonium nitrate, molybdate, and nitric acid. After washing, the precipitate is dissolved in 1 c.c. of 0·04*N*-sodium hydroxide and the solution titrated with 0·04*N*-hydrochloric acid, using phenolphthalein as indicator. J. S. CARTER.

Determination of bile salts in blood. (Correction.) I. LIFSCHÜTZ (Biochem. Z., 1926, **171**, 501—502).—A criticism of Szilárd's method (A., 1925, i, 1485). P. W. CLUTTERBUCK.

Metabolism of bile acids. I. Determination of bile acids. F. RAUE (Z. klin. Med., 1925, **102**, 79—85; from Chem. Zentr., 1926, I, 453).—The method depends on the fluorescence developed by bile salts with strong sulphuric acid. Mucin and protein are removed from duodenal juice (2 c.c.) by precipitation with ethyl alcohol. The filtrate is evaporated and the residue dissolved in strong sulphuric acid (4 c.c.) and kept for 24 hours. The fluorescence is determined, using sulphuric acid for dilution. G. W. ROBINSON.

Determination of blood-sugar. D. G. C. TERVAERT (Nederl. Tijdschr. Geneeskunde, 1925, **69**, II, 1110—1112; from Chem. Zentr., 1926, I, 184).—A consideration of the applicability of the methods in use. Factors for the determination of dextrose from the amount of copper reduced are given, which are to replace those previously quoted (A., 1922, ii, 166). Where the quantity of sugar is small, the author's method (*loc. cit.*) is untrustworthy and the quantity of blood taken should be doubled. Under certain conditions, using the Bang method of collection, the method is, however, applicable. J. S. CARTER.

Determination of blood-sugar. P. J. KRUYSSE (Pharm. Weekblad, 1926, **63**, 575—576).—A procedure is described for applying the ordinary determination of dextrose using Fehling's solution to the determination of sugar in blood. S. I. LEVY.

Determination of uric acid in blood. H. BROWN (J. Biol. Chem., 1926, **68**, 123—133).—The colorimetric method of Folin and Wu (A., 1919, ii, 438) has been modified by the use of smaller quantities of reagents and by working in the cold; it is claimed that, by this means, the turbidity, which was apt to

interfere with the previous methods, is entirely avoided. The results obtained by this method, on human blood, are similar to those obtained by the method of Folin and Wu, and are consistently lower than those yielded by the method of Benedict (A., 1922, ii, 405). C. R. HARINGTON.

Micro-determination of ions in organs and similar material. L. PINCUSSEN and G. CRONHEIM (Biochem. Z., 1926, **171**, 7—14).—A wet combustion process is described, using fuming nitric acid and hydrogen peroxide. The several metallic components are precipitated and determined colorimetrically or volumetrically, phosphoric acid nephelometrically, by addition of strychnine-molybdic acid solution. The halogens cannot be determined by this method, as they are driven off during the combustion. They may be retained by the addition of silver nitrate before the combustion. E. C. SMITH.

Determination of dextrose in biological material. H. F. HOLDEN (Biochem. J., 1926, **20**, 263—270).—Higher values are obtained if dextrose is determined in the presence of amino-acids, by the Wood–Ost method, although these compounds do not reduce the copper solution alone. The error may amount to 10—15%. Tyrosine is decomposed in the presence of dextrose by an alkaline copper solution. This error, which was not observed with the Hagedorn and Jensen method, may be due to a coupled oxidation of the amino-acids and dextrose. If the above methods are applied to the concentrated filtrate from the blood of a rabbit in hypoglycæmic convulsions following the injection of insulin, there is a great divergence between the amounts of dextrose found. This is due to unknown reducing substances, since no such divergence is observed for normal blood filtrates. S. S. ZILVA.

Determination of sugar in urine. C. G. STOFFELLA (Boll. Chim. Farm., 1926, **65**, 225—228).—The author recommends Rupp's method (Apoth.-Ztg., 1924, **39**, 1548), in which 10 c.c. of urine are boiled gently with Fehling's solution for 2 min., the solution cooled without shaking, and potassium iodide, dilute hydrochloric acid, and potassium thiocyanate solution are added successively. The liquid is then rapidly titrated, in presence of starch paste, with 0·1*N*-sodium thiosulphate (say x c.c.) until it remains colourless for 2—3 min. A similar titration is carried out with the above reagents, but without the urine; this should give about 28 c.c. (the theoretical value) using a volume of Fehling's solution containing 0·7 g. of crystallised copper sulphate. The amount of dextrose in the 10 c.c. of urine is then 3·3(28—x) mg.

When the proportion of dextrose is considerable, preliminary dilution of the urine is necessary. When the percentage of sugar present is very small, a slight error may be introduced on account of decolorisation of the iodine by the uric acid. In such case, 20 c.c. of the urine are acidified with 2—3 c.c. of dilute sulphuric acid and titrated with 0·1*N*-iodine solution (y c.c.). Then the amount of dextrose in 10 c.c. of the urine will be 3·3(28—x—y) mg. T. H. POPE.

Determination of volatile fatty acids in bacterial cultures. A. I. VIRTANEN (Mitt. No. 242 Zentralanst. Ackerbau-versuchswesen. Bakt. Abt. 28, 1923, 9 pp.; from Chem. Zentr., 1926, I, 744).—The author discusses the determination of volatile fatty acids in bacterial cultures and in milk by distillation with steam in a vacuum. Even under these conditions a certain amount of lactic acid passes over in the distillate. The lower temperature, however, reduces the error due to volatile acids from the decomposition of protein substances. In the method recommended sodium chloride is added to the material and distillation with steam is carried out at ordinary pressure. Successive fractions of 300—500 c.c. are collected and titrated until a constant titration is obtained due to the small amount of lactic acid coming over. This is subtracted from the titre of the earlier fractions. When large quantities of lactic acid are present originally, the total distillate containing the volatile acids is concentrated at a low temperature, acidified with sulphuric acid, and again distilled, when the lactic acid remains behind. G. W. ROBINSON.

Urinary nitrogen titratable by the Kjeldahl-Foerster, Kjeldahl-Denigès, and Kjeldahl-Grigaut methods. W. MESTREZAT and R. MOREL (Bull. Soc. Chim. biol., 1926, **8**, 206—208).—The Kjeldahl-Foerster method gives results nearest the real values. C. P. STEWART.

Simultaneous micro-determination of ammonia and carbamide by means of permutite. B. POHORECKA-LELESZ (Bull. Soc. Chim. biol., 1926, **8**, 178—183).—The liquid is filtered through permutite, which absorbs the ammonia. After washing, the permutite-ammonia is decomposed by *N*-sodium hydroxide, and the ammonia determined by the author's hypobromite method (A., 1925, ii, 76). In the filtrate the carbamide is determined by the xanthydrol method or by the author's urease method (this vol., 212). C. P. STEWART.

Titration, determination of hydrogen-ion concentration, and "titration of indicators" in gastric juice. H. KALK and B. KUGELMANN (Klin. Woch., 1925, **4**, 1806—1810; from Chem. Zentr., 1926, I, 187).—"Titration of indicator" (Sahli, A., 1925, i, 458) and titration with dimethylaminoazobenzene give identical figures with a test-meal containing little protein or salts. The second method is not applicable when the juice contains lactic acid or much protein. In such cases, the method of Sahli should be used or the p_H value determined. J. S. CARTER.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1926.

General, Physical, and Inorganic Chemistry.

Large reflecting spectrometer for grating measurements in the long-wave spectrum. C. LEISS (Z. Physik, 1926, **37**, 681—684).—The spectrometer is constructed to measure wave-lengths up to and beyond 300 μ in conjunction with a micro-radiometer. The grating is of copper wire, 13 cm. square, with constants 2 and 1. The concave mirror is 15 cm. in diameter and of focal length 45 cm., giving a strong beam of light. E. B. LUDLAM.

Photographic plate as an instrument for measurement of visible and invisible radiations. C. FABRY (Phot. J., 1926, **66**, 328—342).

Fine structure of spectral lines. M. BRONSTEIN (Z. Physik, 1926, **37**, 217—224).—Mathematical. Einstein's law of the inertia of energy is applied to the motions of electrons and nuclei, with the result that the sum of the masses of the electrons and the nuclei is a function of their distance apart (packing effect). An expression is obtained for the separation of the lines in the fine structure which gives a value smaller than that of Sommerfeld, but the difference is very slight, 0·1% for hydrogen.

E. B. LUDLAM.

Fine structure of hydrogen lines. A. H. BUCHERER (Z. Physik, 1926, **37**, 395—404).—The application of the special relativity theory to the motion of an electron in its orbit is criticised, and a theory based on Hasenöhrl's formula for the total energy leads to the value of the separation of the lines 0·296 Å., in good agreement with the older determinations. The essential part of the theory is the conception that the electron revolves round the nucleus as though it were in a space free from force.

E. B. LUDLAM.

Widening by absorption of the lines of the Balmer series. (MLLE.) M. HANOT (Compt. rend., 1926, **182**, 1329—1331; cf. A., 1925, ii, 170).—Comparison has been made by means of a spectrophotometer of two spectra of hydrogen obtained from the same spark, the rays of one of which traverse a second spark arranged in series with the first. Absorption by the second spark occurs to the extent of about 30% for the centre of the H_β and H_γ lines. Such an absorption would correspond with a widening of the lines to the extent of 10 and 15%, respectively. Actually the widening observed is between 8 and 12%. The increase in the width of the lines as the current increases (cf. Hanot, *loc. cit.*) may be due to this absorption effect, but for less condensed sparks where the absorption effect must be small, the widening of the lines increases even more rapidly than in the former case with increase in current. F. G. SOPER.

Series-limits and molecular fields. F. PASCHEN (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1926, 135—141).—The series in the arc spectrum of helium obtained from the glow inside a cylindrical cathode at gas pressures exceeding 2 mm. exhibit a striking broadening and strengthening of the terminal lines and a continuous spectrum extending beyond the series limit. The broadening corresponds with the Stark effect occurring in the dark space and is ascribed to electric fields. Since, however, the $2s$—$3d$ line, which is very sensitive to electric fields, occurs less strongly in the glow light than in the positive light, the field concerned affects only the high quantum orbits and must be considered as molecular. The natures of the discharge and of the electric field of the singly-charged helium ion seem to require a mechanism involving simultaneous enhancement and disturbance of electron captures by the ions.

R. A. MORTON.

Spectrographic examination of the striated discharge in mixed gases. D. A. KEYS and M. S. HOME (Physical Rev., 1926, [ii], **27**, 709—715).—In a mixture of nitrogen and hydrogen the Balmer lines H_α and H_β and the nitrogen bands 4708 and 4278 Å. appear in the negative glow, but are absent from the striation. In a mixture of helium with a trace of hydrogen the mercury lines are strong; the helium line spectrum is strong in the negative glow, but weak in, or absent from, the striations, whilst the hydrogen lines are strong in the striations, but weak in the negative glow. The results indicate that there are relatively few electrons possessing energy equivalent to 15·5 volts in the striations in the nitrogen mixture, whilst in the striations in the helium mixture there are many with energies equivalent to 10·4 and 15·5 volts, but few with energy equivalent to 25·3 volts. An explanation is suggested.

A. A. ELDRIDGE.

First lithium spark spectrum. H. SCHÜLER (Z. Physik, 1926, **37**, 568—571).—Tables are given of the series and term values of the parlithium spark spectrum. Very strong lines, which could not be grouped as spark lines, are regarded as arc lines radiated when the two inner electrons are excited (the helium shell). E. B. LUDLAM.

Neon and helium spectrum in the extreme ultra-violet. H. B. DORGELO and J. H. ARBINK (Z. Physik, 1926, **37**, 667—671).—The ground level of neon is a simple p-level with inner quantum number $j = \frac{1}{2}$. A discharge tube was used with a mixture of neon and 30% helium at a pressure of 5 mm. and a current of 6 milliamperes; the pressure of gas in the vacuum spectrograph was 0·02 mm. A table of neon lines and their grouping is given from 743·74 to 589·84 Å. The following helium lines were found: 584·33, 537·08, 522·17 Å. The line 600·03, suggested by Lyman as a helium line, is regarded as the neon line $1p$—$4s_2$, excited by collisions of the second kind. E. B. LUDLAM.

Spark spectra of neon. L. BLOCH, E. BLOCH, and G. DÉJARDIN (J. Phys. Radium, 1926, [vi], **7**, 129—134; cf. this vol., 329).—The list of rays of Ne II published earlier is completed and corrected and a fuller account of the work given. When the degree of rarefaction is high and intense excitation is employed, a new spectrum ascribed to Ne III makes its appearance. This spectrum is tabulated together with a list of rays of unknown origin. R. A. MORTON.

Structure of the argon spectrum. K. W. MEISSNER (Z. Physik, 1926, **37**, 238—242).—The strong lines in the long wave-length portion of the red spectrum of argon are given as $1s_i$—$2p_k$, and are analogous to the corresponding lines of neon. Comparison tables of the two spectra are given. The two lines measured by Lyman and Saunders, 1048·28 and 1066·73 Å., are combinations of a fundamental ground term and the terms $1s_2$ and $1s_4$; the ground state of neon has a value $j=0$. Of the argon lines 80% have been grouped. E. B. LUDLAM.

***X*-Ray absorption spectrum of argon.** D. COSTER and J. H. VAN DER TUUK (Z. Physik, 1926, **37**, 367—373).—In a K-absorption the principal edge corresponds with the removal of a K-electron to the periphery; the less clearly marked secondary edge, on the hard side, is due to a simultaneous ejection of a K-electron and an outer electron outside the atom. When one of the K-electrons of an argon atom is missing, the outer electrons are subject to a field closely resembling that of a potassium atom, for, although the nuclear charge of the argon atom is one less than that of the potassium atom, this is compensated by the absence of the K-electron. The effective nuclear charge has become greater, and for free atoms the result is quite definite; for molecules or crystals, however, the effect is complicated by the presence of the neighbouring atoms. Transferences of two or more electrons simultaneously appear to play no part in X-ray absorption spectra. The fine-structure of the argon K-absorption edge was photographed and analysed in a recording photometer. The energy difference between the principal and secondary edge is 1·5 volts, about the same as the difference $2p$—$3p$ or $1s$—$1p$ of the potassium optical spectrum. E. B. LUDLAM.

Structure of the arc spectrum of manganese. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 89—120).—Forty wave-lengths absorbed by normal manganese vapour, some of which have been already recorded (Zumstein, this vol., 107), are tabulated. Existing data on the Mn I spectrum are reviewed and values are given for the terms of a sextuplet and an octet system which may be derived from the series schemes of Catalán (A., 1922, ii, 726). The classified wave-lengths of 257 lines between 17,600 and 1875 Å., with their frequencies, intensities, and term combinations, are tabulated. An energy diagram for all the known terms of the Mn I spectrum is given. J. S. CARTER.

Complex structure of the copper spectrum. G. BEDREAG (Compt. rend., 1926, **182**, 1333—1335).—Mathematical examination of the spectra of iron, cobalt, nickel, copper, and zinc indicates the existence in the copper spectrum of complex doublets and quadruplets corresponding with the electronic arrangement (2 . 8 . 17 . 2), in addition to the Rydberg doublets of the normal spectrum given by the configuration (2 . 8 . 18 . 1). Two examples of such quadruplets are given, one in the region 3483—3512—3545 Å., comprising the lines p_3—d_4, p_2—d_3, p_1—d_2, p_2—d_2, p_3—d_3, p_2—d_1, p_3—d_2, and a new line p_1—d_1, foreseen by calculation, at 3513·26 Å.; the other in the region 3621—3635—3645 Å., comprising the p_3—d_4, p_3—d_3, p_3—d_2, p_2—d_3, p_2—d_2, p_1—d_2, p_1—d_1, p_2—d_1 lines. The $4p_2$—$6d$ and $4p_2$—$6f$ lines at 3514·8 and 3511·6 Å., respectively, have also been observed. F. G. SOPER.

Analysis of the copper spectrum. W. M. HICKS (Phil. Mag., 1926, [vii], **2**, 194—236).

Optical excitation of zinc vapour. N. PONOMAREV and A. TERENIN (Z. Physik, 1926, **37**, 95—97).—Zinc vapour at a pressure of 5×10^{-4} mm., obtained by heating zinc at 280°, was exposed to the light from a zinc vacuum arc; the only two lines excited were 3076 ($1S$—$2p_2$) and 2139 ($1S$—$2P$). Roughly estimated, the ratio of the intensities of these two lines in the arc is 12, and in the optically excited light 2. This is probably because the absorption of the line of shorter wave-length is about six times as great as that of the longer wave-length. E. B. LUDLAM.

Under-water spark spectra of the palladium-platinum group of metals. L. H. G. CLARK and (MISS) E. COHEN (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 55—67).—Wave-lengths absorbed in the under-water spark spectra of ruthenium, rhodium, palladium, osmium, iridium, and platinum are tabulated. J. S. CARTER.

Series spectrum of palladium. J. C. MCLENNAN and H. G. SMITH (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 157—176).—Thirty-five wave-lengths absorbed by normal palladium vapour are tabulated. The complete list of the terms of the palladium arc spectrum is given and the wave-lengths, frequencies, and combinations of 195 arc lines between 8700 and 1720 Å. are recorded. The energy diagram has been constructed. J. S. CARTER

Structure of the arc spectrum of platinum. J. C. MCLENNAN and A. B. MCLAY (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 201—215).—Although

it has been possible to assign only arbitrary term designations, term values for the arc spectrum of platinum are tabulated and 338 wave-lengths between 8760 and 2140 Å. have been classified.

J. S. CARTER.

Recent experiments on soft *X*-rays. F. HOLWECK (Compt. rend., 1926, **182**, 1337; cf. this vol., 552; Dauvillier, this vol., 330, 551).—The continuity of the intensity–voltage curve of soft *X*-rays from a tungsten anode up to 280 volts and the discontinuity at this point due to carbon are reaffirmed. Compounds of nitrogen have been examined by the method previously described (*loc. cit.*). Ammonia and nitrous oxide show a marked discontinuity in their absorption bands at 397 ± 1 volts and nitric oxide and nitrogen at 397, 400, and 405 volts. F. G. SOPER.

Intensity of the forbidden mercury line 2270 Å. T. TAKAMINE (Z. Physik, 1926, **37**, 72—79).—The intensity of the line was examined in relation to strength of current and also in comparison with those of the arc. A special form of silica lamp was used with three electrodes. The production of the forbidden line is attributed to the increased concentration of atoms in a metastable state with strong currents, also to an increased number of collisions and transferences of energy, to which the name "inter-*p*-changes" is given, changes such as $2p_1$—$2p_2$.

E. B. LUDLAM.

Action of the electric field on the optically excited spectrum of mercury. A. TERENIN (Z. Physik, 1926, **37**, 676—680).—The only lines in the optically excited spectrum of mercury which were appreciably affected by an electric field of 50,000 volts/cm. were the two yellow lines in the visible, $2p_i$—$3(d_j, D)$, and the lines 3650—55—63, 3126—31, 2967, which are $2p_1$—$3d_{1,2,3}$,*D*, $2p_2$—$3d_{2,3}$,*D*, and $2p_3$—$3d_3$. Thus, of the two states resulting from the excitation, the higher ($3d$) is affected by the magnetic field to a much greater extent than the lower ($2p$), indicating that the emission is essentially determined by the higher state. E. B. LUDLAM.

4722 Line of bismuth and the nature of "raies ultimes." A. L. NARAYAN and K. R. RAO (Proc. Physical Soc., 1926, **38**, 321—323).—The 4722 Å. "raie ultime" and resonance line of bismuth has been examined by means of a quartz Lummer plate. No trace of absorption was found either in the main component or in the satellites even at 1200°. The fluorescence of the vapour under excitation by radiation from 6000 to 3500 Å. consisted of a banded spectrum in the orange-yellow, whilst under excitation from the ultra-violet radiation of a bismuth arc it became bluish and consisted of the 4722 and 3068 Å. lines. Thus, the latter line represents the minimum excitation energy and corresponds with transition to the normal orbit. R. A. MORTON.

Origin of *K*-radiation from the target of an *X*-ray tube. M. BALDERSTON (Physical Rev., 1926, [ii], **27**, 696—708).—Values (ϕ) of the ratio between the energy re-emitted as *K*-radiation by an elementary portion of the radiator to the energy absorbed by that portion from the exciting *X*-radiation are tabulated, as well as values (u) of the quantum transformation coefficient, for silver, molybdenum, zinc, copper, nickel, and iron. For silver, and probably for other elements of high atomic number, practically all of the *K*-characteristic radiation is fluorescent in origin, whilst for copper, and probably for other elements of low atomic number, a considerable part (less than 50%) of the *K*-radiation is due to direct impact of the cathode electrons. A. A. ELDRIDGE.

Zeeman effect in spark and arc spectra of molybdenum. E. WILHELMY (Ann. Physik, 1926, [iv], **80**, 305—328).—The spark and arc spectra of molybdenum in the region 2500—6000 Å. have been investigated under a field strength of 34,000 gauss. In Mo^+ a quadruplet and a sextuple system are found, whilst in Mo septuplet and quintuplets occur. The triplet system has not yet been recorded. In the arc spectrum the multiplets indicated by Catalán (A., 1923, ii, 596) are confirmed, and two groups indicated by Kiess are corrected. In the spark spectrum new terms are recorded which harmonise with the accepted relations between the spectra of neutral and singly ionised atoms. R. A. MORTON.

Zeeman effect and the structure of the arc spectrum of ruthenium. L. A. SOMMER (Z. Physik, 1926, **37**, 1—34).—Several thousand lines of the arc spectrum of ruthenium have been examined and recognised as combinations of 113 energy levels. Measurements of the Zeeman effect show that the terms are triplets and quintuplets. The determination of the l values, by comparison of the observed and calculated g values, was only partly successful. The principle of selection was found to hold: $\Delta j=0$ or ±1; $\Delta l=1$ or 3, or 0 or 2 for the respective combinations. The ground term is a quintuplet *F* term. The ionisation potential is calculated as 7·5 volts. The distribution of electrons in the atoms of the elements from scandium onwards is discussed and the conclusions are reached: the ground terms of the spectra of V^+ and Ni^+ are like the ground terms of Zr and Rh; these are like the ground terms of Ta^+ and Pt^+, and these again like those of Th and U. In this portion of the periodic system the Sommerfeld–Kossel displacement law does not hold (*e.g.*, the ground term of V^+ does not correspond with that of Ti, for V in the 4_1 shell is ionised). The strength of the binding of the different orbits depends on the screening effect of the inner shells. E. B. LUDLAM.

Zeeman effect of the lead spectrum. E. BACK (Z. Physik, 1926, **37**, 193—209).—Examination of the Zeeman effect is of importance in that the separation of the lines gives the inner quantum number, j, of the combined terms and is of value for characterising the ungrouped terms. Many of the lines are very close together, and the separation is difficult to determine accurately. Tables are given showing the grouping of electrons in the lead atom, the Zeeman types of the lines, values of j, and the scheme of the terms of the ground members of the spectrum. Rational values of g are found for all terms investigated.

E. B. LUDLAM.

Quantum mechanics and the anomalous Zeeman effect. W. HEISENBERG and P. JORDAN (Z. Physik, 1926, **37**, 263—277).—Mathematical. The

atomic model built up of rotating electrons possessing a magnetic moment is found to give a satisfactory explanation of the anomalous Zeeman effect and of the fine structure of spectra such as those of hydrogen, the alkalis, and of *X*-ray spectra. The separation calculated for the magnetic doublets is in agreement with that obtained by the Sommerfeld formula. E. B. LUDLAM.

Quantum theory of the unmodified line in the Compton effect. G. E. M. JAUNCEY (Physical Rev., 1926, [ii], **27**, 687—690).—The theory of the unmodified line previously developed (A., 1925, ii, 368, 747) is supported by the fact that experimental results for boron, lithium, and carbon agree with the requirement that the value of ϕ for which the unmodified line should disappear is given by vers $\phi = (3+2\sqrt{2})(\lambda_0^2/\lambda_s)(me/h)$. The ratio of the energies in the modified and unmodified lines is considered. A. A. ELDRIDGE.

Compton effect and photo-electric effect in polarised *X*-rays. F. KIRCHNER (Physikal. Z., 1926, **27**, 385—388).—Stereoscopic photographs of cloud tracks set up in a Wilson chamber by electrons liberated by polarised *X*-rays have been obtained with the photographic plate in a plane perpendicular to the direction of the rays. The Compton scattering electrons exhibit an accumulation of tracks in a direction perpendicular to the electric vector, whilst the electrons concerned in absorption show the larger number of tracks in the same direction as the vector. As a first approximation, it is concluded that there is no correlation between the hardness of the radiation and the extent to which the accumulation of cloud tracks occurs. R. A. MORTON.

Distribution of photo-electric sensitivity and the red limit. E. RUMPF (Z. Physik, 1926, **37**, 165—171).—The formulæ which have been advanced to represent the distribution of photo-electric sensitivity are discussed. Werner's quadratic formula is only an approximation even in the region where it is applicable; Becker's cubic formula fails in the neighbourhood of the red limit. An empirical formula is suggested in which the red limit is calculated according to Suhrmann and which passes into the cubical form for short waves. E. B. LUDLAM.

Collisions of the second kind with excited mercury atoms in the 2*P* state. J. G. WINANS (Nature, 1926, **118**, 46—47).—When a mixture of zinc and mercury vapours is illuminated by the light from a water-cooled silica mercury arc, the zinc lines 4810, 4722, 4680, 3345(?), 3302, 3282, 3075, and 2138 Å. may be observed. Some of the normal mercury atoms absorb radiation of 2536 Å., and others that of 1849 Å., the electron going respectively to the $2p_2$ and the $2P$ level, zinc atoms being excited by collision with either kind. When the exciting light is filtered through dilute acetic acid, radiation of wave-length 1849 Å. is absorbed, and the sharp zinc triplet (4810, 4722, 4680 Å.) is much reduced in intensity. When exciting light from the hot arc is filtered through dilute acetic acid, no zinc lines appear. Zinc atoms cannot directly absorb radiation of wave-length 1849 Å. Hence the effect of mercury atoms in the $2P$ state must be considered in the interpretation of the results obtained on illumination of a mixture of gases and mercury vapour with light from a silica mercury arc. A. A. ELDRIDGE.

Ionisation of oxygen by electron impact as interpreted by positive ray analysis. T. R. HOGNESS and E. G. LUNN (Physical Rev., 1926, [ii], **27**, 732—738).—Since the relative intensity of the ions O^+ and O_2^+, as measured by the ratio of the peak intensities, is constant between 10^{-5} and 10^{-2} mm., and over a large range of partial pressures of oxygen mixed with helium or argon, the formation of these ions must be independent primary processes. An impact electron of sufficient velocity can cause the change (*a*) $O_2 = O_2^+ + \epsilon$ or (*b*) $O_2 = O^+ + O + \epsilon$, the respective ionisation potentials being 13 and 20 volts. The heat of dissociation of oxygen is hence computed as 150,000 cal. per mol., whereas Birge and Sponer's value, calculated from band-spectra data, is 162,600 ± 700 cal. Atomic and molecular negative ions were observed, but of small intensity. The results are correlated with Franck's theory on the dissociation of molecules by the absorption of radiation, and with Lewis' conception of the structure of the oxygen molecule. A. A. ELDRIDGE.

Dissociation of the water molecule. H. SENFTLEBEN and (FRL.) I. REHREN (Z. Physik, 1926, **37**, 529—538).—By measurement of the thermal conductivity, it is shown that when water vapour is exposed to radiation from a water-cooled mercury lamp partial decomposition takes place with the production of hydrogen, but no oxygen. The presence of mercury vapour in the water vapour, however, was necessary, and if the light from the mercury-vapour lamp was made to traverse a vessel containing mercury vapour before it entered the chamber containing the water vapour, no decomposition took place; both these results indicate that the effect is due to collisions of the second kind between water molecules and mercury atoms which have absorbed the resonance radiation. Mixtures of hydrogen and oxygen exposed to the same source of light show a diminution of thermal conductivity and a diminution in pressure at the temperature of liquid air, due to combination. On thermochemical grounds it is concluded that the dissociation is $H_2O + \text{energy} = H + OH$. The energy available from the mercury resonance radiation is 112 Cal. The hydroxyl groups combine to form hydrogen peroxide, but in quantity too small for detection by chemical means. E. B. LUDLAM.

Electron affinity of oxygen. H. SENFTLEBEN (Z. Physik, 1926, **37**, 539—546).—Using the value 112 Cal. (cf. preceding abstract) as the approximate heat of dissociation of water vapour into hydrogen and hydroxyl, the energy necessary for the decomposition of the alkali hydroxides and of water into atoms of hydrogen and oxygen and also into ions is calculated by means of cyclic processes. The electron affinity of oxygen for one electron, *i.e.*, the work necessary to remove one electron from O--, is found to be −204 Cal.; to remove the second electron the work necessary is positive, 164 Cal.; thus, to remove both electrons −40 Cal. are necessary. E. B. LUDLAM.

Ionisation potentials of certain elements of the rare-earth group. L. ROLLA and G. PICCARDI (Atti R. Accad. Lincei, 1926, [vi], **3**, 410—413).—In order to extend the flame method (cf. A., 1925, ii, 1018, 1105) for determining ionisation potentials to elements forming salts and oxides of low volatility, the Bunsen burner used is replaced by an oxygen–coal gas blowpipe, which yields a temperature of about 2300°. Measurements made with sodium and calcium under these new conditions give the value −1·98 for the tangent of the straight line expressing log K as a function of V, K being the equilibrium constant of the reaction, neutral atom $\rightleftharpoons$ atom + electron, and V the ionisation potential in volts; the calculated value for 2300° is −1·96. Examination of the oxides of the rare-earth metals gives the following values for V: lanthanum 5·49, cerium 6·91, praseodymium 5·76, neodymium 6·31, samarium 6·55. T. H. POPE.

Affinity of the iodine atom for the electron. G. PICCARDI (Atti R. Accad. Lincei, 1926, [vi], **3**, 413—416).—The flame method devised for the experimental determination of the reaction, neutral atom $\rightleftharpoons$ positive ion + electron may be applied also to the determination of the affinity of the neutral atom for the electron: neutral atom + electron $\rightleftharpoons$ negative ion. The use of iodine vapour would be inconvenient and would involve difficulty in ascertaining the loss of weight, but by means of a steady current of oxygen passed over the surface of methyl iodide in a glass bulb and then into the flame, the value of the affinity of the iodine atom for the electron is found to be 3·58 volts or, on the assumption that the iodine enters the flame solely in the atomic form, about 82,000 cal. Gerlach and Gromann (A., 1923, ii, 803) gave 82,000 cal. and Born (A., 1920, ii, 156) 81,000 cal. The wave-length of the red end of the continuous spectrum accompanying the union of an electron with an atom or a positive ion is, according to Einstein's formula, 3450 Å., which agrees exactly with Gerlach and Gromann's measurement of this wave-length in the continuous iodine spectrum. T. H. POPE.

Affinity of the neutral bromine atom for the electron. G. PICCARDI (Atti R. Accad. Lincei, 1926, [vi], **3**, 566—568).—Making use of ethyl bromide, the author finds, by means of the flame method (cf. preceding abstract), that the affinity of the neutral bromine atom for the electron is 3·76 volts or 86,700 cal. Born (A., 1920, ii, 156) found 87,000 volts. T. H. POPE.

Effect of pressure on excitation of the hydrogen spectrum by electron impact. P. LOWE (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 217—228).—Experiments in which the gas pressure was varied between the limits 0·005 and 0·06 mm. show that, when the hydrogen spectrum is excited by electrons at potentials greater than 50 volts, the intensities of all lines vary directly with the pressure. At lower potentials the intensities fall away more rapidly than the pressure. The intensities at constant voltage and pressure are directly proportional to the strength of the electron current. Intensity-ratios in the Balmer series depend only on the potential. Although Smyth states (A., 1925, ii, 459) that atomic ions are hardly ever produced as a result of direct electron impact, it is concluded that under certain conditions excited atoms and probably a few ionised atoms are formed by this means. J. S. CARTER.

Analysis of positive ions emitted by a new source. H. A. BARTON, G. P. HARNWELL, and C. H. KUNSMAN (Physical Rev., 1926, [ii], **27**, 739—746).—Crystal granules of iron oxide, containing about 1% of the oxide of an alkali or alkaline-earth metal (as employed in the catalytic synthesis of ammonia), are constant and abundant emitters of singly-charged positive ions of the corresponding alkali or alkaline-earth metals. Emission was increased by a preliminary reduction in hydrogen. Ions of iron, oxygen, or aluminium did not appear. The surface emission of sodium and potassium ions from hot platinum was confirmed. A. A. ELDRIDGE.

Formation of negative ions in mercury vapour. W. M. NIELSEN (Physical Rev., 1926, [ii], **27**, 716—723).—Using a method similar to that of Mohler, the ratio between the negative ion and total current decreases with increase in the accelerating potential for low voltages, but increases at 2·7, 4·7, 5·5, and 8·8 volts. The last three breaks are considered to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. A. A. ELDRIDGE.

Probability of ionisation of gas molecules by electron impacts. II. K. T. COMPTON and C. C. VAN VOORHIS (Physical Rev., 1926, [ii], **27**, 724—731).—After suitable correction, the authors' previous results (A., 1925, ii, 1106) are in fair agreement with corrected results of Hughes and Klein (A., 1924, ii, 375). Curves indicate the probability that an ionising collision will occur in a cm. path in helium, neon, argon, hydrogen, nitrogen, mercury vapour, or hydrogen chloride at 25° and 0·01 mm. by an electron of any speed up to 400 volts, as well as the probability of ionisation at impact. A. A. ELDRIDGE.

Ionisation of air by means of X- and cathode-rays. H. KULENKAMPFF (Ann. Physik, 1926, [iv], **80**, 261—278; cf. this vol., 456).—The ionisation effected by X-rays is independent of the wave-length so long as the same total energy is supplied. It is thus an indirect effect due to liberated photo-electrons; hence by the equation $h\nu=\frac{1}{2}mv^2$, cathode rays of equal energy should bring about the same ionisation. From the mean path of the electrons in air and the ionisation per cm. of trajectory the ionisation can be calculated for cathode-rays. The mean path in air depends on the absorption coefficient. If Lenard's view of the absorption process, a sudden reduction of the velocity to a value approaching zero, is used as a basis of calculation, the results are completely at variance with those obtained with X-rays. If, however, absorption is regarded as a "diffusion" effect, the velocity of the cathode-ray electron being reduced by gradual stages, satisfactory agreement with the X-ray ionisation is obtained. R. A. MORTON.

Chemical action of gaseous ions produced by α-particles. VII. Unsaturated carbon compounds. S. C. LIND, D. C. BARDWELL, and J. H. PERRY (J. Amer. Chem. Soc., 1926, **48**, 1556—1575; cf. this vol., 4).—A quantitative study of nine

reactions of polymerisation, hydrogenation, or oxidation of acetylene, cyanogen, hydrogen cyanide, and ethylene at 25° under the influence of α-radiation of radon. The process of the reaction has been quantitatively determined by manometric measurement at the ordinary and low temperatures and the final gaseous products by chemical analysis. The velocity constant $k\mu/\lambda$, where k is the combined ionisation constant of the gas or mixture, μ is the efficiency constant of conversion of the gaseous ions into the chemical products, and λ is the decay constant of radon, and the ratio M/N, the number of particles reacting per ion pair produced, have been calculated from the general kinetic equation $k\mu/\lambda=(\log P_1/P_2)/E_0(e^{-\lambda t_1}-e^{-\lambda t_2})$, where P_1 and P_2 are any two partial pressures of the reacting gases, E_0 is the initial quantity of radon, and $(e^{-\lambda t_1}-e^{-\lambda t_2})$ is the fraction of radon decaying in the time interval t_1-t_2. Acetylene gives a pale yellow solid polymeride resembling cuprene: about 2% of the hydrogen is eliminated. $M/N=19{\cdot}8$. Cyanogen polymerises to a black solid resembling paracyanogen; 5% of nitrogen is liberated. $M/N=7{\cdot}4$. Nitrogen has a catalytic effect on the action. Hydrogen cyanide gives a dark reddish solid polymeride. The empirical formula is $(HCN)_x$ less about 7% of nitrogen and 2·7% of hydrogen. $M/N=11{\cdot}1$, but the velocity constant varies, probably due to hydrogen cyanide not behaving as a perfect gas. Ethylene condenses to a colourless liquid with elimination of 16% of its hydrogen. $M/N=5{\cdot}1$. Hydrogen has a catalytic effect on the action. The reaction between ethylene and hydrogen is one of condensation of ethylene with elimination of hydrogen and methane. Only 1% of possible ethane is obtained, whereas hydrogen is liberated to the extent of 16% of the ethylene condensed. $M_{C_2H_4}/N_{C_2H_4+H_2}=4{\cdot}9$, only 4% lower than for condensation of ethylene. With acetylene and hydrogen, polymerisation predominates; hydrogen acts as catalyst and reactant; the hydrogen ions which serve as clustering centres for the acetylene are chemically combined in an indefinite ratio. Cyanogen is hydrogenated in the ratio $3C_2N_2:2H_2$, regardless of their relative concentrations. A true compound of empirical formula $(C_6H_4N_6)_x$ is formed. An equimolecular mixture of cyanogen and oxygen gave a yellow solid of empirical formula $(CNO)_x$. The reaction is in two parts: (i) $C_2N_2+2O_2=2CO_2+N_2$ and (ii) $0{\cdot}5xC_2N_2+0{\cdot}5xO_2=(CNO)_x$. The ratio (i) : (ii) = 4 : 5. $M_{C_2N_2+O_2}/N_{C_2N_2+O_2}=7{\cdot}2$, indicating that the ionic cluster contains the same number of oxygen and cyanogen mols. as does pure cyanogen. The oxidation of acetylene gives a colourless liquid of empirical formula $(C_2H_3)_x$, indicating that the hydrogen has been condensed on two thirds of the initial carbon atoms by oxidising the third to carbon monoxide or dioxide. The oxygen in these mixtures ($C_2H_2+O_2$ and $C_2H_2+2O_2$) is used entirely in forming carbon monoxide and dioxide in a 2 : 5 ratio. $M_{C_2H_2+O_2}/N_{C_2H_2+O_2}$ is about 27. M. CARLTON.

Chemical action of gaseous ions produced by α-particles. VIII. Catalytic influence of ions of inert gases. S. C. LIND and D. C. BARDWELL (J. Amer. Chem. Soc., 1926, **48**, 1575—1584).—The ions of inert gases mixed with the reactants contribute as much to the reaction as do the ions of the reactants themselves. Data for polymerisation of acetylene catalysed by nitrogen and helium ions and of cyanogen by xenon, and for the synthesis of water catalysed by argon, are given, and show that under the influence of α-rays the inert gas greatly accelerates the reactions. The values of the velocity constant are normal until 50% of the ionisation falls on the catalyst, when the values drop. This is quite general for all reactions quoted—polymerisation of acetylene, cyanogen, and hydrogen cyanide, oxidation of carbon monoxide and hydrogen, and decomposition of carbon monoxide and ammonia—in presence of the inert gases nitrogen, helium, neon, argon, krypton, xenon, carbon dioxide, and hydrogen. A kinetic equation is deduced which is applicable to the catalysed reactions; exceptions, however, occur where carbon dioxide and nitrogen fail to autocatalyse reactions in which they are formed. The fact that the ionisation potential of the catalyst is either higher or lower than that of the reactants does not affect the general addition law: this shows that the primary step in a reaction does not consist of an exchange of charges between ionised catalysts and neutral reactants. The effect of depletion of the reactants is considered and an empirical law given. M. CARLTON.

Electrical double layer at the surface of mercury. A. BÜHL (Ann. Physik, 1926, [iv], **80**, 137—180).—Very pure mercury free from gas yields positive charge carriers exclusively, when atomised by a draught of pure air. The carriers are shown to consist of mercury. The outermost layer of mercury molecules is positively charged and there is no marked electron atmosphere. The mutual effects of molecules are reduced in the surface layer correspondingly with the small inner pressure of the molecular forces. Electrons are assumed to be drawn towards the interior of the liquid metal. The thickness of the layer from which electrons have been removed is estimated as $1—2\times10^{-6}$ cm., approximately agreeing with the radius of the sphere of influence of mercury. When the metal is left in contact with a gas for a period exceeding 10^{-2} sec., negative carriers make their appearance. All the gases tried behave similarly. Traces of base metals dissolved in the mercury bring about increased formation of negative carriers; 10^{-11} part of zinc is readily detectable, so that the experiment supplies a delicate criterion of purity of mercury. Hence adsorbed gases and dissolved metals (according to their position in the electrochemical series) favour the liberation of electrons from mercury molecules. R. A. MORTON.

Frictional electricity. H. F. VIEWEG (J. Physical Chem., 1926, **30**, 865—889).—The charges produced when definite crystal faces of certain substances are rubbed together have been examined, and by this means some forty different materials have been arranged to give a frictional electric series. In every case, moisture superimposes a positive charge on the natural charge of each surface, the size of the charge increasing with humidity and decreasing as the distance in the series increases; acids, alkalis, or salts add a negative charge. The charges developed by passing air through solutions (N to $0{\cdot}001N$) of

certain salts and acids, and through water, show that the gas receives a negative charge in dilute solution. This first diminishes to zero with increasing concentration and then becomes positive. These results are explained on the basis of selective adsorption of ions by the gas.

An explanation of frictional electricity is proposed using the electronic structure of matter as a basis, and the physical significance of Coehn's rule is discussed. L. S. THEOBALD.

Comparison of the atomic weight of silicon from different sources. P. L. ROBINSON and H. C. SMITH (J.C.S., 1926, 1262—1282).—Five samples of silicon tetrachloride were prepared from siliceous materials of specified origin, and were all subjected to rigorous purification by uniform treatment with mercury and sodium amalgam and by fractional distillation first in dry air and later in a vacuum. The densities of these liquids were determined from the flotation-temperatures of accurately calibrated floats of glass immersed in the silicon tetrachloride liquids. The calculated apparent variation of atomic weight for silicon was not greater than 0·005. It is concluded that further purification would probably have reduced the variation to 0·001. The flotation method used, described in detail, is shown to be suitable for the refined determination of desnity, thermal expansion, or compressibility. R. A. MORTON.

Isotopes of sulphur. F. W. ASTON (Nature, 1926, **117**, 893—894).—The negative mass-spectrum obtained by using pure sulphur dioxide, and exposing for 1 hr. with both fields reversed, shows lines corresponding with sulphur isotopes of mass 32, 33, and 34. S^{34} is about three times as abundant as S^{33}, the two together probably amounting to about 3% of the whole. A. A. ELDRIDGE.

Attempts to fractionate mixed isotopes of lead, and the atomic weight of this metal. T. W. RICHARDS, H. S. KING, and L. P. HALL (J. Amer. Chem. Soc., 1926, **48**, 1530—1543).—Attempts to separate the isotopes of lead by irreversible evaporation of the metal and by fractionation by the Grignard reaction yielded negative results. Determination of the ratio lead chloride/silver gave the mean value of 207·217 for the atomic weight of lead. S. K. TWEEDY.

Line spectra of isotopes. F. A. JENKINS (Nature, 1926, **117**, 893).—The spectra of samples of mercury (atomic weight difference 0·18 unit) and of chlorine (atomic weight difference 0·097 unit) obtained by fractional diffusion were examined. No real shift of the mercury lines 5461, 4359, 4078, or 4047 Å. or their satellites was observed, but small shifts (*e.g.*, 0·0012 Å. for 4741 Å.) were detected with some of the chlorine lines. A. A. ELDRIDGE.

Separation of barium and radium salts. I. BACHILOV.—See B., 1926, 538.

Obliquity corrections in radium determination. I. BACKHURST (Proc. Physical Soc., 1926, **38**, 277—290).—Obliquity errors arise in determinations by the γ-ray method of the radium content of tubes larger in size than the standard. Formulæ are given for corrections applicable to sources of the shapes most frequently occurring in practice. Experimental results on the effect of scattered radiation are shown graphically and compared with theory. The scattered radiation must be reduced to a minimum if accurate obliquity corrections are to be obtained. By keeping away from walls the effect of scattered radiation can be reduced to one half. R. A. MORTON.

Ionisation by radon in spherical vessels. W. MUND (J. Physical Chem., 1926, **30**, 890—894).—See A., 1925, ii, 732. L. S. THEOBALD.

Method of preparation of sources of radium-*B* + *C*. H. JEDRZEJOWSKI (Compt. rend., 1926, **182**, 1536—1539).—An apparatus for preparing concentrated sources of radium-*B* + *C* is described, which gives greater yields than are obtained by the use of liquid air or an electric field. The radon is liberated in an evacuated bulb, and after 3—4 hrs., one of a number of small bulbs projecting from the main apparatus is removed in the flame. The active deposit is obtained by breaking the bulb and washing it out with hot aqua regia, which is subsequently evaporated. Similar deposits are obtained from other small bulbs attached to the apparatus, but 81% of the total yield is contained in the first. Radium-*B* is more soluble than radium-*C*. J. GRANT.

Decay of radium-*E*. L. F. CURTISS (Physical Rev., 1926, [ii], **27**, 672—674).—The half-period of decay of radium-*E* free from radium-*D* is 5·07 days. This value is in agreement with the observations of Antonov, Meitner, and Bastings, but not with those of Thaller and Fournier. A. A. ELDRIDGE.

Absorption of the penetrating radiation from actinium in equilibrium with its derivatives. M. FRILLEY (Compt. rend., 1926, **182**, 1461—1463).—The absorption curve of a substance for β- and γ-rays may be expressed in the form $\log i=f(x)$, where x is the thickness of the absorbing screen and i the ionisation current in a chamber which shuts out α-rays. The absorption curve in aluminium of the penetrating radiation from actinium in equilibrium with its products is abnormal in that, with increasing values of x, the curve $\log i=f(x)$ is first a straight line and then undergoes an increase of slope, followed by a second straight line, which continues until $x=1{\cdot}5$ mm., after which the usual diminution of slope due to filtration of the rays takes place. If the rays are first passed through 0·5 mm. of silver, the aluminium absorption curve is quite normal, the linear portion coinciding with the second linear portion of the ordinary curve. The abnormality is therefore due not to diffusion, as supposed by Hahn and Meitner (A., 1908, ii, 1007), but to the structure of the main radiation (of actinium-*C*″) composed of a few rays, which distinguishes this radiation from that of similar velocity composed of bands, as in radium-*E*. The coefficient of absorption is usually deduced from the slope of the first linear portion of the ordinary curve, but is better determined from the second linear portion, which gives $\mu=44{\cdot}5$ cm.$^{-1}$ for the β-radiation of actinium-*C*″. W. HUME-ROTHERY.

α-Rays of thorium-C + C' and their behaviour in passing through various gases. (FRL.) L. MEITNER and K. FREITAG (Z. Physik, 1926, **37**, 481—517).—Photographs of a very large number of tracks of α-particles taken stereoscopically, using a special form of Wilson expansion apparatus, are reproduced. The tracks appear like the flower of a thistle, the shorter ones of range about 4·8 cm. being easily distinguished from those of about 8·7 cm.; in addition, occasional tracks appear of which the range is 11·5 cm. in air, and others about one third as frequently as these, with ranges 9·5 cm. and more than 12 cm., respectively. The ratio of α-particles from thorium-C to those from thorium-C' was 34·3 : 65·7. The observed ranges in air, nitrogen, oxygen, carbon dioxide, and argon were in agreement with the values calculated by Bohr. The mean relative stopping power of the various gases was calculated from the observed ranges. Of the α-particles from thorium-C', those with ranges 9·5 cm. and 11·5 cm. are about 70 and 200, respectively, per million of the whole. The tracks with a range longer than 12 cm. were much finer than the others and are H-particles. They are produced from a film of water condensed on the radioactive preparation, but this does not exclude the possibility that some may be produced from the disintegration of a nitrogen atom. E. B. LUDLAM.

Long-range α-particles from the active deposit of thorium. K. PHILIPP (Z. Physik, 1926, **37**, 518—528; cf. preceding abstract).—Particles having ranges in air of 11·5 and 9·5 cm. were observed by the scintillation method. As also found by the Wilson method, the appearance of the 9·5-cm. range was not dependent on the nature of the gas in the chamber. Rays with a range greater than 11·5 cm. are not α-particles. The number of particles per million of those of range 8·6 cm. were 65 and 180 for ranges of 9·5 cm. and 11·5 cm., respectively. The H-particles with a range greater than 11·5 cm. were in a ratio to the α-particles of about 30 per million.

E. B. LUDLAM.

Influence of metallic screens on the form of the ionisation curve of α-rays. M. CONSIGNY (Compt. rend., 1926, **182**, 1614—1616; cf. Bragg and Kleemann, Phil. Mag., 1905, [vi], **10**, 318; Bianu, Le Radium, 1913, **10**, 122).—Introduction of a metallic screen causes a deformation and not merely a displacement of the ionisation curve. The magnitude of the deformation appears to be more influenced by the number of layers comprising the screen than by the actual thickness of metal. No simple relationship exists between the magnitude of the deformation and the atomic weight of the metal used. J. S. CARTER.

Anomalous scattering of α-particles. A. SMEKAL (Physikal. Z., 1926, **27**, 383—385).—Debye and Hardmeier (this vol., 450) explain the sub-normal scattering of α-particles by an assumed deformation of the nucleus in collisions between isotropic quasi-point-formed α-particles and atoms. The conception requires the existence of attractions varying as the reciprocal of the fifth power of the distance. The experimental validity of such a law is confirmed, but the inference of a deformable nucleus is questioned on account of (*a*) evidence favouring anisotropy in the α-particle, (*b*) similarity in size between the nuclei of aluminium and magnesium and of the α-particle itself, (*c*) the existence of supernormal scattering, (*d*) the uncertainty concerning perfect elasticity in individual scattering processes. The author favours a quantum-mechanism on the lines of the Heisenberg mechanics and the Born–Franck idea of unquantised meta-stationary states. R. A. MORTON.

Singly-charged α-rays. S. ROSENBLUM (Compt. rend., 1926, **182**, 1386—1388).—The magnetic spectra of the α-rays of thorium-C and thorium-C' have been photographed, using a magnetic field of about 15,000 gauss. In addition to the principal rays, other "half-way" rays due to singly-charged α-particles were observed, the ratio of the numbers of singly- and doubly-charged rays being roughly of the order 1 : 1000. Additional very faint lines of uncertain origin were observed half-way between the central ray and that of the singly-charged α-particles.

W. HUME-ROTHERY.

New method for measuring the absorption of β- and γ-rays of radioactive substances. D. K. YOVANOVITCH and (MLLE.) A. DORABIALSKA (Compt. rend., 1926, **182**, 1459—1461).—The absorption coefficient of β- and γ-rays is usually determined by measuring the ionising power of the rays after passing through increasing thicknesses of matter, but may also be determined by measuring the heat energy retained by the absorbing matter itself. Using the calorimeter previously described (A., 1924, ii, 719), the heat energy absorbed by screens of aluminium, copper, and lead exposed to radioactive rays has been determined. To an approximation the results may be expressed in the form $q=Q_\beta\left(1-e^{-\frac{\mu}{\rho}\frac{m}{s}}\right)$, where q is the flow of heat per g. of radium (element) per hr. absorbed in excess of that due to α-rays, $Q_\beta=13{\cdot}4$ cal. is the flow of heat due to all the β-rays, μ/ρ is the mass absorption coefficient, and m/s the mass of the absorbing screen per cm.^{2} With an aluminium screen, μ/ρ for the β-rays of radium is determined as 51·02; copper and lead give higher values. The extrapolated value for the flow of heat from radium with an absorbing screen of zero thickness is 129 cal. per g. per hr. W. HUME-ROTHERY.

Variation with pressure of the residual ionisation in gases. W. W. MERRYMON (Physical Rev., 1926, [ii], **27**, 659—671).—Using a glass globe with a sputtered silver coating as the ionisation chamber, the residual ionisation in aged, dried, filtered air, hydrogen, helium, argon, oxygen, nitrogen, carbon dioxide, methane, and ethylene, up to 1800 mm. pressure, has been determined. Values of q, the number of pairs of ions formed per c.c. per sec. at 760 mm., and dq, the increase in q per atm. increase in pressure, are, respectively, 12·2, 9·88; 5·0, 2·033; 3·2, 2·215; 22·8, 18·59; 14·2, 10·95; 12·0, 10·00; 19·6, 14·22; 12·5, 8·68; 20·42, 14·70. The rate divided by the number of electrons in the molecule is approximately constant at 0·855. A. A. ELDRIDGE.

Radioactivity of the alkali metals. I. J. PATTON and L. J. WALDBAUER (Chem. Reviews, 1926, **3**, 81—93).

Transmutation experiments. M. W. GARRETT (Nature, 1926, **118**, 84).—No trace of gold was detected when a discharge was passed (*a*) between tungsten electrodes immersed in a fine emulsion of mercury droplets in white paraffin oil, (*b*) between aluminium rods in an emulsion of mercury in distilled water, or (*c*) between an iron pole and a mercury surface in an atmosphere of hydrogen; neither was gold detected after an arc had been maintained and extinguished (6—8 times per sec.) for 288 hrs. in a silica tube containing mercury and hydrogen and attached to a shaking machine, although Miethe's results would indicate an expected yield 10^4 times as great as the sensitiveness of the test. Attempts to prepare indium from tin and scandium from titanium were equally unsuccessful. A. A. ELDRIDGE.

The new atomic mechanics. L. BRILLOUIN (J. Phys. Radium, 1926, [vi], **7**, 135—160).—A critical *résumé* of the new mechanics as developed by Heisenberg, Born, Kramers, and others. R. A. MORTON.

Multiple periodic systems in the quantum mechanics. G. WENTZEL (Z. Physik, 1926, **37**, 80—94).—Mathematical. E. B. LUDLAM.

Atomic structure and the magnetic properties of co-ordination compounds. L. C. JACKSON (Phil. Mag., 1926, [vii], **2**, 86—96).—The electron distributions proposed by Welo and Baudisch (A., 1925, ii, 1031) and by Bose (this vol., 106, 111, 114) to explain the magnetic properties of the co-ordination compounds of Cr^{+++}, Fe^{+++}, Fe^{++}, Co^{+++}, etc., are only partly successful. A satisfactory scheme must not only take into consideration the distribution of the electrons among the sub-groups of the various levels, but also should bring out clearly the character of the combination, *i.e.*, whether sixfold or fourfold co-ordination. Cabrera's scheme (A., 1923, ii, 123) fulfils these requirements, but has difficulty in accounting for the magneton numbers of the fourfold nickel compounds. The tendency of the M_{32} sub-groups to be completed, as suggested by Cabrera, is here possibly hindered by the screening effect of the M_{33} sub-group, or by the difference between the type of symmetry of the $4M_{32}$ electron orbits and that of the outer binding orbits. Cabrera's scheme requires further modification when it is recognised that some " simple " salts (*e.g.*, $NiCl_2,6H_2O$) may really be co-ordination compounds. A. B. MANNING.

Spectral intensity distribution and electron jumps in the Bohr model. H. BARTELS (Z. Physik, 1926, **37**, 35—59).—An atom can return in stages from the excited to the normal state. A relation is sought between the distribution of the energy of excitation over the single terms and the distribution of spectral intensities. A method is developed which gives a survey of the complicated phenomena, particularly of the decrease of intensity along one series and the relation of the intensity in one series to that in another. E. B. LUDLAM.

Electrodynamics of the rotating electron. J. FRENKEL (Z. Physik, 1926, **37**, 243—262).—Mathematical. The electron is treated as a point associated with a moment-tensor which determines its magnetic properties. The explanation of the origin of the anomalous Zeeman effect is deduced. The electromagnetic field produced by a rotating electron is determined and the result is obtained that the structure of the nucleus is maintained by the magnetic forces between electrons and protons, which must be enormously greater than the electrostatic forces. E. B. LUDLAM.

Modified periodic system. A. VON ANTROPOFF (Z. angew. Chem., 1926, **39**, 722—725).—Bohr's modification of the periodic table is arranged on a cylindrical surface, the lengths of the periods being equalised by placing the symbols of the short-period elements in larger areas. Hydrogen occupies a whole period, a space being left for " neutronium " in the inert gas group, which flanks the table when the surface is opened out. The rare-earth metals are placed with lanthanum. The mutual relationships between the elements are indicated by schematic colouring or shading. Some advantages of the modification are described. S. K. TWEEDY.

Applications of the modified periodic system to the graphical representation of the properties of elements and their compounds. A. VON ANTROPOFF (Z. angew. Chem., 1926, **39**, 725—728).—The application of the modified periodic table (cf. preceding abstract) to the graphical representation of the chemical and physical properties of elements and their compounds is illustrated by means of an atomic-volume curve, a m.-p. and b.-p. diagram for the elements, and diagrams representing the properties of the hydrides, and the isotopic characters of the elements. Harkins' generalisations with regard to isotopic elements (cf. A., 1921, ii, 445) become apparent in the latter diagram. S. K. TWEEDY.

***X*-Ray term values, absorption limits, and critical potentials.** E. C. STONER (Phil. Mag., 1926, [vii], **2**, 97—113).—Methods of computing the term values for the *K*, *L*, and *M* energy levels are discussed, and values are deduced from the available *X*-ray data for the elements from titanium (22) to zinc (30). A consideration of the fine structure of the absorption edges leads to the conclusion that the term values correspond with the energy required to remove an electron to the lowermost possible unoccupied optical level in the atom. For a neutral atom this will differ by only a few volts from that corresponding with removal to the boundary, but the difference increases with successive stages of ionisation of the atom. This accords with the range and character of the fine structure observed for compounds. The apparently divergent values obtained by different observers for the critical potentials are discussed. It is suggested that some of the points correspond with critical potentials for atoms which have been ionised by the loss of outer or inner electrons. Critical potential experiments are unsuitable for the direct precise determination of atomic energy level values. A. B. MANNING.

Stintzing's hypothesis of the structure of atomic nuclei. R. REINICKE (Z. Physik, 1926, **37**, 210—216; cf. this vol., 7).—This hypothesis is modified and extended. The helium complex is regarded as a separate unit tetrahedron with protons at each

corner. The spaces between them correspond with Stintzing's carbon scheme. The scheme for neon places one tetrahedron symmetrical inside four others; a similar type is assigned to iron. The group H_3 plays a part distinct from that of the more stable helium. The author suggests that the logical extension of this method should embrace the electron groups in the external portion of the atom. E. B. LUDLAM.

Influence of radiation on ionisation equilibrium. M. SAHA and R. K. SUR (Phil. Mag., 1926, [vii], **1**, 1025—1034; cf. Nature, 1925, **115**, 377).—Radiation is regarded as an extra component entering into the equilibrium and for which all the usual constants can be determined. Formulæ are deduced which represent approximately the energy level differences of various states, but which do not include a term embodying the finite width of the absorption band. Such a thermodynamical treatment cannot account for the fact of absorption.
A. E. MITCHELL.

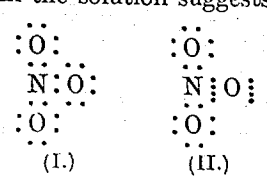
Law of radiation. (SIR) O. J. LODGE (Nature, 1926, **117**, 891).

Radiation. (SIR) O. J. LODGE (Nature, 1926, **118**, 81).

Rectilinear diameter of helium. E. MATHIAS, C. A. CROMMELIN, H. K. ONNES, and J. C. SWALLOW (Ann. Physique, 1926, [x], **5**, 359—370).—See A., 1925, ii, 468.

Molecular spectrum of carbon dioxide. J. W. ELLIS (Nature, 1926, **118**, 82—83).—The frequencies of the two weaker carbon dioxide absorption bands at 2·73 and 2·02 μ are approximately represented by $\nu_a'+2\nu_a$ and $\nu_a'+4\nu_a$, respectively, where ν_a' and ν_a are the frequencies of the bands at 4·25 μ and 14·66 μ. Both for the absorption bands, and the corresponding emission bands, the calculated frequencies are somewhat larger than the observed frequencies, as may be anticipated. The frequencies of the bands in absorption and emission are tabulated. A. A. ELDRIDGE.

Mutability of absorption spectra in solutions in relationship to the distribution of charge of the molecules and connexion between absorption and refraction. III. G. SCHEIBE [with R. RÖMER and G. RÖSSLER] (Ber., 1926, **59**, [*B*], 1321—1334; cf. A., 1925, ii, 352).—Measurement of the absorption spectra of potassium iodide in water, 9*N*-calcium chloride solution, 9*N*-magnesium chloride solution, and ethyl alcohol, of sodium nitrate in water and 10*N*-calcium chloride, and of potassium nitrate in water, 5*N*-calcium chloride, 5*N*-strontium chloride, 5*N*- and 7·6*N*-magnesium chloride, and 7·6*N*-magnesium bromide are recorded. The differing manner in which the two prominent bands of the nitrate ion are influenced by variation of the anions and cations in the solution suggests that the nitrate ion is itself dipolar and that the electronic structure consists of the form I in equilibrium with a very small proportion of form II. A similar existence of two chromophors in simply constructed molecules is found in aldehydes and ketones and in carboxylic esters. In saturated and unsaturated hydrocarbons the polarity is so slight that a uniform distribution of the electrons belonging to a C—C linking must be assumed. If, however, a new atom is introduced, dipolar character is immediately developed, *e.g.*, in alcohols in which the oxygen has a greater affinity for electrons than carbon and appears as the negative part of the molecule of which carbon is positive. The connexion between refraction and absorption is discussed.
H. WREN.


(I.) (II.)

Ultra-violet spectra of praseodymium, neodymium, samarium, europium, and erbium. J. H. GARDINER (J.C.S., 1926, 1518—1522).—The absorption spectra of 1 : 10 solutions of the nitrates of lanthanum, ytterbium, gadolinium, terbium, thorium, cerium, and scandium have been photographed without disclosing bands between 350 and 400 μμ. Praseodymium shows three bands the approximate centres of which are 482, 468, and 442 μμ. Neodymium shows 474·5 (faint) and 353, 350·5, 346·7 μμ. Samarium has a dominant band head at 402 μμ and faint bands at 479, 375, 362, and 344 μμ. Europium has faint but sharp bands at 393 and 361 μμ. Erbium exhibits a strong band at 485 and a very faint band at 449 μμ; the dominant band at 379 μμ is sharp on the less refrangible side; a faint band at 363 μμ and a faint line at 365 μμ are also shown. Erbium oxide appears to be weakly radioactive and europium oxide less so. R. A. MORTON.

Explosion spectra of mercury fulminate and some azides. A. PETRIKALN (Z. Physik, 1926, **37**, 610—618).—The explosion spectrum of mercury fulminate shows the resonance line of mercury, 2536, and the triplet series. The azides of calcium, strontium, and barium gave the triplet series and some of the lines of the singulet series. Zinc azide gave only the first triplets of the diffuse and sharp series. In addition to these lines of the metals, the fulminate gave the cyanide bands, the azides gave the long wavelength oxide bands which are those in the visible obtained in the flame spectra. E. B. LUDLAM.

Spectral sensitivity of chromates with organic substances. J. M. EDER (Z. Physik, 1926, **37**, 235—237; cf. Plotnikov and Karsulin, this vol., 585).—The action of light on chromated gelatin begins at 550, reaches a maximum between 470 and 430, and becomes very slight beyond 380 μμ. This is in contrast with Plotnikov's result with collodion sensitised with potassium dichromate and cresyl-blue-2B.S., in which the action was found to begin in the yellow at 595 and reached a maximum in the green between 540 and 580 μμ. E. B. LUDLAM.

Ultra-violet absorption spectrum of formaldehyde vapour. New type of spectrum for Y-shaped molecules. V. HENRI and S. A. SCHOÚ (Compt. rend., 1926, **182**, 1612—1614).—The ultra-violet absorption spectrum of formaldehyde vapour consists of a large number of bands the fine structure of which corresponds with quantisation formulæ for symmetrical molecules with two different moments of inertia. The distances between hydrogen atoms and between the carbon and oxygen atoms are 1·3 and 0·9 Å., respectively. The above type of spectrum is

common to all Y-shaped molecules, *e.g.*, acetone and carbonyl chloride. J. S. CARTER.

Infra-red absorption in ethers, esters, and related substances. A. W. SMITH and C. E. BOORD (J. Amer. Chem. Soc., 1926, **48**, 1512—1520).—The absorption maxima between 0·9 and 2·4 μ are recorded for a series of ethers and esters. The positions of the bands are not appreciably altered by change in molecular structure and are characteristic of the hydrogen–carbon linkings (cf. Ellis, A., 1924, ii, 219). The decrease in the intensity of the bands in certain compounds is probably due to a decrease in the number of such linkings in the molecule.

S. K. TWEEDY.

Spectrochemistry in the infra-red. X. Influence of intermolecular action on the form of infra-red absorption bands in liquids. XI. Double band of alcohols at 3·0—3·4 μ. XII. Form of the bands of alcohols in relation to the number and position of hydroxyl groups in the molecule. XIII. Absorption coefficients relative to CH for bands of alcohols. G. B. BONINO (Gazzetta, 1926, **56**, 278—286, 286—291, 292—295, 296—300; cf. A., 1925, ii, 351, 1032).—X. Theoretical. The energy of an oscillator such as the CH group will at any moment be the sum of the energy of the oscillator considered as isolated and a term representing intermolecular energy relative to the group. In consequence, the oscillator will absorb infra-red radiation in a continuous band about the frequency $\nu_m=(2E_{o\ kin}+M)/nh$, where $2E_{o\ kin}$ is the mean kinetic energy of the isolated oscillator and M the mean of the intermolecular energy term.

XI. Just as substances containing the CH oscillator exhibit an absorption band at 3·4 μ, those containing hydroxyl have a second at 3·0 μ. From the results of Ransohoff (Diss., Berlin, 1896) with a series of alcohols, it is calculated that each replacement of hydrogen by hydroxyl in the chain causes a regular increase in the absorption coefficient at 3·0 μ, whilst that at 3·4 μ decreases. It is anomalous that the absorption coefficient at 3·4 μ is greater for glycerol than for propylene glycol.

XII. Absorption curves are plotted from the results discussed above. The width of the 3·0 μ band at half its height increases from ethyl to propyl alcohol, and from ethylene to propylene glycol, but only very slightly from the last to glycerol.

XIII. [With I. RAGAZZI.] On repeating Ransohoff's work with propylene glycol and glycerol, the anomaly mentioned in XI vanishes; the former now takes its place between the latter and propyl alcohol.

E. W. WIGNALL.

Ultra-violet absorption of a pair of isomeric monobromoheptenes. A. KIRRMANN and H. VOLKRINGER (Compt. rend., 1926, **182**, 1468—1470).—The ultra-violet absorption of the following two isomeric bromo-$\Delta^{\alpha\beta}$-heptenes has been investigated: (1) $C_5H_{11}\cdot CH{:}CHBr$, consisting of a mixture of two geometrical isomerides, and (2) $C_5H_{11}\cdot CBr{:}CH_2$. The curves connecting frequency and log. molecular absorption coefficient show points of inflexion corresponding with elementary maxima in the following regions for the two substances: (1) 2125 and 1975; (2) 2170 and 1950 Å. Between 1874 and 1980 substance (2) has the higher coefficient of absorption, but the difference changes sign at 1980. The curves generally resemble those of Henri (A., 1925, ii, 1137) for ethylenic acids, and indicate that the double linking is stronger in (2) than in (1), and that the same applies to the linking between carbon and bromine. The following physical constants are determined: (1) b. p. 54—56°, d_4^{21} 1·1581, n_D^{21} 1·4612; (2) b. p. 46·0—46·2°, d_4^{21} 1·1598, n_D^{21} 1·4590. W. HUME-ROTHERY.

Ultra-violet absorption spectra of hydroxybenzene derivatives. (MLLE.) E. KEPIANKA and L. MARCHLEVSKI (Bull. Inter. Acad. Polonaise, 1926, *A*, 75—92).—The ultra-violet absorption spectra of the dihydroxybenzenes in aqueous solution show the same general character as that of phenol, although the absorption is more intense and the single band is extended further into the red, the extension increasing in the order *m*-, *o*-, *p*-. Introduction of a methyl group into phenol increases the intensity of absorption and to some extent alters its character; the absorption band is shifted towards the red, markedly so in *p*-cresol. In alcoholic solution, the absorption band both of phenol and the cresols is moved towards the red. The hydroxybenzoic acids in comparison with benzoic acid show an increased intensity of absorption, especially towards the less refrangible part of the spectrum. In each case, introduction of the hydroxyl group has a bathochromic effect, whilst with *p*-hydroxybenzoic acid the character of the spectrum is changed. Beer's law is considered to be valid for these substances when changes in concentration not too great are involved. M. CLARK.

Absorption spectra of some naphthalene derivatives in vapour and solution. H. G. DE LASZLO (Proc. Roy. Soc., 1926, **A**, **111**, 355—379; cf. A., 1924, ii, 513).—The derivatives of naphthalene containing the groups CH_3, Cl, Br, OH, CO_2H, CN, and NH_2 show a marked difference in absorption spectra according as to whether the groups are in the α- or β-positions. The spectra of the β-derivatives are more like that of naphthalene, consisting of two clearly differentiated sections, both as regards position and intensity; the first part is always more shifted towards the red than the second part when compared with naphthalene. In the α-spectra this is reversed, the second part having a greater shift towards the red than the first. β-Naphthol has its second part shifted towards the ultra-violet, which is quite anomalous. The first parts of the β-spectra always contain better defined, more intense and numerous bands than the α-spectra. They also contain one very prominent band which corresponds with the carbon band of naphthalene. The hexane solution (solvent) spectra are always further towards the red than the vapour spectra. The average intensity of the β-spectra (the first part) increases in the order Br, Cl, CH_3, CN, CO_2H, OH, and NH_2. The second parts of all derivatives except the naphthylamines have the same intensity as naphthalene. The following derivatives possess a fine structure in the state of vapour: β-CH_3, α- and β-OH, β-NH_2, β-Br, and β-Cl. The following have a sharp band representing

the carbon band of naphthalene: α-Br, α- and β-CN, and α-CH_3. The moments of inertia in g. cm.$^2 \times 10^{-40}$ calculated from the infra-red absorption bands are: α-naphthol 94·8, α-naphthylamine 59·0, β-naphthol 142·5, β-naphthylamine 80·4. W. THOMAS.

Spectrophotometric investigation of colouring matters of blood. J. STRUB (Z. wiss. Phot., 1926, **24**, 97—133).—Curves and tables are given showing the absorptions of aqueous oxyhæmoglobin in 12 concentrations for 33 positions in the visible spectrum; centrifuged and uncentrifuged blood solution for 26 spectral positions; aqueous carboxyhæmoglobin and the corresponding oxyhæmoglobin for 33 positions; hæmatoporphyrin in pure, concentrated sulphuric acid in 6 concentrations and for 33 points in the spectrum. The magnitude of the errors of observation, and their dependence on absorption, intensity, and wave-length, using a König-Martens spectrophotometer, were studied, making use of the absorption curve of oxyhæmoglobin. The principle is given for a spectrophotometric method of determining the age of blood spots on cloth, depending on the conversion of oxyhæmoglobin into methæmoglobin. Tests of Beer's law for oxyhæmoglobin and hæmatoporphyrin gave mean deviations of 6% and 11%, respectively, for the whole spectrum. Dilute oxyhæmoglobin solutions absorb more than is demanded by Beer's law, but with increasing dilution the theoretical absorption is approached, and is passed with the most dilute solution examined (1 : 4000). With acid hæmatoporphyrin, dilute solutions absorb more than is expected, and the deviation from the theoretical increases with progressive dilution. The deviation also varies with wave-length. W. CLARK.

Quenching of the resonance fluorescence of mercury by the addition of gases. G. CARIO and J. FRANCK (Z. Physik, 1926, **37**, 619—624; cf. Stuart, *ibid.*, 1925, **32**, 262).—Hydrogen is one hundred times as effective as nitrogen in reducing the resonance fluorescence of mercury. This is because the energy of the mercury in the $2p_2$ state is sufficient to dissociate the hydrogen molecule by collisions of the second kind. With nitrogen the energy is insufficient; what happens is that the mercury passes into the metastable $2p_3$ state, in which it can exist for about 1/200 sec. Absolutely pure nitrogen should produce almost no effect at the ordinary temperature, but it would be too difficult to obtain it pure enough to test the theory. Mercury in the $2p_3$ state can pass into the higher $2p_2$ state by collisions of the first kind, receiving the additional energy to pass into the form capable of emitting radiation, but at ordinary temperatures this happens seldom. The authors therefore measured the intensity of the fluorescence in presence of nitrogen at different pressures at 18° and at 750°. At the higher temperature, even at a pressure of 45 mm., there is practically no quenching. Similar experiments were repeated with hydrogen, and there was no reduction of the quenching action at the high temperature. When nitrogen was added to the hydrogen, the quenching action was greater than with pure hydrogen, for both $2p_2$ and $2p_3$ states possess sufficient energy to dissociate the hydrogen; therefore the $2p_3$ atoms do not revert at all to the $2p_2$ state and less energy is radiated. E. B. LUDLAM.

Degree of polarisation of resonance fluorescence of sodium vapour excited by the D_2-line. G. L. DATTA (Z. Physik, 1926, **37**, 625—638).—At a pressure of 10^{-6} mm. the polarisation of the light is 33%; the difference between this result and the value according to Heisenberg's theory is attributed to the influence of neighbouring atoms. On this assumption, the radius of the sphere of action is of the order 10^{-4} cm. In magnetic fields of 150 gauss and 250 gauss, the polarisation was slightly below 60%, indicating a reduction of the radius of the sphere of action. Potassium vapour produced an effect on the polarisation similar to that of sodium vapour, but argon at a pressure of 0·5 mm. produced no appreciable effect. E. B. LUDLAM.

Activated fluorescence and the Döppler effect. F. RASETTI (Nature, 1926, **118**, 47).—Illumination of a mixture of mercury and sodium vapours with light from a water-cooled mercury lamp yields a visible glow of *D*-light; the *D*-lines were strongly reversed and had Δλ 0·16 Å. The value calculated from the correspondence between the kinetic energy and the difference between the excitation potentials of mercury and sodium is 0·17 Å. The theory of activated fluorescence is also supported by visual observations of the distribution of intensity. A. A. ELDRIDGE.

Excitation of atoms and molecules to emission of light by means of illumination. II. A. TERENIN (Z. Physik, 1926, **37**, 98—125; cf. *ibid.*, 1925, **31**, 26).—The vapours of arsenic and antimony, heated at 1100°, were exposed to the light from an arc of the same metal and the spectrum of the light so excited was photographed. By throwing a vertical spectrum of the exciting light upon the vapour and receiving the light produced by it on a vertical slit of a spectrograph, points were obtained on a horizontal line corresponding with monochromatic excitation. Conclusions are reached as to the scheme of energy levels for antimony. The only line obtained from arsenic vapour was 2288 Å. The thallium line 5351 does not produce fluorescence of thallium vapour; the emission of 5351 is due to absorption of 3776. Experiments are described on the optical excitation of mercury lines. Illumination of sodium iodide heated at about 600° with light of wave-length shorter than 2500 produced the *D*-line, and in certain cases the lines 3302 and 3303, but no iodine lines. It is suggested that the light dissociates the sodium iodide into atoms and that the sodium atom is then in the excited state. E. B. LUDLAM.

Fluorometry. II. Relation between fluorescence and hydrogen-ion concentration. L. J. DESHA, R. E. SHERRILL, and L. M. HARRISON (J. Amer. Chem. Soc., 1926, **48**, 1493—1500; cf. Desha, A., 1920, ii, 552).—The maximum change in the intensity of fluorescence of certain sulphonic acids and quinine occurs within a range of 0·2 p_H unit, which is characteristic of each substance. Even at equal hydrogen-ion concentrations, the total salt concentration affects the intensity of fluorescence. The fluorescence of the compounds investigated is

inhibited by chlorine ions and is probably related to the ionisation of the substances. S. K. TWEEDY.

Inhibition of the glow of phosphorus. H. J. EMELÉUS (J.C.S., 1926, 1336—1344).—Rayleigh's experiments on the glow of phosphorus (A., 1923, ii, 755) have been extended. Contamination of air with ethylene, benzene, chloroform, and aniline, all of which act as strong inhibitors, makes it easier to blow the glow from a phosphorus surface. The requisite blast of air acts as a measure of the rate of propagation of the glow in the contrary direction. An increase of temperature reduces the efficiency of the poisons. These inhibitors are analogous in their action with oxygen: both processes hinder the propagation of the glow. The "glow-temperature" (initial appearance of glow) of phosphorus in various ethylene–air and ethylene–oxygen mixtures has been systematically investigated. Inhibition extends to 90°, which is much above the ignition temperature. The temperature at which the slow non-luminous oxidation is replaced by a sudden glow does not depend on whether air or oxygen is used as a diluent for ethylene.
R. A. MORTON.

Yield of visible light by excitation of phosphors by slow cathode rays (cathodofluorescence). W. KORDATZKI, A. SCHLEEDE, and F. SCHROETER (Physikal. Z., 1926, **27**, 392—401). The term "energy-economy" is defined as the ratio of visible radiation energy to the entire radiation, whilst the term "photometric-economy" indicates the ratio of surface brightness to the entire radiation. The principal results of the investigation for energy-economy and photometric-economy, respectively, are as follows: Carbon lamp, 3%, 0·4%; tungsten lamp, 8%, 1·7%; "Nitra" lamp, 14%, 2·8%; ZnS—Cu, 1·5%, 1·0%; ZnS,CdS—Cu, 1·0%, 0·8%; Zn_2SiO_4—Mn, 0·26%, 0·21%; MgS—Ce, 0·21%, 0·15%; SrS,CaS—Bi, 0·08%, 0·04%, the customary notation for the phosphors being used. R. A. MORTON.

Energy levels of the carbon monoxide molecule. O. S. DUFFENDACK and G. W. FOX (Nature, 1926, **118**, 12—13).—Although a part of the third positive bands appears at 10·2 volts (cf. Johnson, this vol., 334), another system ("3A"), constituted by the bands at 2295·2, 2389·0, 2489·9, 2597·1, and 2711·35 Å. having the same final states as the former, appears at 11·1 volts. The remaining bands may then be arranged in two series having the same final states, and having initial states differing by 2210 cm.$^{-1}$, the difference being ascribed to a vibrational shift. Using pure carbon dioxide, the third positive bands are observed only under conditions indicating dissociation with formation of carbon monoxide. Possibly the carbon monoxide molecule has two distinct types of spectral terms corresponding with different types of electronic orbits. A. A. ELDRIDGE.

Energy levels of the carbon monoxide molecule. R. C. JOHNSON (Nature, 1926, **118**, 50).—The 3*A* positive bands of Duffendack and Fox (preceding abstract) are those previously interpreted as an $n'=4$ sequence; the view that their initial level is $2p_{123}$ (Birge, this vol., 224, 337) is, however, preferable.
A. A. ELDRIDGE.

Dissociation of hydrogen molecules by mercury atoms in the metastable state 2^3P_0. E. MEYER (Z. Physik, 1926, **37**, 639—657).—Mercury atoms are obtained in the metastable state by first exciting them by means of radiation 2537 Å. to the unstable 2^3P_1 state; when these collide with nitrogen they lose energy and fall to the 2^3P_0 state, the nitrogen acquiring only a small portion (0·2 volt) of their energy. The metastable atoms are capable of dissociating the hydrogen, and, on account of their long life compared with those in the unstable state, the rate of the dissociation of the hydrogen follows a different course in the two cases. Different pressures of both hydrogen and nitrogen were used, and the behaviours at 18° and at 45° contrasted. The rate of dissociation was measured by the thermal conductivity method, using two Pirani gauges arranged as a bridge. In the presence of hydrogen alone, the rate of dissociation falls off steadily with decreasing pressure of the gas; when nitrogen is present, there is practically no diminution in the rate until a very low pressure is reached, at which traces of impurities or some other agency may come into play. Thus, at low pressures the rate is much greater in a nitrogen–hydrogen mixture than in pure hydrogen, due to longer life of the metastable atom and the increased chance of a collision with a hydrogen atom. E. B. LUDLAM.

Photo-electric effect in crystals. P. LUKIRSKY, N. GUDRIS, and L. KULIKOWA (Z. Physik, 1926, **37**, 308—318).—Finely powdered crystals of fifteen halogen salts were suspended between the plates of a condenser, by Millikan's method, and exposed to the light from sparks between a variety of metals. The crystals became positively charged, indicating the loss of an electron, and the charge on the condenser plates was altered so that they retained their position. The increased voltage on the plates gave a measure of the photo-electric effect; the threshold value for the effect was deduced from the wave-length of the line in the spectrum of the metallic spark which just gave an observable value. For lithium fluoride and cadmium bromide the threshold wave-length was shorter than 1860 Å.; for all the others it lay between 2000 and this value. The bearing of these results on lattice energy, electron affinity, and photo-chemical change in solids is discussed. E. B. LUDLAM.

Specific inductive capacity and ethylenic stereoisomerism. J. ERRERA and M. LEPINGLE (Bull. Soc. chim. Belg., 1926, **35**, 135—138; cf. Walden and Werner, A., 1924, ii, 648).—The dielectric constants ϵ of pairs of ethylenic stereoisomerides have been measured. The following values are found at 20°: dichloroethylenes, *cis* 9·22, *trans* 2·25; diiodoethylenes (at 83°), *cis* 4·46, *trans* 3·19; ethyl β-chlorocrotonates, *cis* 7·67, *trans* 4·70. For these three known pairs of isomerides, ϵ and the molar polarisation $P=(\epsilon-1)M/(\epsilon+2)d$ are greater for the *cis*- than for the *trans*-forms. α-Bromo-Δ^{α}-butenes, b. p. 94·6—94·8°, 5·89, b. p. 86·0—86·2°, 5·05; β-bromo-Δ^{β}-butenes, b. p. 93·6—93·9° (CH_3 and Br *trans*) 6·76, b. p. 85·8—85·9° (CH_3 and Br *cis*) 5·38; crotononitriles, b. p. 107·7—108·2°, 36·08, b. p. 121·7—122·1°, 28·08.

Densities and refractive indices of the specimens used are given, and the values of $[R_L]_D$ and of P are calculated. E. W. WIGNALL.

Dielectric constants of good conducting materials. H. ZAHN. **Dielectric constants of good conducting solutions of electrolytes.** H. HELLMANN and H. ZAHN (Ann. Physik, 1926, [iv], **80**, 182—190, 191—214; cf. A., 1925, ii, 1117).—A new method of investigating the dielectric constant of materials in which the relatively high conductivity has hitherto proved a serious obstacle, has been devised and examined theoretically and experimentally. It depends on the connexion between the decrement of an oscillating system and the magnitude of the capacity used. The method has advantages over the resonance process, and the upper limit of conductivity ($\sigma=0{\cdot}1$) for which it is applicable is merely a matter of technical difficulty. R. A. MORTON.

Perforation of glass. (MLLE.) L. INGE and A. WALTHER (Z. Physik, 1926, **37**, 292—301).—The voltage necessary to perforate microscope object and cover glasses was measured at various temperatures up to 300°. From the temperature of liquid air up to about 50° there is no influence of temperature, but above a critical temperature, different for different specimens, the variation of *E.M.F.* with temperature is in accord with the theory of heat. For rock-salt the critical temperature lies between 220° and 250°. E. B. LUDLAM.

Additive rule for the molecular volumes of crystallised inorganic compounds. E. MOLES (Anal. Fis. Quím., 1926, **24**, 199—209).—By means of Biltz's additive rule, the author finds the molecular volumes of pyridine and ethylenediamine to be 65·4 and 56·0, respectively. The values, calculated for absolute zero by Lorenz's rule, are 65·0 and 55·0, respectively. It is concluded that the molecular or atomic volumes of radicals or atoms in perfect crystalline complexes may be generally taken as coinciding with the values calculated for absolute zero. Applying the additive rule, it follows that in chloro-acids, such as chlorostannic acid, hydrochloric acid occurs as the hydrate, $HCl,2H_2O$. This would imply $SnCl_4,(HCl,2H_2O),4H_2O$ for chlorostannic acid. From a comparative study of the molecular volumes of the ethyl sulphates and sulphates of the rare earths, it is concluded that the former may be considered as having the general formula $R_2(SO_4)_3,8H_2O+3Et_2SO_4,10H_2O$. G. W. ROBINSON.

Volume contraction in the formation of aromatic compounds at the absolute zero. W. HERZ (Z. anorg. Chem., 1926, **153**, 339—340; cf. this vol., 559).—Using van Laar's equation (Z. anorg. Chem., 1918, **104**, 134) the density at absolute zero of carbon in aromatic compounds is found to be 3·01, and the atomic volume 3·99. The molecular volume of aromatic compounds at absolute zero calculated therefrom is always smaller than the sum of the atomic volumes of the constituent atoms. The contraction has been calculated for a number of aromatic hydrocarbons, halogen derivatives, etc., and expressed as a percentage of the molecular volume. M. CARLTON.

Dispersion of the electric birefringence of camphor. R. DE MALLEMANN (Compt. rend., 1926, 182, 1534—1536).—The dispersion and specific birefringence of camphor in light petroleum solution have been determined by the method previously described (Z. Physik, 1924, **22**, 1), a continuous field being substituted for the interrupted field. For the rays 436, 546, and 578 of the mercury arc, values for the dispersion of 1·425, 1·07, and 1·0, respectively, have been obtained for active camphor, and 1·40, 1·05, and 1·0 for inactive camphor. The corresponding specific birefringences are 153·7 and 158·6, respectively, 159 being obtained with the interrupted field. Active and inactive camphor have therefore almost the same specific birefringences, and normal dispersion. J. GRANT.

Anomalous dispersion and absorption of electric waves. II. S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 83—89; cf. this vol., 560).—The dielectric constants and absorptions for electromagnetic waves of 9·5 metres are recorded for glycerol, alcohol, and ether between 65° and −67°. The preliminary results previously described are confirmed. The absorption for glycerol attains a maximum value at a temperature slightly below that at which the temperature coefficient of the dielectric constant is a maximum. S. K. TWEEDY.

Rotatory power and p_H of complex molybdomalates. Physico-chemical applications of the polarimeter. E. DARMOIS (Bull. Soc. chim., 1926, [iv], **39**, 723—741).—The change in the rotatory power of the complex molybdomalates by the addition of acids is due to the decomposition of the complex; the ability to affect the complex does not seem to be wholly dependent on the strength of the acid. Ethyl oxalate added to an aqueous solution of the complex produces a gradual change in the rotatory power, and the rate of hydrolysis can be obtained from the rate of this change. It is found that ethyl oxalate is hydrolysed by water in two stages to give (*a*) the acid ester, (*b*) the free acid. The rate of hydrolysis of ethyl oxalate in the presence of various acids can also be measured. W. THOMAS.

Influence of the viscosity on the specific rotation of certain active substances. P. ACHALME and J. ACHALME (Compt. rend., 1926, **182**, 1539—1541).—The effects of the addition of various amounts of a viscous, saturated solution of citric acid on the specific rotation of optically active solutions, and of a solution of constant viscosity on optically active solutions of various concentrations, have been studied. The concentration of active material exercises no direct effect on the specific rotation, but acts indirectly by increasing the viscosity of the medium. J. GRANT.

Dependence of the rotatory power of glucosamine on hydrogen-ion concentration. E. VELLINGER (Compt. rend., 1926, **182**, 1625—1627; cf. A., 1925, ii, 356, 964).—The rotatory power of glucosamine has been examined in its relation to the p_H value of its aqueous solutions; the relationship appears to be similar in character to that shown by the amphoteric compound asparagine (A., 1925, ii,

743). If the amphoteric nature of glucosamine be assumed, the rotatory power is equal to the sum of the rotations of the ions and of the undissociated molecule, and is represented accurately by a three-term equation involving hydrogen-ion concentration and the two dissociation constants of glucosamine. The isoelectric point of glucosamine is at p_H 9·9.

M. CLARK.

Interferometry. I. Zeiss-Löwe liquid interferometer. II. Examination of very dilute solutions. W. BARTH (Z. wiss. Phot., 1926, **24**, 145—158, 158—166).—I. A description of the method of using the above interferometer to determine the refractive index of a liquid.

II. The refractive indices of very dilute aqueous solutions of carbamide, mercuric cyanide, magnesium sulphate, and potassium chloride have been measured by means of the interferometer with an accuracy much greater than that attainable with the dipping refractometer. The relation between the concentration and the refractive index for the first two substances differs from that for the last two.

R. CUTHILL.

Polarisation of light in sulphur suspensions. G. I. POKROWSKI (Z. Physik, 1926, **37**, 172—178).—The polarisation produced by the scattering of light in a turbid medium is defined as positive when the greater component vibrates normal to the plane containing the incident and scattered radiation, negative when the component in this plane is the greater. Sulphur was precipitated by addition of very small quantities of sulphuric acid to sodium thiosulphate, and the change in polarisation with increase in size of the particles was examined. As the size increased, an inversion of the polarisation took place, in accordance with Rayleigh's theory of electromagnetic scattering. The variation of polarisation with angle of scattering showed large deviations from the calculated values, but this is attributable to the irregularity in size which the particles assume after the lapse of considerable time. E. B. LUDLAM.

Influence of molecular structure on dielectric polarisation. J. ERRERA (Bull. Soc. chim. Belg., 1926, **35**, 154—157).—Molar polarisation P is the sum of terms due to electronic motions (P_E), and to the atoms and whole molecules (P_A and P_0, respectively) (cf. this vol., 225; Ebert, A., 1925, ii, 14). $P_0+P_A=P-P_E$, and $P_E=[R_L]_D$. The values of (P_0+P_A) obtained from this relation are calculated for the substances investigated by Errera and Lepingle (cf. this vol., 777). In agreement with the view that the greater the dipolar character of the molecule the greater the value of (P_0+P_A), this term is found to be higher for *cis*- than for *trans*-isomerides, particularly with dichloroethylenes, in which the dipolar character is most pronounced. E. W. WIGNALL.

Polarisation of a medium and its molecular structure. Electric moments of dihalogen derivatives of benzene. J. ERRERA (Compt. rend., 1926, **182**, 1623—1625; cf. this vol., 225).—The following electric moments have been obtained: *o*-dichlorobenzene, 2×10^{-18}; *m*-dichlorobenzene, $1{\cdot}21\times10^{-18}$; *o*-dibromobenzene, $1{\cdot}52\times10^{-18}$; *o*-di-iodobenzene, $1{\cdot}32\times10^{-18}$; *m*-di-iodobenzene, $1{\cdot}01\times10^{-18}$. The corresponding *p*-compounds have zero moment. There is, thus, a correspondence between *cis*- and *trans*-disubstituted ethylenic compounds and *o*- and *p*-disubstituted benzene derivatives, the moments of the *cis*-ethylenic compounds being, however, smaller than those of the corresponding *o*-derivatives of benzene. The ratio of the moments of *o*- and *m*-compounds is 1·65 for dichlorobenzene and 1·31 for di-iodobenzene, indicating an increased deformation of the benzene ring with increasing atomic weight of the substituent. The fact that *p*-derivatives have zero moment is an argument against the polar theory of the structure of benzene.

J. S. CARTER.

Dipole moment and molecular structure. K. HÖJENDAHL (Nature, 1926, **117**, 892).—Tabulated results are given for the experimental dipole moment, calculated for infinite dilution in benzene solution, the association constant, and the theoretical dipole moment (calculated as the vector sum of the moments of monosubstituted benzene derivatives) for a number of di- and tri-substituted benzene derivatives. The relative directions of the component moments indicate that chlorine, bromine, and the nitro-group are similarly charged, the methyl group being oppositely charged. A. A. ELDRIDGE.

Born's dipole theory of anisotropic fluids. W. KAST (Z. Physik, 1926, **37**, 233; cf. Szivessy, A., 1925, ii, 1123).—Anisotropic liquids (azoxyanisole, and azoxyphenetole, when melted) possess considerable conductivity, with a number of ions about the same as distilled water. Free electric charges on the surface, which would be produced by the action of a magnetic field on dipoles, would be compensated very rapidly by charges on ions; the free charges would exist at most for 10^{-4} sec. It is improbable that a quadrant electrometer would register such a brief charge. The magnetic field would also require a much longer period to attain its strength. E. B. LUDLAM.

Electrical structure of molecules, particularly of mesomorphic substances (anisotropic fluids). E. BAUER (Compt. rend., 1926, **182**, 1541—1544).—The elongation of molecules, and the existence of an optical axis along the axis of elongation, according to Born's hypothesis, are admitted. The variation of the dielectric constant of nematic substances in a magnetic field indicates that their magnetic moments are perpendicular, or almost perpendicular, to the molecular chain. This accounts for the thread structure often observed through crossed Nicols, since in an electric field these run parallel to the field. In smectic liquids the electric moment is parallel to the axis, whilst in paramagnetic substances the vectors of the electric and magnetic moments are assumed to be perpendicular. This theory accounts for many experimental facts. J. GRANT.

Diatomic molecules. F. J. VON WISNIEWSKI (Z. Physik, 1926, **37**, 126—136).—The empirical formula, $K=1+3\sqrt{3}\pi.N_0d^3$ is found to be in satisfactory agreement with data for hydrogen chloride, bromide, and iodide, carbon monoxide, and nitrogen;

K is the dielectric constant, N_0 is Loschmidt's number, d the diameter of the molecule. The Bohr–Debye model of these gases is found to be satisfactory in regard to refractive index, ionisation potential, distance apart of the atoms, and moment of inertia. The generally accepted theory of dielectrics, does not however, lead to the above equation.

E. B. LUDLAM.

Rare earths. XXIV. Theory of colour. L. F. YNTEMA (J. Amer. Chem. Soc., 1926, **48**, 1598—1600).—Differences in physical properties, such as colour, must be due to different arrangements of the electrons in inner shells or levels; the presence of colour in rare-earth elements is due to an incomplete kernel; in each instance where the kernel is complete the element has no absorption bands. A relationship between the absorption spectra is indicated which may be expected from analogy with X-ray and spark spectra.

M. CARLTON.

Molecular diameters at the b. p. S. MOKRUSCHIN (Z. anorg. Chem., 1926, **153**, 273—275).—The diameters of the molecules of various elements and organic compounds at the b. p. have been determined from the equation $d=k_s\sqrt[3]{(M/d_s)}$, where M is the mol. wt. of the substance in the state of vapour, d_s the density at the b. p., and k_s is a constant ($1{\cdot}79\times10^{-8}$). The values obtained for d are in good agreement with those calculated by Jäger from the kinetic energy of the molecules and the surface energy of the liquid, and in fair agreement with those of Sirk (A., 1925, ii, 184).

A. R. POWELL.

Rare earths. XXIII. Element 61. II. X-Ray analysis. J. A. HARRIS, L. F. YNTEMA, and B. S. HOPKINS (J. Amer. Chem. Soc., 1926, **48**, 1594—1598).—An X-ray spectrograph of the Uhler type was used; the L-emission spectrum only was examined, the oxide being fused to the target. Two series of experiments were made with samples taken (i) from the least soluble fraction of the double magnesium nitrate, and (ii) from fractions of the bromate series which first gave the 5816 Å. band. Lines are found in the X-ray emission spectra corresponding with the theoretical positions for $L\alpha_1$ and $L\beta_1$ of element 61. The mean value of $L\alpha_1$ agrees within 0·0004 Å. with the value calculated from Siegbahn's precision values. The single reading for $L\beta_1$ differs from the calculated value by 0·0040 Å. The name "illinium" is suggested for this element.

M. CARLTON.

New element of atomic number 61. Illinium. B. BRAUNER (Nature, 1926, **118**, 84—85).—Historical.

A. A. ELDRIDGE.

New elements. I—V. F. H. LORING (Chem. News, 1926, **132**, 407—410).—A further discussion of the results of earlier work on elements 43, 75, 85, 87, and 93.

A. R. POWELL.

Distinguishing between ionic and atomic lattice by means of the X-ray spectrograph. A. E. VAN ARKEL (Z. Physik, 1926, **37**, 672—675).—The determination of the scattering power of the atoms by comparison of neighbouring lines in the X-ray spectra is correct only when the extension in space of the atoms can be neglected. This is not true for elements of low atomic number, and in these cases the relative intensities are a function of the angle of reflexion; the correct value is obtained by extrapolating the observed values for the angle zero. When this correction is applied, it is possible to decide whether the lattice is composed of atoms or ions. The case of titanium nitride is discussed as an example.

E. B. LUDLAM.

Effect of crystal size on intensity of X-ray reflexion. R. J. HAVIGHURST (Proc. Nat. Acad. Sci., 1926, **12**, 375—380; cf. Darwin, A., 1922, ii, 416).—Experiments on the dependence of the intensity of X-ray reflexion on the size of the reflecting crystal for powdered crystals of sodium chloride and calcium fluoride show that primary extinction is absent in crystals grown from solution and ground to less than 10^{-3} cm. in thickness; such powder-measurements may be used in the determination of electron distributions. With crystals as poor as the alkali halides, single crystal measurements similar to those of Bragg, James, and Bosanquet (A., 1922, ii, 703) are satisfactory after correction for secondary extinction. Although powder-measurements with calcite are difficult to carry out, measurements using ground calcite and also precipitated calcium carbonate show that the more intense reflexions measured by W. H. Bragg (Phil. Trans., 1915, **A**, **215**, 253) are enormously in error because of extinction.

J. S. CARTER.

Intensity of reflexion of X-rays by lithium, sodium, and calcium fluorides. R. J. HAVIGHURST (Proc. Nat. Acad. Sci., 1926, **12**, 380—385; cf. preceding abstract).—Since the scattering power for X-rays of an atom in a crystal varies with the angle of scattering in a manner determined by the electron distribution, measurements have been made of the scattering power of powdered crystals of lithium, sodium, and calcium fluorides in an attempt to determine the distribution of electrons in the four atoms concerned. The present experiments lead to relative values only of the atomic structure factor, but an attempt has been made to make these values absolute. The atomic scattering curves, which are now being examined by a method involving a Fourier analysis, show that the curves for fluorine from different compounds are nearly alike, indicating that the fluorine ion is in a force field of the same magnitude in all three crystals. It is apparent from the scattering curves that the assignment of scattering power to atoms in accordance with their total number of electrons is only a rough approximation. This is especially so in the cases of oppositely charged ions, the excess of positive or negative charge producing a tightening or loosening of the electron atmosphere, which affects the scattering properties. A system with electrons nearer its centre has a larger scattering power than one in which the electrons are less tightly bound.

J. S. CARTER.

Interatomic distances in crystals. W. L. BRAGG (Phil. Mag., 1926, [vii], **2**, 258—266; cf. A., 1920, ii, 537).—The assumptions involved in assigning definite "spheres of influence" to the atoms in crystal structures are discussed. Lists of atomic or ionic radii have proved of great value in making a first approximation to the relative positions of the atoms in a structure which is under investigation. Some recent work on

atomic radii is summarised, and attention directed to the values proposed by Wasastjerna (A., 1923, ii, 593), which are found to be in good agreement with the results of *X*-ray analyses of crystal structures. Menzer's structure for garnet (Z. Krist., 1926, **63**, 157) confirms the estimate of 2·7 Å. for the distance between oxygen ions (cf. Bragg and Brown, this vol., 227). A. B. MANNING.

Higher order *X*-ray reflexions from fatty acids. J. A. PRINS and D. COSTER (Nature, 1926, **118**, 83—84).—Curves show that for palmitic acid the odd and even orders of reflexion are approximately equally intense in the neighbourhood of the ninth order, whereas at the sixteenth (about as intense as the fifth) the even orders have a much greater intensity. Calculations based on a new model for the scattering power of the molecule give for the intensity of the rth order $I_r=[\sin(r\pi/12)/r]^2$ when r is odd; $I_r=[\sin(r\pi/12)-\sin(r\pi/24)/r]^2$ when r is even. Agreement between calculated and observed values is satisfactory. Similar results were obtained with palmitic and stearic acids. With palmitic acid, the 34th order is the only one to appear above the 28th, and with lauric acid the 26th above the 21st. The singularity may depend on the fact that the scattering substance is not uniformly distributed along the chain, but contains a periodicity due to the successive CH_2 groups. A. A. ELDRIDGE.

Crystal structure and chemical constitution. K. WEISSENBERG (Mitt. Materialprüf., 1926, [ii], [2], 34).—See A., 1925, ii, 1129, 1130.

Mineral substance in bones. W. F. DE JONG (Rec. trav. chim., 1926, **45**, 445—448).—The structure of modern and fossilised bones has been investigated by the Debye–Scherrer method of *X*-ray analysis. The films show lines characteristic of the fluorapatite type of structure and nothing else. The fundamental mineral is probably $3Ca_3(PO_4)_2,CaCO_3$, in which the carbonate radical may be replaced, as in fossilisation, by fluorine, chlorine, or sulphate, and perhaps by other radicals, whilst some of the calcium may be replaced by magnesium, and possibly also by iron and aluminium. The diffuse nature of the *X*-ray lines indicates that the crystals present contain only some tens or hundreds of molecules, but on incineration the crystal size is increased. No evidence could be found of the existence in bones of the colloidal collophanite, $Ca_3P_2O_8,H_2O$, described by Dana ("A System of Mineralogy," 6th ed., 108). W. HUME-ROTHERY.

Crystal structure of manganese fluoride, lead iodide, and tungsten sulphide. A. E. VAN ARKEL (Rec. trav. chim., 1926, **45**, 437—444).—The crystal structure of the above substances has been determined by the powder method. Manganese fluoride has the rutile type of structure, with two molecules in the unit cell, and base and height 4·88 and 3·29 Å., respectively. The space-group is D_{2h}^{14}, and the co-ordinates are: Mn (0, 0, 0) ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), F (u, u, 0), ($\bar{u}$, $\bar{u}$, 0), ($u+\frac{1}{2}$, $u-\frac{1}{2}$, $\frac{1}{2}$), ($u-\frac{1}{2}$, $u+\frac{1}{2}$, $\frac{1}{2}$), where u is about 0·30—0·31. Lead iodide has the same type of structure as cadmium iodide. The dimensions of the elementary hexagonal cell are: base 4·59, height 7·02, $d_{calc.}$ 5·94, which is slightly lower than the experimental value. These values agree with those of Terpstra and Westenbrink (Versl. Akad. Wetensch. Amsterdam, 1921, **35**, 74) except that the present work gives a slightly higher cell. The co-ordinates are: Pb (0, 0, 0), I ($\frac{1}{3}$, $\frac{2}{3}$, u), ($\frac{2}{3}$, $\frac{1}{3}$, $\bar{u}$), where u is slightly greater than 0·25 but cannot be accurately determined. Tungsten disulphide has a structure resembling that of molybdenite with two molecules in the unit cell, and base 3·18 and height 12·5 Å. The co-ordinates are: W (0, 0, 0) ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$), S (0, 0, u), (0, 0, $\bar{u}$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}+u$), ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}-u$), where u is about $\frac{3}{8}$. W. HUME-ROTHERY.

Refraction of *X*-rays in prisms of various materials. C. M. SLACK (Physical Rev., 1926, [ii], **27**, 691—695).—For 0·7078 Å., the following values of $(1-\mu)\times10^6$ were obtained: silver, 5·85±0·3; copper, 5·95±0·5; sulphur, 1·39±0·05; aluminium, 1·68±0·07; carbon, 1·23±0·15; celluloid, 0·980±0·03; paraffin, 0·701±0·03. Values for 1·537 Å. were: aluminium, 8·40±0·2; celluloid, 4·78±0·1; paraffin, 3·28±0·15. The results agree with the Lorentz dispersion formula. The broadening of the curves due to granular structure, *e.g.*, in the case of graphite, might lead to a method of comparing the internal arrangements of the particles. A. A. ELDRIDGE.

Crystalline structure of anhydrite. E. C. S. DICKSON and W. BINKS (Phil. Mag., 1926, [vii], **2**, 114—128).—The structure of anhydrite, determined by the ionisation spectrometer, is based on a simple orthorhombic lattice, the unit cell containing four molecules. The space-group V_h^{17}, previously determined by Rinne, was confirmed by the Debye powder method. Assuming a regular tetrahedral arrangement of the SO_4-group, two parameters suffice to fix the positions of all its atoms in the unit cell. The positions of the calcium atoms involve only a single parameter. In calculating amplitude factors, some deviations from Hartree's F-values for scattering power had to be made (cf. James and Wood, this vol., 13). A. B. MANNING.

Comparison between the diameters of ions of the same element having different charges. A. FERRARI (Atti R. Accad. Lincei, 1926, [vi], **3**, 275—277).—The diameters of quadrivalent ions of manganese and lead, viz., 2·50 and 3·10 Å., are appreciably smaller than those of the corresponding bivalent ions, these being 2·95 and 3·80 Å., respectively. T. H. POPE.

***X*-Ray investigations on cellulose.** R. O. HERZOG (Pulp and Paper Mag., 1926, **24**, 694—699).—A general account of the results obtained. *X*-Ray study of vegetable fibres shows that cellulose has a crystalline structure, the lengths of the edges of the unit cell being 8·60, 7·78, and 10·22 Å., respectively, corresponding with 4 $C_6H_{10}O_5$ groups for the unit cell. When the cellulose is mercerised, many of the weaker spots in the *X*-ray diagram disappear; there is a contraction in the direction of the length of the fibre of 3% and an expansion at right angles to this of 2%, and the lengths of the edges of the unit cell become 8·88, 8·05, and 9·88 Å., respectively; this also corresponds with 4 $C_6H_{10}O_5$ groups for the unit cell. The unit cells of cellulose acetate and cellulose

nitrate (rhombic symmetry) contain 16 $C_6H_7O_2(OAc)_3$ groups and 32 $C_6H_8O_3(NO_3)_2$ groups, respectively. A. GEAKE.

Crystal structure of cellulose acetate and nitrate. R. O. HERZOG (Helv. Chim. Acta, 1926, **9**, 631—633).—See preceding abstract.

Cellulose acetate and nitrate. E. OTT (Helv. Chim. Acta, 1926, **9**, 633; cf. this vol., 563).—A claim for priority in discovering the crystalline structure of cellulose triacetate (cf. Herzog, B., 1925, 349, 440). A. R. POWELL.

Isomorphic relations between metals of the mercury and magnesium groups. I. Isomorphism of mercury and magnesium. G. CAROBBI and A. MARCOLONGO (Gazzetta, 1926, **56**, 69—76; cf. A., 1924, ii, 414, 816).—Researches have established the possibility of the existence of solid solutions between the compounds $Hg_3La_2(NO_3)_{12},24H_2O$ and $Mg_3La_2(NO_3)_{12},24H_2O$ containing up to about 10% of the mercury compound, and between the compounds $Hg_3Bi_2(NO_3)_{12},24H_2O$ and $Mg_3Bi_2(NO_3)_{12},24H_2O$ containing up to 25% of the mercury compound. Crystals of the type $2La(NO_3)_3,3Hg(NO_3)_2,24H_2O$ similar to those in the magnesium series could not be isolated, although there was some evidence of their presence, in small quantities, when crystallised with the corresponding magnesium compound, $2La(NO_3)_3,3Mg(NO_3)_2,24H_2O$. S. B. TALLANTYRE.

Mercury oxychlorides: $2HgCl_2,HgO$ and $HgCl_2,HgO$. E. CAROZZI (Gazzetta, 1926, **56**, 175—179).—The mercuric oxychloride, $2HgCl_2,HgO$, separated mechanically from its mixtures with the compound $HgCl_2,2HgO$, obtained as a deposit on pieces of saccharoid marble left under 5% mercuric chloride at 12—14°, forms pale yellow, cubic crystals, d^{16} 6·39, n_D^{18} 2·001 (cf. Thümmel, A. 1889, 1050). The compound $HgCl_2,HgO$, prepared by Tarugi's method (A., 1902, ii, 20), forms golden-yellow crystals of the rhombic system, $a : b : c = 0{\cdot}78363 : 1 : 0{\cdot}52724$. T. H. POPE.

Isomorphic relations between the double cyanides, $K_2Zn(CN)_4$, $K_2Cd(CN)_4$, and $K_2Hg(CN)_4$. E. CAROZZI (Gazzetta, 1926, **56**, 180—186).—The compounds $K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ are completely miscible in the solid state, as also are $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$, but no mixed crystals of $K_2Zn(CN)_4$ and $K_2Hg(CN)_4$ are formed containing more than 53·21% of the former compound. T. H. POPE.

Composition and structure of organic molecular compounds. H. RHEINBOLDT (Z. angew. Chem., 1926, **39**, 765—767).—A statistical survey of 455 organic molecular compounds shows that in 65% of the compounds the molecular ratio of the components is 1 : 1 and in a further 25% the ratio is 2 : 1 or 1 : 2. These compounds can thus be divided into two principal classes, viz., compounds of the first order in which the lattice points of the single molecules are occupied, and compounds of higher orders which are similar in structure to inorganic complex compounds and in which the lattice points of certain molecules are saturated with several molecules of the other component of the compound. A. R. POWELL.

What is a metal? A. EUCKEN (Z. Metallk., 1926, **18**, 182—188).—The characteristic properties of the elements generally classed as metals are reviewed from a physical point of view, and it is shown that the power of conducting electricity is the most characteristic of them all, and that many other properties, *e.g.*, power of reflecting light, heat conductivity, and ductility, are closely related mathematically to the electrical conductivity, which, in itself, is due to the presence of one or more free electrons in the atoms. Under certain conditions, non-metals and compounds, having normally no free electrons and therefore being non-conductors of electricity, may be made conductors by causing some of their electrons to become temporarily free; thus, under the action of ultra-violet light, both diamond and zinc blende conduct electricity. The difference of behaviour of metals and non-metals as electrical conductors is shown to be in agreement with Bohr's theory of atomic configuration. A. R. POWELL.

Photo-electric conductivity in rock-salt. A. ARSENJEWA (Z. Physik, 1926, **37**, 701—704; cf. Gyulai, this vol., 225).—The photo-electric conductivity of a crystal of rock-salt previously exposed to *X*-rays was found to be proportional to the energy absorbed and independent of the wave-length over the range 580—420 μμ. This result is not in agreement with the experiments of Gyulai, who took the mean absorption curve and compared it with the mean conductivity, using several crystals. If the author's result is correct, the quantum rule can apply to the primary effect only. E. B. LUDLAM.

Magnetic oxide of chromium. L. BLANC (Bull. Soc. chim., 1926, [iv], **39**, 718—722).—The magnetic properties are probably due to an oxide of the formula $nCrO_3,mCr_2O_3$. This oxide could not be isolated; it is formed by the transformation of Cr_5O_9-α to Cr_5O_9-β. The formula Cr_5O_9-μ is suggested. W. THOMAS.

Magnetic susceptibilities of some alkali metals. W. SUCKSMITH (Phil. Mag., 1926, [vii], **2**, 21—29).—The magnetic susceptibilities of sodium, potassium, and rubidium have been determined at temperatures from 0° to 500°, and those of cæsium from 0° to 300°. The metals were contained in small bulbs of pyrex glass, which were suspended in a non-uniform magnetic field. The bulbs were rigidly connected to a torsion arm the force on which could be neutralised electromagnetically. Water was used as the standard. The susceptibilities decrease with increasing atomic number. With rise of temperature they increase gradually for each metal up to the m. p., at which they drop suddenly, thereafter again exhibiting a gradual increase. The specific susceptibilities are $+0{\cdot}62\times10^{-6}$ $+0{\cdot}53\times10^{-6}$, and $+0{\cdot}11\times10^{-6}$ for sodium, potassium, and rubidium, respectively, at 500°, and $-0{\cdot}02\times10^{-6}$ for cæsium at 300°. Evidence is adduced to support the view that the shape of the susceptibility curves in the region of the m. p. is due to the breaking up of molecular aggregates. A. B. MANNING.

Changes in the crystal orientation of copper during recrystallisation. G. TAMMANN and H. H. MEYER (Z. Metallk., 1926, **18**, 176—181).—Hard-rolled copper sheet (87% reduction) does not recrystallise below 450° and below 650° it is impossible to determine the orientation of the crystals. After complete recrystallisation at 700°, the composition of the crystal facets in the plane of rolling is 76% of (111) and 24% of (011); as the temperature rises, the former commence to disappear and (001) faces take their place, until at 800° the composition is 38% of (111), 40% of (011), and 22% of (001). Prolonged heating at 1050° causes the complete disappearance of the (111) faces and of all but 3% of the (001) faces, and practically all the cube faces are oriented so that two edges are parallel to the direction of rolling. With less severely worked sheet, similar changes take place, but the proportion of (111) faces originally formed is greater and a higher temperature is necessary to cause their disappearance. The large number of twinned crystals formed during the earlier stages of recrystallisation are twinned about the icositetrahedral plane, whereas twins of native or electrolytic copper are formed about the octahedral plane. In chill- or sand-cast copper, a section parallel to the cooling surface shows a majority of cube faces and a fair proportion of rhombodecahedral faces; in electrolytic copper the orientation varies considerably, the (001) and (011) faces predominating in a section parallel to the cathode. These crystal changes during heating explain the necessity for annealing copper at 700—800° during rolling; higher temperatures cause large, evenly oriented crystals, which readily break away from one another, whereas at 700° the crystals are smaller and, by reason of their uneven orientation, the metal is in a sufficiently coherent state to be able to withstand further deformation without suffering fracture. A similar explanation is advanced to account for the variation in the pliability of annealed copper sheet.

A. R. POWELL.

Elastic limits and the strength of crystalline substances. J. FRENKEL (Z. Physik, 1926, **37**, 572—609).—The rigidity of crystalline substances is compared with the friction between two surfaces and a "file model" suggested. The potential energy of two halves of a crystal is calculated as a function of their relative displacement on the electrical theory of cohesion, and as an additional "non-Coulomb" energy; by this means, the elastic moduli and the corresponding normal and tangential elastic limits are calculated. Variation with temperature is determined on general statistical principles. Quantitative agreement with experiment is realised for the moduli; for the elastic limits the agreement is only qualitative.

E. B. LUDLAM.

Plastic deformation of single metallic crystals. S. J. WRIGHT (Nature, 1926, **117**, 891—892).

Determinations of mol. wt. in liquid ammonia and the mol. wt. of inulin. H. REIHLEN and K. T. NESTLE (Ber., 1926, **59**, [*B*], 1159—1162; cf. Schmid and Becker, A., 1925, i, 1386).—Determinations of the mol. wt. of carbamide dissolved in liquid ammonia between −33·5° and −73° by tensimetric measurement give normal values. Schmid and Becker's value for the mol. wt. of inulin is confirmed. The cryoscopic constant of ammonia appears to be approximately 14, whereas the calculated value is 9·4.

H. WREN.

Resistivity and conductivity of dilute amalgams at various temperatures. T. I. EDWARDS (Phil. Mag., 1926, [vii], **2**, 1—21).—The variation of the specific resistance of mercury with temperature has been determined over the range 0—300°. A quartz tube was used and was maintained at a constant temperature for each determination by immersion in a bath of ice, water, or other suitable liquid. The results are represented by the formula: $\rho_t=\rho_0(1+0{\cdot}8877t\times10^{-3}+0{\cdot}977t^2\times10^{-6}+0{\cdot}19t^3\times10^{-9}$ (cf. Williams, A., 1925, ii, 946). The specific resistances of dilute amalgams of thallium, germanium, antimony, yttrium, cerium, and aluminium have also been measured, those of thallium at 13·3° and 100° over a range of concentrations up to 1%, and at temperatures up to 300° for a concentration of 0·5%, and those of the other metals at 300°. The amalgams which oxidise readily in air (cerium and aluminium) were prepared and maintained in an atmosphere of hydrogen. Amalgams of beryllium of suitable concentration could not be prepared. The relative change of conductivity with respect to mercury ($\Delta L/L$) at constant temperature is proportional to the concentration for the dilute amalgams examined. If the concentration (c) is expressed in g.-atoms per g.-atom of mercury, the value of $\Delta L/cL$ at infinite dilution is of the same order of magnitude ($4{\cdot}7\times10^{-2}$ to $6{\cdot}6\times10^{-2}$ at 300°) for all the amalgams. This is in accord with the Skaupy theory.

A. B. MANNING.

Effect of a magnetic field on the electrical resistance of mercury and some amalgams. (MISS) P. JONES and T. J. JONES (Phil. Mag., 1926, [vii], **2**, 176—194).—When measured in tubes of about 1 mm. diameter, and with currents up to nearly 0·1 amp., the increase of resistance of mercury produced by transverse magnetic fields ranging from 3000 to 10,000 gauss is independent of the current and is proportional to h^2. For larger currents, the change of resistance becomes dependent on the current, and is ultimately given by the expression $R\propto h^{1{\cdot}58}/i^{0{\cdot}4}$. With varying temperature, the increase of resistance for small values of the current varies inversely as the viscosity. These results are in agreement with the theory of Williams (A., 1925, ii, 753), who assumes that the increase of resistance is due to the production of motion in the mercury by the action of the magnetic field. For straight tubes of diameter 0·96 and 0·5 mm., respectively, and for small currents, the increase of resistance was approximately proportional to the diameter of the tubes. The increase of resistance of amalgams of bismuth (0·5 and 0·64%) and zinc (1·187%) scarcely differed appreciably from that of mercury alone, although with the more concentrated amalgams there was an indication of a slight diminution in the change of resistance. Such a change is predicted by the theory on account of the increased viscosity.

A. B. MANNING.

Measurement of magnetisation of ferromagnetic powders. R. CHEVALLIER (Bull. Soc. chim., 1926, [iv], **39**, 711—717).—The Curie-Chene-

veau balance is suitable for measurements with paramagnetic substances, but unsuitable for ferromagnetic powders, because absolute values cannot be obtained on account of hysteresis. A suitable apparatus for the latter is described whereby measurements by induction can be expressed in absolute units. W. THOMAS.

Dependence of the susceptibility of a diamagnetic gas on pressure. E. LEHRER (Z. Physik, 1926, **37**, 155—156).—Measurements were made on carbon dioxide and argon at pressures from 60 to 720 mm., but no variation of susceptibility with pressure was observed. The method adopted was to note the difference in pressure on a sensitive manometer connected to the two ends of a horizontal tube between the poles of a magnet, the ends of the tube being kept at different temperatures. E. B. LUDLAM.

Emissivity of bismuth in a magnetic field. C. W. HEAPS (Physical Rev., 1926, [ii], **27**, 764—768).—A magnetic field of 4900 gauss fails to affect the emissivity of bismuth at 100°, probably on account of the absence of magneto-resistance in the surface layers of the metal. A. A. ELDRIDGE.

Thermo-electric properties of zinc and cadmium. E. GRÜNEISEN and E. GOENS (Z. Physik, 1926, **37**, 278—291).—The *E.M.F.* against copper of crystals of zinc and cadmium was determined at temperatures ranging from −253° to 100°. Crystals about 20 cm. long and from 2·5 to 4 mm. thick were used and measurements made both along and parallel to the hexagonal axis. Tables and curves are given showing the thermo-electric force, the Peltier effect, and the differences of the Thomson coefficients for the two axes. Relationships are evident between these magnitudes, and a connexion with the frequency of atomic vibrations is indicated, but no rational formula has been deduced. E. B. LUDLAM.

Optical and electrical constants of sucrose. E. L. PALUMBO (Ann. Physik, 1926, [iv], **79**, 533—549).—The refractive index of aqueous solutions of sucrose for wave-lengths between 706·5 and 396·4 μμ and within the range of concentrations 19—61% has been measured to 5 decimal places. The results are expressed by $R'=R_0(1-c)+Rc$ (R_0 is the refraction constant of water, R' that of the solution, R that of sucrose, c is concentration). R and R' are independent of concentration, but a small variation with wave-length is shown. The relation $R=A/(1-\lambda_1^2/\lambda^2)$ (in which A is a constant 0·20176, λ the wave-length for which R is determined, and λ_1 a wave-length characteristic of the sugar molecule) leads to a value of 832·84 Å. for λ_1. For the dielectric constant (cf. A., 1924, ii, 932), the analogous expression $D'=D_0(1-c)+Dc$ is used. D and D' increase with rise of temperature and increase less markedly with increasing concentration. Born's theory of rotation leads to a characteristic wave-length of 1349·0 Å. The specific rotation varies with concentration in the sense opposed to the requirements of the theory. The depolarisation of scattered light has been investigated and the work of Gans (Z. Physik, 1923, **17**, 353; 1924, **27**, 164) extended and confirmed, thereby establishing quantitatively the anisotropic nature of the chemical linkings.

An addendum by R. GANS on the Born theory directs attention to certain errors. A modified expression is advanced. R. A. MORTON.

Correction for width of slit in measurements with the König-Martens photometer. F. HOFFMANN (Z. Physik, 1926, **37**, 60—71).—It is shown how a correction reducing the readings to the value for width of slit zero may be applied; a method is given for determining the colour-temperature of the comparison lamp, which must be known. A table is given of the correction for three widths of slit in three colours and over a temperature range 1000—2000°. E. B. LUDLAM.

Total brightness of the black body at the m. p. of palladium and platinum and its applicability as a unit of light. E. BRODHUN and F. HOFFMANN (Z. Physik, 1926, **37**, 137—154).—Measurements of the total brightness of palladium and platinum at their m. p. were made, using a special form of hollow space inside a larger enclosure maintained at uniform brightness. The values obtained in Hefner candles per cm.^{2} were: palladium (m. p. 1557°) 15·66, platinum (m. p. 1771°) 65·24. The mean error of each series was ±0·5%, which is less than that obtained with flames. From the mean of the two values the "mechanical equivalent of light" is found to be 0·0045 watt/lumen. E. B. LUDLAM.

Specific heats of hydrogen cyanide. J. R. PARTINGTON (J.C.S., 1926, 1559—1562).—The criticism advanced by Ingold (this vol., 231) is contested. Experimental evidence of various kinds points to the association of hydrogen cyanide. R. A. MORTON.

Specific heat and entropy of hydrogen chloride derived from infra-red band spectra. H. C. HICKS and A. C. G. MITCHELL (J. Amer. Chem. Soc., 1926, **48**, 1520—1527).—Theoretical. The rotational-oscillational specific heat of hydrogen chloride is calculated from the experimentally determined energy levels, the rotation being quantised with half-quantum numbers. The entropy, calculated by Tolman's method (A., 1920, ii, 468), agrees well with the experimental value. S. K. TWEEDY.

Thermal data on organic compounds. III. Heat capacities, entropies, and free energies of *tert.*-butyl alcohol, mannitol, erythritol, and *n*-butyric acid. G. S. PARKS and C. T. ANDERSON (J. Amer. Chem. Soc., 1926, **48**, 1506—1512; cf. Parks and Kelley, this vol., 232).—The specific heats of the above compounds were determined over the approximate temperature range 87—300° Abs.; the heats of fusion of *tert.*-butyl alcohol and *n*-butyric acid are 21·88 and 30·04 cal./g. at the m. p., 298·5° Abs. and 267·4° Abs., respectively. The entropies at 298° Abs. of the respective compounds are 47·2, 60·5, 42·5, and 61·0 cal./1°, and the free energies −49,900, −226,200, −152,900, and −92,500 cal.; both sets of results agree closely with those predicted in the manner previously described. S. K. TWEEDY.

Heat capacity of solid aliphatic crystals. II. E. O. SALANT (Proc. Nat. Acad. Sci., 1926, **12**, 370—374).—Using the author's previously deduced equa-

tion (this vol., 668), the heat capacities at various temperatures of methyl, ethyl, and butyl alcohols, glycerol, acetone, dextrose, formic and oxalic acids have been calculated from the respective m. p. and mol. wts., and the characteristic frequencies of the CH, C·C, CO, and OH linkings. The calculated values, especially at low temperatures, are generally in much closer agreement with the experimental numbers than are those previously given (A., 1925, ii, 1042). The observed and calculated values for glycerol, dextrose, and oxalic acid deviate considerably with increase of temperature. J. S. CARTER.

Heats of fusion of ethyl ether, methyl alcohol, and ethyl alcohol. S. MITSUKURI and K. HARA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 205—208).—The lowering of the f. p. of ethyl ether, methyl alcohol, and ethyl alcohol by addition of various organic liquids has been determined and the heats of fusion have been calculated (cf. this vol., 568). For ethyl ether, L is 1400 cal./mol. (cf. Beckmann and Waentig, A., 1910, ii, 581), for methyl alcohol 600 cal./mol. (cf. Maass and Waldbauer, A., 1925, ii, 492), and for ethyl alcohol 650 cal./mol. M. CARLTON.

Latent heat of vaporisation and its relation to curvature and pressure. J. SATTERLY (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 229—231).—Considering the case of a capillary tube standing in water, Houllevigue (J. Phys., 1896, [iii], **5**, 159) deduced thermodynamically that $L'-L=(\omega/\sigma)\log\omega/\omega'$, where L and L' are the heats of vaporisation over the flat and concave surfaces, respectively, ω and ω' the corresponding vapour pressures, and σ is the vapour density at the pressure ω. Without introducing any serious error, the equation may be written: $L'-L=gh=2\gamma/r\rho$, where h is the height of the liquid column, γ the surface tension, ρ the liquid density, and r the radius of curvature of the concave surface. The equation may be derived simply from considerations of potential energy. J. S. CARTER.

Velocity of sound in a liquid and its relation to the latent heat of vaporisation. J. SATTERLY (Trans. Roy. Soc. Canada, 1926, [iii], **20**, III, 133—137).—Mathematical. The formulæ quoted by Ionescu (A., 1925, ii, 644) giving the relationship between the velocity of sound in a liquid and the latent heat of vaporisation are discussed and the derivation of the Lewis formula ($V=\sqrt{L/\alpha T}$, where L is the heat of vaporisation, α the coefficient of dilatation, and T the absolute temperature) is criticised. Lewis' formula fails for water, the calculated value for the velocity of sound being 6500, whereas the measured value is 1450 metres/sec. J. S. CARTER.

Heats of combustion of hydrocarbons. D. P. KONOVALOV (Compt. rend., 1926, **183**, 40—41).—See this vol., 668.

Heat of combustion of salicylic acid. P. E. VERKADE and J. COOPS (J.C.S., 1926, 1437—1443; cf. Berner, this vol., 116).—The heat of combustion of salicylic acid has been redetermined; the value found is 5241·7 cal.^{15}/g. (air) (v=constant, 19·5°). The value found by Berner (*loc. cit.*) is low. R. A. MORTON.

Critical temperatures of silicon derivatives. M. PRUDHOMME (Bull. Soc. chim., 1926, [iv], **39**, 710—711).—The critical temperatures of compounds is stated to be independent of those components having critical temperatures of several thousand degrees. The author suggests a hypothetical silicon the critical temperature of which is 730° Abs. W. THOMAS.

Heat conductivity of air and hydrogen. E. SCHNEIDER (Ann. Physik, 1926, [iv], **80**, 215—216; cf. this vol., 462).—Corrections.

Complexity of the solid state. IV. Behaviour of pure sulphur trioxide. III. A. SMITS and P. SCHOENMAKER (J.C.S., 1926, 1603—1607; cf. this vol., 669).—The intensively-dried, high-melting, asbestos-like form of sulphur trioxide behaves on distillation as a mixture of pseudo-components having very different vapour pressures and m. p. At the ordinary temperature, these states are stable, but at 50° changes occur in the direction of the inner equilibrium. The unchanged state and that changed at 50° yield identical X-ray photographs. The X-rays effect a very rapid increase of the vapour pressure, *i.e.*, a rapid change in the direction of the inner equilibrium. X-Rays establish the inner equilibrium and also transform the metastable forms into the stable form, since the three forms described as ice-like, low-melting, and high-melting asbestos-like forms yield identical X-ray photographs. R. A. MORTON.

Properties of selenium monochloride. V. LENHER and C. H. KAO (J. Amer. Chem. Soc., 1926, **48**, 1550—1556).—Selenium monochloride prepared by the method previously described (A., 1925, ii, 426) has d_4^{25} 2·7741, m. p. −85°, specific conductance K $5{\cdot}12\times10^{-7}$ mho, and n^{25} 1·59617. The action of selenium monochloride on many substances, including the metals, metallic selenides, some oxidised compounds, and hydrocarbons, shows that it is a typical acid chloride and strong chlorinating agent. M. CARLTON.

Volume relations of the cobaltammines. F. EPHRAIM and O. SCHÜTZ (Helv. Chim. Acta, 1926, **9**, 626—631).—The densities of 58 cobaltammine salts have been determined and from these figures the mol. vols. and percentage contractions in mol. vol. based on the sum of the mol. vols. of the constituent elements have been calculated. For the same anion, the percentage contraction of all bivalent ammines is approximately the same and of all tervalent ammines 2—3% more. The mean differences in contraction between bromide and chloride are 2·3% for bivalent and 2·9% for tervalent ammines, and between iodide and bromide 4·5% and 4·6%, respectively. Substitution of chromium or iridium for cobalt in the complex makes no difference to the contraction, nor does the substitution of one or two NH_3 groups in the complex by H_2O, Cl, Br, I, or NO_2. Removal of water of crystallisation changes the contraction considerably. Similar regularities

have been found between double halides of metals and cobaltammines. A. R. POWELL.

Relation between the volume [of a substance] at absolute zero and other properties. W. HERZ (Z. anorg. Chem., 1926, **153**, 269—272; cf. Lorenz and Herz, A., 1925, ii, 25).—The relations between the volume of a substance at absolute zero, V_0, and the latent heat of vaporisation, L, the Poisson capillarity constant, a, the molecular elevation of the b. p., c, and the difference in the specific heats, C_p-C_v, are given by the equations: (1) $L=5{\cdot}7T_s/V_0d_c$, (2) $a=0{\cdot}31464T_s/V_0d_c$, (3) $V_0=4{\cdot}275c/T_cd_c$, and (4) $C_p-C_v=0{\cdot}50595/V_0d_c$, where T_c and d_c are the critical constants and T_s is the b. p. of the substances. The results calculated for the above physical properties by the use of these equations are in fairly close agreement with the observed values in the case of many organic compounds and volatile elements. A. R. POWELL.

Relation between the coefficient of expansion and compressibility of a fluid. V. S. VRKLJAN (Z. Physik, 1926, **37**, 458—468).—A formula is deduced rigorously whereby the coefficient of expansion can be calculated from the coefficient of compressibility; two approximation formulæ are also given. The values calculated from Amagat's results are compared with the direct determinations of the coefficients of expansion for water, alcohol, and ether. E. B. LUDLAM.

Gas thermometry with helium, neon, nitrogen, and oxygen. W. HEUSE (Z. Physik, 1926, **37**, 157—164).—The limiting value of the coefficient of pressure and expansion, $\gamma=0{\cdot}0036604$, is probably correct to 0·01%. Increasing the surface exposed to the gas sixfold, by putting glass tubes inside the thermometer bulb, produced a marked increase in the coefficient due to adsorption. The difference between the slope of the 0° isotherm at high pressures and at a pressure of 1 metre, previously observed with helium, is also observed with neon, nitrogen, and oxygen, but remains unexplained. E. B. LUDLAM.

Molecular changes in vapours and liquids. G. N. ANTONOV (Phil. Mag., 1926, [vii], **1**, 1121—1145).—The discontinuous variation of the physical properties of liquids with temperature (A., 1925, ii, 865) has been examined further and it is shown that liquid–liquid and liquid–gas systems are governed by the same laws. The variation of the composition of two conjugate liquid layers with temperature is thus discontinuous and it appears that both temperature and concentration changes favour complex formation. Colligative properties such as b. p. and f. p. indicate that the number of molecules per unit volume remains the same with increasing concentration in the critical regions and sometimes outside them. It is suggested that complex formation is essential for separation into two phases. By extending the analogy to liquid–gas systems, it is shown that $d_l/Mx=d_v/My$, where d_l and d_v are the liquid and vapour densities, M is the mol. wt., and x and y are the association factors of the liquid and vapour, respectively. From this it is possible to calculate the association factor at all temperatures and to show that its value increases with decreasing temperature. A. E. MITCHELL.

Rate of diffusion and nature of solvent. G. E. MUCHIN and G. P. FAERMANN (Z. physikal. Chem., 1926, **121**, 180—188).—The rates of diffusion of acetic acid and aniline in ethyl alcohol, benzene, and acetonitrile and in binary (50% by weight) mixtures of these solvents have been investigated. Determinations of the viscosities of these solvents have also been made, where published data were lacking. No proportionality between viscosity and diffusion constant was found, in opposition to the Stokes–Einstein law; this is ascribed to chemical action between solvent and diffusing solute. L. F. GILBERT.

Density measurements at high temperature. VII. Densities of molten lead–cadmium, cadmium–tin, and zinc–tin alloys, and of molten cadmium. F. SAUERWALD (Z. anorg. Chem., 1926, **153**, 319—322).—A modification of the buoyancy method for determining the density of metals with high vapour pressure is described. The specific volume of molten cadmium has been redetermined and the fact established that molten alloys of lead and cadmium, zinc and tin, tin and cadmium of mean concentration are formed from their components without volume change. M. CARLTON.

Heats of mixing of molten metals. A. MAGNUS and M. MANNHEIMER (Z. physikal. Chem., 1926, **121**, 267—288).—Direct and indirect methods have been employed in a study of the heat changes on mixing molten lead and tin, zinc and tin, lead and cadmium, tin and cadmium, and bismuth and tin in various proportions. L. F. GILBERT.

Metallographic observations on cuprous oxide in copper. P. SIEBE (Z. anorg. Chem., 1926, **154**, 126—129).—In normal cast copper, the cuprous oxide forms bands of the eutectic surrounding the grains of copper. The beads of eutectic are larger the slower the cooling. When copper is rolled, the beads of eutectic become oval and form lines in the direction of rolling. At temperatures below 600°, the beads become more and more angular with falling temperature, and cold-working may thus be distinguished from hot-working. When copper is heated at 1000°, the beads of cuprous oxide increase in size; in air, oxygen is absorbed and the eutectic is gradually formed throughout the mass. A. GEAKE.

Miscibility of copper and of tin with iron in the molten state. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1926, **153**, 260—262).—Polemical against Wever and Reinecken (this vol., 475). Two experiments are described which show that the systems iron and copper and iron and tin have only a limited range of miscibility in the liquid state and that the separation into two layers is not caused by segregation during solidification (cf. Isaac and Tammann, A., 1907, ii, 469). A. R. POWELL.

Supersaturated mixed crystals and the nature of martensite. R. RUER (Z. physikal. Chem., 1926, **121**, 484—488).—Theoretical. Supersaturated mixed crystals cannot separate from solution. Martensite is not a true solution of carbon or cementite in α-iron. Hardening theories based on the possibility

of true solutions of carbon or cementite in α-iron are untenable. L. F. GILBERT.

Binary mixtures. G. C. SCHMIDT (Z. physikal. Chem., 1926, **121**, 221—253).—The heat and volume changes which occur on mixing pairs of organic compounds in various proportions have been determined. The vapour pressures of these mixtures have also been determined, and in some cases redetermined, at different temperatures by a method previously employed (A., 1922, ii, 119). At low temperatures, the redetermined values do not agree exactly with those first obtained. Use is made of the results to amplify the author's previously expressed views (*loc. cit.*, and A., 1922, ii, 472) on the inadequacy of the Dolezalek theory in its present form. L. F. GILBERT.

Organic molecular compounds. XVII. Behaviour of decahydronaphthalene. G. WEISSENBERGER, R. HENKE, and E. SPERLING (Monatsh., 1926, **46**, 483—497; cf. this vol., 465, 466).—The vapour pressures at 20° of mixtures of decahydronaphthalene with each of the following: *n*-hexane, benzene, toluene, chloroform, carbon tetrachloride, trichloroethylene, carbon disulphide, methyl, ethyl, *iso*propyl, and *iso*butyl alcohols, methyl, ethyl, *iso*propyl, and *iso*butyl acetates, ethyl ether, and acetone, are compared with the values required by the Raoult–van 't Hoff and the van Laar formulæ. The former of these is regarded as quite adequate and preferable to the latter. There appears to be no evidence of any field of residual affinity for decahydronaphthalene in any of these mixtures, with the possible exception of that with chloroform. In addition, values are recorded for the vapour pressures of a number of ternary mixtures containing phenol, decahydronaphthalene, and the solvents methyl, ethyl, *iso*propyl, and *iso*butyl alcohols. These are homogeneous in all cases except mixtures with methyl alcohol and more than 1 mol. of hydrocarbon to 3 mols. of phenol, which separate into two phases. These data confirm the conclusion previously arrived at as to the inertness of the hydrocarbon. The following constants are recorded for decahydronaphthalene: d_4^{20} 0·8865, d_4^{30} 0·8772, *a* 19·96, *b* 0·1265. G. M. BENNETT.

Organic molecular compounds. XIX. Application of theory of residual field. G. WEISSENBERGER (Z. anorg. Chem., 1926, **152**, 333—341).—Vapour-pressure measurements for binary liquid systems which contain molecular compounds have been made at 20°. From the extent to which two substances combine to form a compound, their residual fields are estimated. In general, it appears that constitutive influences are such that the greater the complexity of a molecular compound the greater is the partition of the available residual field and the less is the stability. Of the substances examined, acetone is the most reactive. R. CUTHILL.

Binary liquid mixtures. XXII. Systems with nitrobenzene and nitrophenols. G. WEISSENBERGER, R. HENKE, and F. KAWENOKI (J. pr. Chem., 1926, [ii], **113**, 171—180).—An examination of mixtures of nitrobenzene, *o*-, *m*-, and *p*-nitrophenol with benzene, carbon disulphide, chloroform, methyl alcohol, ether, acetone, and ethyl acetate, followed by a discussion of the relation between the vapour pressures and the heat effects, and of the part played by the nitro- and hydroxyl groups in the attraction or repulsion of the components. J. S. H. DAVIES.

Binary liquid mixtures. XXIII. Vapour pressure. G. WEISSENBERGER and F. SCHUSTER (J. pr. Chem., 1926, [ii], **113**, 180—184).—A discussion of the relationship between the form of vapour-pressure curves and association and molecular compound formation in binary liquid mixtures with special reference to the system acetone–chloroform. J. S. H. DAVIES.

Vapour-pressure lowering as a function of the degree of saturation. II. I. BENCOWITZ and H. T. HOTCHISS, jun. (J. Physical Chem., 1926, **30**, 642—657).—Additional experimental evidence is given in confirmation of two previous deductions (cf this vol., 29). L. S. THEOBALD.

Temperature of the vapour evolved from solutions. E. REISSMANN (Z. angew. Chem., 1926, **39**, 770).—A refutation of Block's criticism (this vol., 474) of the author's earlier paper (cf. A., 1925, ii, 105). The temperature of the vapour above a boiling solution of a salt is shown to be approximately the same as that of the solution and not 100°. A. R. POWELL.

Is orthoboric acid volatile in steam? R. NASINI (Atti R. Accad. Lincei, 1926, [vi], **3**, 247—250).—Contrary to the statement of Anschütz and Riepenkröger (A., 1925, ii, 1084), orthoboric acid distils in steam at reduced pressure if the temperature is not below 60°, whilst at higher temperatures boric acid volatilises even at the ordinary pressure. It is hence probable that orthoboric acid is transported as such in steam, although at the higher temperatures steam may carry over meta- or even pyro-boric acid. T. H. POPE.

Selective solvent action. V. Salting in. R. WRIGHT (J.C.S., 1926, 1203—1207; cf. A., 1925, ii, 1144).—Instances of increased solubility at 20° of water-soluble and alcohol-soluble solutes in 50% (by weight) aqueous alcohol are recorded and discussed. S. K. TWEEDY.

Method for determining solubility of sparingly soluble substances. S. MITCHELL (J.C.S., 1926, 1333—1336).—The solubilities of sparingly soluble substances have been measured by an optical method, based on the shifting of interference bands. A preliminary calibration is carried out with solutions of the substances of known concentration, the compensator readings being usually a linear function of the % saturation. For solutions of benzene in water, the calibration curve is not linear. S. K. TWEEDY.

Solubility of beryllium oxide in solutions of its salts. N. V. SIDGWICK and N. B. LEWIS (J.C.S., 1926, 1287—1302).—In presence of beryllium oxide, saturated solutions of beryllium sulphate, selenate, and oxalate contain more of the respective salts.

The proportions thus dissolved are 1, 1, and 3 mols. for 4 mols. of the oxide. The viscosities of neutral and basic solutions of these salts and the conductivities of neutral and basic beryllium chloride and oxalate solutions are recorded at 25°, together with the f. p. of neutral oxalate solutions. The assumption of the complex cation $[Be,x BeO]^{\cdot\cdot}$, where x on the whole is less than 4, explains the results with the sulphate and selenate solutions; a structure is ascribed to the crystalline hydrate of beryllium oxalate which explains its anomalous properties. The large increase in solubility of this salt in presence of the oxide may be due to the latter replacing a molecule of water besides combining with the beryllium ion. Examination of the system beryllium oxalate–oxalic acid–water at 25° did not reveal the existence of acid salts (cf. Rosenheim and Woge, A., 1898, ii, 71). *Beryllium benzenesulphonate* and *p-toluenesulphonate* were obtained as crystals containing $4H_2O$; the solubilities at 25° of the respective anhydrous salts were 53·8% and 39·2%. S. K. TWEEDY.

Crystallisation of supersaturated solutions of sodium sulphate and carbonate. N. V. TANCOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 215—220).—From supersaturated solution, sodium sulphate separates at first as the heptahydrate alone. Supersaturated solutions of sodium carbonate deposit first a hydrate of unknown composition which has a slight positive temperature coefficient of solubility and undergoes ready transformation into the heptahydrate at temperatures above 15° or into the decahydrate at temperatures below 15°. In order to avoid extraneous seeding of supersaturated solutions, it is necessary to wash the apparatus and its supports with hot chromic acid mixture and to steam for about an hour. T. H. POPE.

Molecular contraction in solutions at different temperatures. J. N. RAKSHIT (Z. Elektrochem., 1926, **32**, 276—281).—The molecular contractions of aqueous solutions of potassium chlorate, sodium carbonate, sodium sulphate, calcium sulphate dihydrate, manganous sulphate (anhydrous and tetrahydrate), ferrous sulphate heptahydrate, cadmium sulphate 8/3 hydrate, and of ethyl alcohol have been measured at different concentrations and at temperatures ranging from 10° to 60°. In all cases, the molecular contraction decreases with increase of temperature, and this may be attributed either to an increased coefficient of expansion of the hydrated solute or to its progressive dissociation. The results are discussed particularly with regard to the connexion between the heat of solution and the work involved in the chemical and physical changes which the constituents of the solution undergo; they show that most of the earlier thermochemical measurements must have been influenced by temperature and concentration. N. H. HARTSHORNE.

Contraction constants of salt hydrates. A. BALANDIN (Z. physikal. Chem., 1926, **121**, 299—306).—A test has been made of the applicability of the formula previously put forward (A., 1925, ii, 637) for the contractions which occur in reactions of the types $M+O=MO$, $MO+SO_3=MSO_4$, and $MSO_4+nH_2O=MSO_4,nH_2O$, where M is a metal; the formula is approximately valid for most of the reactions. The variations of the contraction constants are correlated with differences of chemical constitution. L. F. GILBERT.

Distribution of electrolytes between two liquid phases. S. A. VOZNESENSKI and K. V. TSCHMUTOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 343—346).—The expression $c_1^{m_1/m_2}/c_2=k$, where c_1 and c_2 are the respective concentrations of the undissociated part of an electrolyte in the two phases, m_1 and m_2 the mol. wts. of the electrolyte in the two phases, and k the partition constant, depending on the temperature and pressure (cf. Schilov and Lepin, A., 1922, ii, 626, 824) and the equation $c_1=c_2f_a^2/k_1$, where f_a is the coefficient of activity of the electrolyte according to Debye's theory (cf. Debye and Hückel, A., 1923, ii, 459, 724) and k_1 Debye's dissociation constant, lead to the expression $c_2f_a^2/c_2=kk_1$. The coefficient of activity may be calculated approximately in accordance with the formula $\log f_a=-GZ\sqrt[3]{C}/(DT)^{3/2}$, where C is the concentration determined analytically, Z the valency of the ion, D the dielectric constant, T the absolute temperature, and G has the value $1{\cdot}86\times10^6$. These relations hold only when (1) the two phases are virtually insoluble in one another so that the dielectric constant of the aqueous phase remains unchanged, (2) the influence of the distributed electrolyte on the mutual solubility of the phases is negligible, (3) the concentrations of the electrolyte are sufficiently low, (4) the electrolyte is "strong," and (5) influences of hydration, solvation, etc., are absent.

Investigation of the distribution of hydrochloric and picric acids between water and benzene at 17° shows that the above relationships are valid only at very low concentrations of these electrolytes, their inapplicability at higher concentrations being apparently due to the influence on the mutual solubilities of the two phases. T. H. POPE.

Adsorption of some organic acids by two active carbons of different origin. P. SURUN (Compt. rend., 1926, **182**, 1544—1546).—The adsorption of two varieties of carbon activated by heat and by impregnation with zinc chloride have been measured, using various concentrations of acetic, oxalic, tartaric, and citric acids. The adsorbent was shaken with the solutions for 30 min. and separated by centrifuging. The adsorption agrees with the usual formula, but the conclusions of Fromageot and Wurmser (A., 1925, ii, 384) are not substantiated. On the contrary, the adsorption is found to decrease with an increase in the number of carboxyl groups, independently of the concentrations of the solutions employed. J. GRANT.

Adsorption. II. Adsorption by coconut charcoal of saturated vapours of some pure liquids. III. Stages in the adsorption by coconut charcoal from vapour mixtures of alcohol and benzene and of acetone and benzene. F. G. TRYHORN and W. F. WYATT (Trans. Faraday Soc., 1926, **21**, 134—146).—See this vol., 346.

Adsorption from viscous media by charcoal. II. G. WEISSENBERGER, S. BAUMGARTEN, and R. HENKE (Monatsh., 1926, **46**, 679—700).—The relationship between the amounts adsorbed at equilibrium and the viscosity of the medium previously deduced (Weissenberger and Waldmann, A., 1925, ii, 655) has been verified by measurements of the adsorption of iodine or Sudan II in *o*-, *m*-, and *p*-methyl*cyclo*hexanols, oleic acid, 90% lactic acid, and 67% aqueous sucrose solutions (the viscosities being, respectively, 27·31, 29·72, 39·75, 36·32, 72·06, and 95·05 times as great as that of water) by four varieties of charcoal. For different chemical media, no simple relation exists between the viscosity and either the time taken to attain equilibrium or the amount of adsorption, whilst the order of adsorption capacity of the various charcoals also varies from medium to medium; it follows that the chemical nature of the medium affects the time taken to attain equilibrium, the amount of adsorption, and the adsorption capacity of the various charcoals. Figures are recorded showing the variation of the adsorption from equivalent solutions as the composition of the solvent is varied by diluting the methyl*cyclo*hexanols with alcohol, oleic acid with benzene, and lactic acid and sucrose solutions with water. The results do not always agree satisfactorily with Freundlich's formula (A., 1907, ii, 155), especially in the case of mixtures, but agreement with the authors' exponential relationship is in all cases good. The values for β and $1/\gamma$ (*loc. cit.*) for the solvents employed are, respectively, 1·555 and 0·585, 0·939 and 0·359, 0·876 and 0·441, 0·160 and 0·264, 1·670 and 0·592, 3·980 and 0·069. J. W. BAKER.

Adsorption phenomena. G. TESTONI (Annali Chim. Appl., 1926, **16**, 45—52).—The action of solutions of basic dyes, acid dyes, and mineral salts on silica, aluminium hydroxide, and kaolin has been studied. The basic dyes were adsorbed by silica, forming a coloured substance which resisted the action of water, but only a few acid colours gave similar results. With aluminium hydroxide, no basic dyes were adsorbed, but acid dyes were taken up promptly. Kaolin adsorbed more generally than silica or aluminium hydroxide, but made no distinction between basic and acid dyes. The quantity of dyes adsorbed varied with concentration in accord with Ostwald's law. In certain cases, a colourless liquid could be obtained with silica or aluminium hydroxide. Experiments with a solution of Congo-red and equal weights of aluminium hydroxide, kaolin, and barium sulphate gave very divergent results. Aluminium hydroxide decolorised the solution completely, forming a bright red lake; kaolin adsorbed 55% of the colour, forming a violet lake, whilst barium sulphate adsorbed 40%, forming a pale rose lake. The behaviour of these adsorbents in contact with solutions of copper sulphate, nickel sulphate, cobalt chloride, and the corresponding ammonia compounds was also examined. Silica adsorbed more than aluminium hydroxide, but kaolin was found to be inactive. The ammonia solutions showed much greater adsorption than neutral solutions. With 0·2% solutions of copper sulphate, nickel sulphate, and cobalt chloride, decomposition took place with the formation of the respective hydroxides and of colloidal aluminium hydroxide. R. SANSONE.

Adsorption. IV. Sorption phenomena and chemical processes. S. LIEPATOV (Kolloid-Z., 1926, **39**, 127—140).—The sorption of various electrolytes by starch, manganese dioxide, and nitroalizarin has been studied. The sorption velocity depends on the nature of the sorbent and of the solvent containing the electrolyte; it increases with rise of temperature and with the smallness of the sorbent particles. The sorption velocity is a diffusion velocity and its kinetics must therefore be based on Nernst's diffusion theory. Manganese dioxide and nitroalizarin form chemical compounds with free alkali hydroxides. The case of the sorption of a base from a salt is a chemical process of distribution of the base between the acid of the sorbent and that remaining in solution. The sorption reversibility is a specific property of the system and cannot be anticipated on the basis of Gibbs' theory. An extension of Schmidt's sorption equation (A., 1895, ii, 39; 1910, ii, 1041; 1911, ii, 969; 1912, ii, 236) is advanced which takes into account a maximum of the sorption. It is valid for the cases studied and elucidates satisfactorily the processes concerned. N. H. HARTSHORNE.

Surface actions. R. DUBRISAY (Compt. rend., 1926, **182**, 1463—1465; cf. this vol., 672).—The adsorption of various dyes from aqueous solutions by sand, kieselguhr, asbestos, and cotton has been investigated colorimetrically. In all cases, the adsorption is increased by the addition of 0·5% of sodium chloride to the solution, confirming the author's previous results (*loc. cit.*) for the effect of electrolytes on adsorption at the surface of contact of water and benzene. This is further confirmed by observations on the height to which water and colouring material rise when strips of filter-paper are immersed in the solution. W. HUME-ROTHERY.

Interfacial tensions between organic liquids and water or aqueous solutions. J. R. POUND (J. Physical Chem., 1926, **30**, 791—817; cf. J.C.S., 1923, **123**, 578).—The interfacial tensions of 42 organic liquids against water and against aqueous solutions of hydrochloric acid, sulphuric acid, and sodium hydroxide and chloride have been measured at 30° by the capillary tube method (Reynolds, J.C.S., 1921, **119**, 469). The densities of the mutually saturated solutions were also determined. The variations of these interfacial tensions with time were observed over long periods. When two partly miscible liquids saturate each other, their densities usually change in the normal manner, and with allowance for this, constancy of interfacial tension over many days is shown to hold between many pairs of liquids. Purification of an organic liquid tends to raise the interfacial tension and make it less variable with time. Many mixtures of organic liquids, however, have with water and aqueous solutions interfacial tensions which are constant over long periods, but certain impurities greatly influence this factor and usually cause it to decrease continuously with the time of contact. Interfacial tension between saturated solutions is lower the greater the mutual solubility of the two liquids concerned. With certain esters and dilute

acid and alkali solutions, the interfacial tensions, owing to hydrolysis, decrease with time, the products of hydrolysis increasing the mutual solubility or giving a contaminated interface. A mixture of oils often has an interfacial tension against a given solution lower than the average tension of the components. Further, the tension against sodium chloride solution is greater than that against water and any variation with time is usually less. L. S. THEOBALD.

Surface tension of molten metals and alloys. I. Method of maximum bubble pressure and the surface tension of mercury and bismuth. F. SAUERWALD and G. DRATH (Z. anorg. Chem., 1926, **154**, 79—92).—The maximum bubble pressure method is suitable for determining the surface tension of metals at high temperatures. Measurements with mercury at the ordinary temperature showed that for substances which do not wet the glass or silica capillaries the outer diameter of the capillary must be used in calculating the surface tension, and that the end of the capillary must be several mm. beneath the surface. The result was independent of the nature of the gas when this was air, nitrogen, carbon dioxide, or hydrogen, and of the time of formation of a bubble when this was varied from several secs. to 30—40 secs. The values found for mercury for temperatures up to 200° lie between those of Hagemann (Diss., Freiburg, 1914) and Hogness (A., 1922, ii, 29); at 19° and 201°, the surface tension is, respectively, 473 and 429 dynes/cm. Measurements were made with bismuth between 583° and 779°, using hydrogen, and the results accord well with those of Hogness (*loc. cit.*) between 300° and 500°, and of Smith at 750°. The surface tension is 354 dynes/cm. at 590°, and the temperature coefficient is 0·060. A. GEAKE.

Determination and importance of surface tension of sucrose solutions. P. HONIG (Chem. Weekblad, 1926, **23**, 265—269).—The surface tensions of pure sucrose solutions, as measured by the Traube stalagmometer and the torsion method of du Nouy (J. Gen. Physiol., 1919, **1**, 521), show close agreement, increasing regularly with the concentration. With molasses, both methods show irregularities and differences, and it is found impossible to use the measurement of surface tension for testing raw sugars. Norit is found to be more suitable than kieselguhr for removing wax, peptones, and other colloidal materials from sucrose solutions. S. I. LEVY.

Measurement of surface tension. R. GOIFFON (Bull. Soc. Chim. biol., 1926, **8**, 165—169).—A very thin sheet of platinum is suspended vertically from a suitable balance over the liquid the surface tension of which is to be measured. The vessel containing the liquid is raised until the platinum enters the liquid, and is then slowly lowered until the lower edge of the sheet just touches the liquid surface, as is shown by the weight becoming constant although the vessel is again slightly lowered. The surface tension (A) is given by the expression $(P_0-P_l)/2l$, where P_0=wt. of sheet in air, P_l=wt. just touching the liquid surface, and l=width of sheet. In practice, the surface tension is usually obtained by measuring P_0-P_l for pure water and for the liquid under examination. Then $A=(P_0-P_l)/(P_0-P_{H_2O})75$, taking 75 dynes as the surface tension of water at 18°. C. P. STEWART.

Drop-weight method of measuring surface tension. T. IREDALE (Nature, 1926, **118**, 48—49).—Polemical and explanatory (cf. Harkins, this vol., 568). A. A. ELDRIDGE.

Surface tension of crystals of barium sulphate and gypsum. D. BALAREV (Z. anorg. Chem., 1926, **154**, 170—172).—From the data of Hulet for the solubility of coarse and finely-divided material, Jones (A., 1913, ii, 300) has calculated the abnormally high values 1300 and 1050 dynes/cm. for the surface tensions of barium and calcium sulphates respectively. The solubility of Hulet's finely-ground material, besides being high on account of the presence of barium chloride in the sulphate, is also increased by the destruction of the crystal form produced by grinding. The new surfaces formed are more soluble on account of their abnormality and irregularity, and not on account of their size, and ultra-microscopic dust is also formed. By breaking thin plates of gypsum into several parts under a saturated solution, the conductivity of the solution is increased several per cent. A. GEAKE.

Spreading of oxyhæmoglobin. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 371—382).—The spreading of oxyhæmoglobin solutions has been studied by use of the Langmuir–Adam apparatus. On water of p_H 7 a considerable time is necessary for the maximum spreading to be reached, the surface occupied by 1 mol. being then $1400—1600\times10^{16}$ cm.^{2} Spreading is very much more rapid on buffer mixtures of p_H 4—5 and is practically instantaneous at p_H 3. In the latter case, the spreading is double the value for solutions of p_H 5·5—8. It is not the p_H of the liquid, however, which alone determines the spreading, for on a 0·001N-hydrochloric acid solution the spreading is often no more than 100×10^{16} cm.^{2} Probably the p_H in the surface is the decisive factor, and this is much nearer the neutral point in hydrochloric acid solution without buffer, because the protein and carbonate in the hæmoglobin solution bind the acid. The rapidity of spreading is dependent on temperature, as also is the maximum final area for solutions of high p_H, but not for strongly acid solutions. The coefficient of compressibility increases with increasing p_H and temperature, and the effect is reversible unless the film has been broken. As observed by Marcelin for fatty acids (A., 1925, ii, 772), the molecules of protein at the surface behave, under low pressure, as a dilute solution or gas. The spreading is probably due to the gradual solution in water of the amino- or amino-acid groups of the protein, which must therefore each occupy about 20 Å.^{2} of the surface. At a p_H value higher than 5, a double layer is probably formed. The possible arrangement of the oxyhæmoglobin molecules in the red corpuscles is discussed and, in connexion with the effect of acid on the spreading of the protein, it is suggested that any theory of muscular contraction should take this into consideration. M. S. BURR.

Liesegang's rings. K. JABLCZYŃSKI and S. KOBRYNER (Rocz. Chem., 1926, **6**, 182—189).—See this vol., 473.

Permeability of collodion membranes. R. COLLANDER (Soc. Sci. Fennica, Comment. Biol., 1926, II [6], 1—48).—In continuation of previous work on copper ferrocyanide membranes (A., 1924, ii, 154; 1925, ii, 201), experiments have been made with collodion membranes. The first was obtained from an ethereal alcoholic solution by drying, and the second and third were swollen by treatment with 68% and 80% aqueous alcohol, respectively. For various compounds, mainly organic acids and alcohols, the permeability P, given by $Pt(c_0-c_2)=100c_2$, where c_0 is the initial concentration of substance and c_2 is the concentration on the other side of the membrane after time t, has been measured. The results show that molecular size, in so far as it may be measured by mol. refraction, is the chief factor in determining the speed of transmission through the membrane. The limiting mol. sizes for the three grades of membranes are 0·44, 0·53, and 0·63 $\mu\mu$, respectively. The collodion membrane behaves as an ultrafilter, and, with increasing mol. size, the permeability velocity decreases much faster than the diffusion coefficient, especially with denser membranes. Mol. size is not, however, the sole factor in the process; in certain cases, solubility and perhaps adsorption are involved.

The difference of permeability of ions of electrolytes towards collodion membranes is unconnected with any specific variation in the condition of the collodion, such as occurs with membranes of protoplasm. The author agrees with Michaelis (cf. this vol., 120, 349) that the volume of the ions concerned is the important factor, and that anions of strong electrolytes are practically impermeable, especially when multi-valent.

Comparison with the behaviour of copper ferrocyanide membranes shows remarkable similarity. A difference is shown in the abnormally great permeability of ferrocyanide membranes for water. This may be explained by their power of binding water, possibly in an adsorbed condition. The author points out the excellent agreement between his results and those recently obtained by Fujita (this vol., 574). C. H. D. CLARK.

Rapid method of dialysis and its application to the preparation of dialysed ferric hydroxide. R. FABRE and H. PENAU (Bull. Soc. Chim. biol., 1926, **8**, 199—202).—The speed of dialysis is greatly increased by passing a stream of air or other suitable gas through the dialysing fluid. In preparing a colloidal solution of ferric hydroxide, the ferric chloride is decomposed by the addition of potassium hydrogen carbonate, first solid, and finally in saturated solution. Dialysis for 3 days with continuous agitation gives a crystalloid-free solution containing about 1·25% of Fe_2O_3. This can be concentrated to any desired extent by ultrafiltration. C. P. STEWART.

Enzyme purification by electrodialysis and electro-osmosis. R. FRICKE, F. A. FISCHER, and H. BORCHERS (Kolloid-Z., 1926, **39**, 152—165).—The purification of trypsin and invertase by electrodialysis and by electro-osmosis using a Prausnitz apparatus (Z. Elektrochem., 1922, **28**, 27) is described. As in earlier experiments with malt diastase (A., 1924, i, 469), the chief advantage of electrodialysis lies in the ease with which electrolytes and proteins are removed by this process, whilst carbohydrates are scarcely removed at all. Greater efficiency is to be expected from the electro-osmotic method if it were further developed. The increase in the inactivation velocity with increasing degree of purity is, however, a great hindrance to the perfection of these and other methods. N. H. HARTSHORNE.

Solutions of sulphur, selenium, and tellurium in pyrosulphuric acid. R. AUERBACH (Z. physikal. Chem., 1926, **121**, 337—360).—Measurements of the specific heats of liquid and solid pyrosulphuric acid and of the heat of fusion of this substance have been made. The cryoscopic constant, as calculated from these data, has been used to determine the apparent mol. wts. of sulphur, selenium, and tellurium in pyrosulphuric acid solution. An apparatus suitable for the necessary f.-p. determinations is described. It is considered that sulphur dissolves as S_2, S_2O_3 not being formed; metalloidal selenium dissolves as Se_2, "metallic" selenium as Se, and tellurium as Te.

L. F. GILBERT.

Calculation of ebullioscopic constants. N. DE KOLOSOVSKI (J. Chim. phys., 1926, **23**, 352—358).—Combination of the equation of van 't Hoff, the law of Trouton, and the relation between critical temperature and b. p. leads to the equation $E=0{\cdot}000095MT=0{\cdot}000057MT_c$ for the molecular rise of b. p., in which T is the b. p. and T_c the critical temperature of the solvent of mol. wt. M. The values of E thus calculated are in substantial agreement with those obtained by other methods, except where marked association or dissociation occurs. Little advantage is gained by replacing the simple Trouton rule by one of the more complex expressions.

W. HUME-ROTHERY.

Application of spectrographic methods to the study of complexes in solution. P. JOB (Compt. rend., 1926, **182**, 1621—1623; cf. this vol., 571).—The existence of KI_3 and of $KBrI_2$ in alcoholic solutions, and of $KHgCl_3$ and of K_2CdBr_4 in aqueous solutions, is demonstrated by the author's spectrographic method, and approximate values for the equilibrium coefficients are given. Potassium iodide exists as triple molecules in alcoholic solutions.

J. S. CARTER.

Thomas Graham's characterisation of the colloid state. P. P. VON WEIMARN (Kolloid-Z., 1926, **39**, 172—173).—Graham's conception of the colloid state is discussed and it is shown that his views on this were not nearly so narrow as is frequently supposed. N. H. HARTSHORNE.

Origin of the charge on colloidal particles. H. B. OAKLEY (J. Physical Chem., 1926, **30**, 902—916; cf. Wilson, A., 1918, ii, 260).—The theory of surface ionisation is developed to explain the charge on colloids. By combining the equation for the Donnan equilibrium with that for the dissociation of weak acids or bases, the views of Loeb are shown to explain the general behaviour of colloids (silicic acid) towards acids, bases, and salts. The results of Bradfield

(A., 1923, ii, 470) with clay suspensions agree closely with those predicted by the theory. The nature of the electrical double layer of colloids is also discussed in the light of the theory, and the present method of measuring the charge on colloids is adversely criticised. L. S. THEOBALD.

Dispersoid synthesis of gold. III. P. P. VON WEIMARN (Kolloid-Z., 1926, **39**, 166—172; cf. A., 1923, ii, 645, 869; 1925, ii, 196).—Solutions of colloidal gold in pure glycerol have been prepared by the decomposition by heat of auric chloride or chloroauric acid and by the citrate or tartrate methods, and in distilled and tap water, using human saliva as a dispersing agent. The glycerol solutions can be kept in open vessels for about a year without the formation of mould. They can be heated to 290° and solidified at about −200° to transparent jellies and glasses. The saliva-prepared solutions by evaporation at the ordinary temperature deposit a red precipitate in concentric rings. The precipitate is redispersible in distilled water. The author states that in this and previous work he has never encountered anything which contradicts his precipitation laws. N. H. HARTSHORNE.

Colloidal gold and an organic gold compound obtained biochemically. G. RIMINI (Gazzetta, 1926, **56**, 161—164).—If gold chloride solution is mixed with a paste of 100 g. of freshly pressed distillery yeast in about 500 c.c. of water and the mixture allowed to undergo auto-digestion at about 30—35°, an organic gold compound of acid character is formed, and may be precipitated from the filtered solution by means of sodium hydroxide solution. If the mixture of gold chloride and yeast suspension is freed from liquid shortly after preparation, and the residue treated for 12 hrs. with sodium hydroxide solution (d 1·28) and then filtered through calcined asbestos, careful acidification of the filtrate in the cold with concentrated hydrochloric acid gives a yellowish-white precipitate which gradually turns violet-brown; when the acid is removed by washing with water, this precipitate dissolves in water to give a solution showing all the characters of colloidal gold solution. T. H. POPE.

Colloidal manganese dioxide. A. STEOPOE (Bul. Chim., Soc. Româna Stiinte, 1925, **28**, 83—85).—Reduction of potassium permanganate solutions by gaseous ethylene yields stable sols of manganese dioxide (cf. Spring and Boeck, A., 1888, i, 228). The stability reaches a maximum at a manganese dioxide concentration of approx. 0·1882 g./litre. A sol of this concentration was preserved in a rubber-stoppered vessel for 195 days. H. E. F. NOTTON.

Reactions between solid substances reduced to the colloidal state. E. STERKERS and R. BREDEAU (Compt. rend., 1926, **182**, 1549—1551).—By means of a "colloid mill," metallic oxides have been made to combine with fatty acids of high mol. wt. A solution of the fatty acid in a suitable solvent is introduced into the mill with the finely-powdered metallic oxide, and the compound is obtained in a colloidal form which solidifies when the solvent evaporates. Calcium resinate, zinc oleate, and magnesium stearate have been prepared. J. GRANT.

Mechanism of emulsification. A. J. STAMM and E. O. KRAEMER (J. Physical Chem., 1926, **30**, 992—1000).—Recent studies of emulsions indicate the inadequacy of the "oriented wedge" theory of emulsions. Insufficient attention has been directed to the mechanism of emulsification, which consists of (1) a pulverisation of both phases into lamellæ and drops and (2) a coagulation or reunion of the drops of one or of both phases. The function of an emulsifying agent is to protect the drops of one phase to a certain extent whilst permitting the coagulation of the other phase, which then forms the dispersion medium. The stabilising action is probably dependent on the formation at the interface of a film the properties of which are determined by the geometrical shape and the size of the constituent molecules. L. S. THEOBALD.

Concentration and purification of solutions of hydrophilic colloids. H. BECHHOLD and E. HEYMANN (Biochem. Z., 1926, **171**, 33—39).—The statement of Reitstötter and Lasch (this vol., 352) that solutions of gelatin cannot be concentrated by ultrafiltration is contradicted. Gelatin and glue solutions can be fractionated by ultrafiltration, but the fractions so obtained are not identical with those obtained by fractional precipitation with magnesium sulphate. Glue can be partly freed from breakdown products and mineral impurities by washing on the ultra-filter, yielding a product of increased tenacity. In contradistinction to electrodialysis, electro-ultrafiltration effects the separation of non-electrolytes, and simultaneously fractionates and concentrates the colloidal constituents. E. C. SMITH.

Scattering of light by silicate solutions. P. B. GANGULY (J. Physical Chem., 1926, **30**, 706—712).—Aqueous solutions of commercial sodium silicate show a scattering power greater than that of ordinary molecular solutions, and the rate of change of this property with increasing ratio $SiO_2 : Na_2O$ increases suddenly after the ratio 3 is exceeded. Ultramicroscopical examination shows the number of particles per c.c. to increase also at this point. The initial scattering power decreases with time until an equilibrium value is reached. With a ratio 2 and a solution 2·5 molar with respect to silica, this required 50 hrs. It is concluded that the solutions contain colloidal aggregates or micelles which increase in concentration or size (or both) as the ratio $SiO_2 : Na_2O$ increases, and that the amount of colloidal matter increases rapidly after the ratio 3 is reached (cf. Harman, this vol., 478). L. S. THEOBALD.

Cholesterol and lecithin suspensions. P. RONA and W. DEUTSCH (Biochem. Z., 1926, **171**, 89—118).—The flocculation of cholesterol suspensions in buffer solutions of $M/500$ concentration occurs between p_H 2·4 and 3·2, irrespective of the buffer used and without buffer at 2·4. The flocculation of suspensions of lecithin occurs under the same conditions between p_H 1·73 and 1·75. Addition of chlorides accelerates the flocculation, activity increasing with the valency of the cation and with diminishing p_H. Addition of

mixtures of chlorides of uni- and bi-valent, and uni- and ter-valent metals causes a great increase in the rate of flocculation. In the case of lecithin suspensions, the alkali metals are practically without effect, the chlorides of bi- and ter-valent metals being increasingly active, and mixtures of salts showing an antagonistic action. Differences of p_H are of little significance. Lecithin exerts a strongly inhibitory action on the flocculation of cholesterol, even in extremely small concentration. The mixed suspension behaves like a pure lecithin suspension, except that flocculation is delayed. *iso*Butylurethane has no effect on the flocculation of cholesterol or of lecithin. Thymol has no effect on cholesterol, but increases the extent and rate of flocculation of lecithin. The addition of alkali or lecithin increases the stability of the suspension. E. C. SMITH.

Comparison of the heat effect of the swelling and mercerisation of cellulose with absorption and *X*-ray spectrographic experiments. J. R. KATZ (Z. Elektrochem., 1926, **32**, 269—274).—The relationship between the beneficial influence of a low temperature on the mercerisation of cellulose and the development of heat in this process is complicated by the fact that it is irreversible. Great significance is to be attached to measurements of the heat effect on swelling as a function of the sodium hydroxide concentration, or rather to a simultaneous consideration of these measurements and the absorption curve for the same cellulose, since mercerisation probably depends more on the quantities of sodium hydroxide and water absorbed than on the concentration of the mercerising solution. The heat effect–concentration curve of Barratt and Lewis (A., 1922, i, 526) is compared with a typical absorption curve of Vieweg (cf. A., 1907, i, 893). Both show two points of inflexion at approximately the same concentrations of sodium hydroxide, viz., 10—15% and 30%. This similarity between the two curves agrees with Vieweg's hypothesis that the inflexions are due to the formation of alkali–cellulose compounds, but if such were the case, it would be expected that the heat effect curve would be parallel to the concentration axis between its two inflexions, whereas actually it rises steeply. Facts connected with the water and sodium hydroxide absorption and with the alteration in the space lattice in this part of the curve are cited as possible explanations of the discrepancy. Further evidence in support of the compound hypothesis is given by the *X*-ray spectrograms of cellulose mercerised in sodium hydroxide solutions having concentrations between 10 and 15%. These show a characteristic pattern the intensity of which increases with increasing sodium hydroxide percentage. Within this region too the heat effect curve shows a relatively large development of heat with increasing sodium hydroxide percentage, which can be explained as due to the heat of formation of a compound giving the characteristic spectrogram referred to above. For a given concentration of sodium hydroxide, this pattern has a greater intensity the lower the temperature of mercerisation, and thus shows a similarity to other characteristics of the mercerised state. The irreversibility of the mercerisation process and the consequent difficulty of treating it thermodynamically are discussed. N. H. HARTSHORNE.

Swelling of cellulose. R. O. HERZOG (Kolloid-Z., 1926, **39**, 98—107).—The swelling of cellulose fibres in aqueous solutions of electrolytes is discussed, with many references to previous work. Swelling is connected with the formation of chemical compounds between the cellulose and the electrolyte; in other words, with the transformation of a homopolar radical lattice into a heteropolar ion lattice. On account of the probable similarity in the structure of all polysaccharides, the results obtained with cellulose may be supposed to be characteristic of the whole class of substances. Thus polysaccharides containing no electrolytes do not swell in water, whilst the tumefactory behaviour of others has been traced to the presence of electrolytes (*e.g.*, phosphoric acid combined with amylopectin has been found by Sameč to cause the swelling of starch). The evidence for the formation of compounds between cellulose on the one hand and bases, Schweizer's reagent, copper diethylenediamine hydroxide, nitric acid, and concentrated solutions of alkali and alkaline-earth salts on the other is recorded and their constitution discussed. The combination of water with the ions and the cellulose molecule, the action of the water on the crystallite aggregate (volume increase and mercerisation contraction), the alteration in elastic properties due to swelling, and the complications caused by the irregularity of and impurities in the natural product also receive treatment.
N. H. HARTSHORNE.

Preparation of very strongly stretched gelatin and its *X*-ray diagram. Gelatin and collagen. O. GERNGROSS and J. R. KATZ (Kolloid-Z., 1926, **39**, 181—183).—A method for stretching gelatin up to five times its original length is described. The *X*-ray diagram of the product is much more like the diagram of collagen than is that of gelatin stretched only to twice its original length, described in an earlier communication (Naturwiss., 1925, **13**, 901).
N. H. HARTSHORNE.

Cleavage of strongly stretched gelatin. J. R. KATZ and O. GERNGROSS (Kolloid-Z., 1926, **39**, 180—181).—Gelatin stretched to five times its original length and dried in air shows a tendency to crack in the direction of stretching. By further drying in a vacuum and then tapping with a hammer, it breaks up into threads similar in appearance to asbestos.
N. H. HARTSHORNE.

Swelling and osmotic pressure of gelatin in salt solutions. J. H. NORTHROP and M. KUNITZ (J. Gen. Physiol., 1926, **8**, 317—337).—The effect of salts on the swelling of gelatin at p_H 4·7 is closely paralleled by the effect on the osmotic pressure, and up to an increase in volume of about 800% the bulk modulus (calculated from the swelling and the osmotic pressure) is constant. If any of the salts increases the swelling above this point, the modulus decreases, showing that the elastic limit has been exceeded, a deduction which explains the fact that gelatin swollen in acid returns to its original volume after removal of the acid, whereas gelatin swollen in

salt solution does not do so. The modulus of elasticity of gelatin swollen in salt solutions varies in the same way as the bulk modulus calculated from the swelling and the osmotic pressure. The increase in osmotic pressure caused by the salt disappears on removal of the salt. The observed osmotic pressure is much greater than that calculated from the Donnan equilibrium except in the case of aluminium chloride, where the calculated and observed values agree closely. The increase in swelling in salt solutions is caused by an increase in osmotic pressure due, probably, to a change in the osmotic pressure of the gelatin itself rather than to a change in ion concentration.

C. P. STEWART.

Elasticity of jellies of cellulose acetate in relation to their physical structure and chemical equilibria. H. J. POOLE (Trans. Faraday Soc., 1926, **21**, 82—106).—See this vol., 353.

Adsorption. XIV. Influence of hydrogen ions on the stability of sols. S. GHOSH and N. R. DHAR (J. Physical Chem., 1926, **30**, 830—844; cf. A., 1925, ii, 386, 778).—Existing work on the coagulation of sols in the presence of various concentrations of hydrogen ions is explained by (1) adsorption of ions carrying the same charge as the sol, (2) hydrolysis of the sols and formation of acids which stabilise them, and (3) hydrolysis of coagulating electrolytes. Addition of acids renders the sols unstable by checking hydrolysis, whilst alkalis stabilise by extending hydrolysis. Results now obtained show that the peptising influence of hydrogen ions is less marked when sols of ferric and chromium hydroxides are coagulated by sodium acetate as compared with potassium or sodium chlorides. Potassium oxalate is a more effective coagulant for ferric hydroxide sol than potassium sulphate, in each case in presence of hydrochloric acid. With increasing concentration of this acid, the precipitation value of the latter remains constant, whilst that of the former increases. In the case of chromium hydroxide sol, the coagulating power of potassium sulphate at first remains constant in the presence of increasing amounts of sulphuric acid and then increases; that of the oxalate increases throughout. At a definite concentration of acid, the coagulating powers become equal. Sodium potassium tartrate, in the absence of hydrochloric acid, is a better coagulant than potassium sulphate, but in the presence of acid the converse is true. The importance of (1) in coagulation has been overlooked by Tartar and Gailey (A., 1922, ii, 829) and the influence of hydrogen ions over-emphasised.

L. S. THEOBALD.

Precipitation of mastic suspensoids. H. V. TARTAR and C. Z. DRAVES (J. Physical Chem., 1926, **30**, 763—776; cf. Tartar and Gailey, A., 1922, ii, 829).—The precipitation of mastic suspensoids at 25° has been examined in relation to the hydrogen-ion concentration of the dispersion medium. Merck's powdered mastic and mastic from tears of the original gum were precipitated by potassium chloride. The two varieties of different dispersity and concentration showed differences in acidity which were maintained practically unchanged after precipitation (cf. Pauli and Matula, A., 1917, ii, 563; Browne, A., 1923, ii, 244). Ultrafiltration and dialysis showed the p_H value of a mastic suspensoid to be due to organic acid in true solution. In agreement with Michaelis and co-workers (A., 1921, ii, 682; 1922, ii, 429), it is found that the greater the hydrogen-ion concentration the less the amount of potassium chloride required for the precipitation of the suspensoid. Dispersity and concentration affect coagulation only through their effect on hydrogen-ion concentration, which, in the absence of added electrolyte, is greater the greater the concentration of the sol, and increases with rate of formation of the sol. The decrease in acidity with dilution explains the rule of Burton and Bishop (A., 1921, ii, 176) that dilution increases the concentration of uni-univalent salt required for precipitation. The logarithm of the dilution of potassium chloride required for coagulation varies linearly with the p_H for each variety of mastic. The corresponding curves run parallel to each other between the range p_H 2·4 to 5·0, sols from Merck's mastic requiring a greater concentration of salt at a given p_H. The suspensoids of a given variety of mastic precipitate at approximately the same value for p_H with hydrochloric acid alone, independent of concentration or dispersity. Beyond p_H 6·0, they all precipitate with nearly the same concentration of potassium chloride.

L. S. THEOBALD.

Adsorption of ions in connexion with their coagulative power. K. C. SEN (Kolloid-Z., 1926, **39**, 140—152).—The lowering of the charge on a colloid may be due, not only to the electrical adsorption of oppositely charged ions, but also to adsorption under the influence of chemical forces. On account of this chemical attraction, many univalent ions, *e.g.*, organic cations and silver, show an abnormally great coagulative power, and the deviations from the simple Schulze–Hardy valency rule may be thus explained. The chemical attraction is independent of the electrical nature of the colloid surface, but depends to some extent on its magnitude. Adsorption on a precipitated substance is chiefly influenced by this factor, but at the same time a small degree of electrical adsorption is also possible because in the presence of water the surface of the adsorbent is not electrically neutral. Many experiments with ions of equal valency have supported completely the view of Freundlich (A., 1907, ii, 939) that ions with the greatest coagulative power are the most strongly adsorbed and *vice versa*. If the adsorption values are expressed in mols., the theoretical relationship between the adsorbed quantities of ions of different valency and their coagulative power is complicated, but if they are expressed in equivalents, in most cases practically identical ion series are obtained, not only for coagulative power, but for cataphoretic and electro-osmotic experiments, and also adsorption. The results are discussed in relation to a paper by Ostwald (Kolloid-Z., 1920, **26**, 28, 69).

N. H. HARTSHORNE.

Coagulation of alkali-blue–tannin sols by electrolytes. H. FREUNDLICH and S. MITSUKURI (Kolloid-Z., 1926, **39**, 123—127).—The coagulation of alkali-blue sols containing tannin by different electrolytes has been investigated at different tannin

concentrations. Towards electrolytes with univalent inorganic cations tannin acts as a sensitiser at all concentrations; towards electrolytes with bivalent cations it sensitises at small and protects at greater concentrations, whilst towards tervalent cations its protective action preponderates. The addition of tannin does not alter the cataphoretic migration velocity to any marked extent; the view of Brossa (A., 1923, i, 397) that tannin sensitises by dehydration and not by discharging the colloid particles is thus confirmed. The increase in protective action with the cation valency of the electrolyte is in harmony with the behaviour of other hydrophile colloids as regards protective action (*e.g.*, gum arabic on silver sol). N. H. HARTSHORNE.

Formula for the critical coagulation concentration of electrolytes for the precipitation of mastic sol. T. TSUJI (Kolloid-Z., 1926, **39**, 110—112).—Determinations have been made of the critical concentrations of sodium and potassium chlorides required to coagulate mastic sol at different hydrogen-ion concentrations. The critical concentrations are for these salts independent of the concentration of the colloid. The following equation has been found: $hi^{1\cdot5}/(i_0^{1\cdot5}-i^{1\cdot5})=K$, where K is a constant, i_0 the maximum critical coagulation concentration of electrolytes of which the action is independent of the colloid concentration, and i and h are the concentrations of the salt and hydrogen ions, respectively, which must be combined to precipitate the colloid. The equation is easier to manipulate than that of Michaelis and Hirabayashi (A., 1922, ii, 429).

N. H. HARTSHORNE.

Reciprocal action between colloidal solutions. I. Relation between mutual flocculation, protective action, and sensitisation in the reciprocal action of two sols. A. RABINERSON (Kolloid-Z., 1926, **39**, 112—123).—The behaviour as regards flocculation, protective action, and sensitisation of the following mixtures of sols has been investigated: ferric oxide and Prussian-blue, silver and ferric oxide, ferric oxide and night-blue, ferric oxide and dextrin, Prussian-blue and albumin, silver and albumin, silver and mastic, ferric oxide and albumin. Each pair in varying proportions was observed for 24 hrs., both in absence of electrolytes and in different concentrations of sodium chloride. In the former case, flocculation occurs if the colloids are oppositely charged and the curve showing the relation between degree of flocculation and composition has a well-defined maximum corresponding with complete precipitation. In all cases the degree of flocculation increases with increasing sodium chloride concentration, but the position of the maximum remains unaltered. Sensitisation and protective action are only manifestations of different flocculation conditions; in different electrolyte concentrations the same quantity of one colloid may either sensitise or protect the other. Protective action is exerted by hydrophobe as well as by hydrophile colloids, but in the former case the protecting colloid must be more stable than that protected. It appears that a colloid present in excess may protect another more sensitive, at electrolyte concentrations which lie between the coagulation values of the two sols.

N. H. HARTSHORNE.

Solution of silver micelles by hydrogen peroxide. Adsorption compounds or astoicheiometric compounds in silver sols and precipitates. A. FODOR (Kolloid-Z., 1926, **39**, 173—178).—The fading of colour which occurs when hydrogen peroxide in the presence of acids or ammonia reacts with silver sols has been studied. It has been found that, not only silver sols, but also coarsely-dispersed silver precipitates are similarly dissolved. The finer particles of a silver precipitate dissolve in hydrogen peroxide which has been de-acidified by shaking with barium carbonate, but the coarser particles and the micelles in a silver sol do not. The process of solution in all cases consists of the oxidation of the silver by the peroxide to silver hydroxide and the solution of this by acid (or ammonia). Only the weakest acids (*e.g.*, amino-acids) are necessary. The reason for the solution of fine particles of precipitate without the addition of any acid is that these particles carry adsorbed carbonic acid. The mechanism of the process and the constitution of the micelles or particles in this and other cases are discussed.

N. H. HARTSHORNE.

Action of protective colloids on mercuric iodide. J. SAMESHIMA and T. SUZUKI (Bull. Chem. Soc. Japan, 1926, **1**, 81—83).—When 1 c.c. of 0·1*N*-mercuric chloride and potassium iodide solutions, respectively, are added to 100 c.c. of 0·0025% gelatin solution, retarded deposition of red mercuric iodide occurs; when 1·5 c.c. and 0·005% gelatin solution are used, there is a pink turbidity, which separates into a red precipitate and a white, turbid liquid; and when the gelatin is of concentration 0·01% or more, the precipitate is yellow, changing to white and eventually to red. Yellow mercuric iodide is always the initial product, envelopment of the particles by gelatin preventing their conversion into the red form. The white substance is a compound of 93% of mercuric iodide and 7% of gelatin. Other albuminoid substances exhibit similar protective action, which, however, is not proportional to the gold number of the colloid.

S. K. TWEEDY.

Change in the caseinogen constituent in the lime–caseinogen–calcium phosphate complex, and the influence of rennin on this complex. C. PORCHER (Compt. rend., 1926, **182**, 1420—1422).—Alkaline [lime] caseinogen complexes are altered by heating in proportion to their alkalinity, phosphoric acid being split off from the protein molecule. Subsequent addition of phosphoric acid and of rennin cause increasing diminution in the firmness of the curd formed. Addition of formaldehyde inhibits coagulation when the temperature is sufficiently high; this is only slightly affected by the addition of phosphoric acid to the heated formolised complex. It is thus possible (cf. this vol., 677) to act on either the phosphatic or the caseinogen constituent. The latter appears to be the determining factor in the case of coagulation by rennin. H. J. EVANS.

Grain size and the quantum theory of photographic exposure. M. C. HYLAN (J. Physical Chem., 1926, **30**, 845—848; cf. Germann and Hylan, A., 1924, ii, 9, 409).—Emulsions of silver iodide free of adsorbed impurities show the finer grained emulsion to be faster than the coarser grained, and thus afford support for the theory of Germann and Hylan (*loc. cit.*) as opposed to the views of Silberstein (Phil. Mag., 1922, **44**, 257) and Rawling (B., 1924, 693).
L. S. THEOBALD.

Quantitative study of the association of mercuric chloride. F. BOURION and E. ROUYER (Compt. rend., 1926, **182**, 1546—1549).—An attempt is made to reconcile the authors' conclusion that at 100° an equilibrium exists between simple and triple mercuric chloride molecules (A., 1923, ii, 568) with Linhart's view that at 25° and 40° there is an equilibrium between the simple and double molecules (A., 1915, ii, 99). J. GRANT.

Dissociation constants of weak acids and bases from solubility measurements. N. R. DHAR (Z. anorg. Chem., 1926, **153**, 323—331; cf. A., 1913, ii, 565; Z. Elektrochem., 1913, **19**, 407; A., 1915, ii, 532).—Sparingly soluble bases are more soluble in the solution of a salt of a weak base and strong acid than in water, and weak acids are more soluble in solutions of sodium salts of weak acids than in water. Dissociation constants of weak acids may be calculated by a simple equation from data of solubility measurements.

Data for the solubility of boric and arsenious acids at 33° are evaluated in this manner. M. CARLTON.

Theory of dielectric polarisation in salt solutions. L. EBERT (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 454—461).—From a consideration of the specific polarisation of a solution and of the solvent, as determined by the dielectric constant, an expression has been deduced for w, the relative number of dipoles fixed by one molecule of the solute. This quantity has been calculated for potassium and barium chlorides, cadmium bromide, and tetrapropylammonium iodide at different concentrations from the experimental data of several investigators, and the results appear to be in qualitative agreement with the values obtained by other methods, *e.g.*, electrolytic transference. For the last two salts, w diminishes considerably with increase in concentration. In the case of cadmium bromide, this is probably to be ascribed to the replacement of Cd^{++} ions by $CdBr^{+}$ ions, which are both larger and have a smaller charge than the former, and therefore less attractive power. M. S. BURR.

Activity coefficients of hydrogen chloride in non-aqueous solutions. W. W. LUCASSE (Z. physikal. Chem., 1926, **121**, 254—266).—The activity coefficients of hydrogen chloride in aqueous glycerol solutions (1 and 5 mol. % of glycerol) have been determined by a potentiometric method. These coefficients and also those similarly obtained by Harned and Fleysher (A., 1925, ii, 538) with solutions of hydrogen chloride in aqueous ethyl alcohol, and by Nonhebel and Hartley (*ibid.*, 1061) with solutions of hydrogen chloride in methyl alcohol, agree with those calculated by Hückel's equation over the hydrogen chloride concentration range 0·005 to 1*M*. Hückel's equation is thus substantiated with solvents of widely different dielectric constants. L. F. GILBERT.

[*E.M.F.* measurements with] aqueous solutions of simple electrolytes. H. S. HARNED and G. ÅKERLÖF (Physikal. Z., 1926, **27**, 411—448).—In reference to the theory of electrolytes put forward by Debye and Hückel, the authors have reviewed the available *E.M.F.* data for reversible cells containing solutions of chlorides and sulphates of the alkali and alkaline-earth metals. In the case of solutions containing a single electrolyte, the results are in satisfactory agreement with Hückel's simplified general formula for the activity coefficient of an electrolyte (A., 1925, ii, 513). In the case of mixed solutions, the agreement is not nearly so good, except for those solutions containing chlorides only. R. CUTHILL.

Activity coefficients and transport numbers of barium bromide. R. W. GELBACH and W. F. HUPPKE (J. Amer. Chem. Soc., 1926, **48**, 1504—1506).—From the *E.M.F.* measurements at 25° of some concentration cells (cf. Pearce and Gelbach, A., 1925, ii, 867), the activity coefficients and transport numbers (cf. MacInnes and Beattie, A., 1920, ii, 466) of barium bromide are calculated. The geometric mean activity coefficients agree closely with those calculated for barium chloride from f.-p. data (cf. Lewis and Linhart, *ibid.*, 97). S. K. TWEEDY.

Aqueous solutions of sodium silicates. III. Sodium-ion activity. R. W. HARMAN (J. Physical Chem., 1926, **30**, 917—924; cf. this vol., 478).—Measurements of the activity of the sodium ion in aqueous solutions of sodium silicates of the ratios $Na_2O : SiO_2$, 1 : 1, 1 : 2, 1 : 3, and 1 : 4 at concentrations ranging from 1·0 to 0·1N_w at 25° have been made by the electrometric method. The curve obtained by plotting the activity coefficient, γ, against weight normality, N_w, shows a minimum (at 0·2N_w) only in the case of the ratio 1 : 1. In concentrated solution, the values of γ for the ratio 1 : 1 show that 40% of the total sodium exists in the active ionic state and in dilute solution practically all the sodium is in this condition. With the ratios 1 : 3 and 1 : 4, however, the values of γ are very low in concentrated solution and even in dilute solution are still abnormally low, indicating that the sodium in solution does not exist wholly as sodium ion. When γ is plotted against the ratio $Na_2O : SiO_2$, the decrease in γ with an increase in the proportion of silica is regular for the 0·1N_w solution and for the higher concentrations beyond the ratio 1 : 2. Increasing the concentration of a solution for a given ratio and increasing the ratio for a given concentration thus reduce the activity of the sodium ion to a marked degree. L. S. THEOBALD.

Ionic activity *versus* concentration in the interpretation of equilibria between amalgams and aqueous sodium and potassium mixtures. G. M. SMITH (J. Physical Chem., 1926, **30**, 849—857).—The interpretation given by Bjerrum and Ebert (Kgl. Danske Videnskab. Selskab, Math-fys. Medd., 1925, **6**, 3) to the data of Wells and Smith (A., 1920,

ii, 361) on amalgam equilibria is adversely criticised; it is maintained that the possibility of complex formation cannot be ignored. L. S. THEOBALD.

Acid-basic function of molecules and its dependence on the electric charge type. J. N. BRÖNSTED (J. Physical Chem., 1926, **30**, 777—790; cf. Rec. trav. chim., 1923, **42**, 718).—The definition of acids and bases by the scheme (1) A (acid) $\rightleftharpoons$ B (base) + $H^{\cdot}$ involves the admission of ions as well as electrically neutral molecules as acids and bases. For example, if A represents acetic acid, then B, the base, must be the acetate ion. Hence, in comparing the first with the second dissociation step of a dibasic acid, the dissociation of an electrically neutral acid and an acid of one negative electric charge are actually considered. The positive aquo-ions, such as $Al(H_2O)_6^{\cdot\cdot\cdot}$ and $[Co(NH_3)_5H_2O]^{\cdot\cdot\cdot}$ are acids, the former dissociating thus: $\underset{\text{(acid)}}{[Al(H_2O)_6]^{\cdot\cdot\cdot}} \rightleftharpoons \underset{\text{(base).}}{[Al(H_2O)_5OH]^{\cdot\cdot}} + H^{\cdot}$. The acid property is more pronounced the higher the positive charge, thus, substitution by anions such as Cl' or NO_2' in the ion $[Co(NH_3)_5H_2O]^{\cdot\cdot\cdot}$ reduces the positive charge by one, the resulting ion exercises a smaller repellent effect on the positively charged hydrogen ion, and a weaker acid is the result. Further, quadrivalent complex platinum ions form stronger acids than the corresponding tervalent cobaltic ions.

In correspondence with the theory of Kossel (A., 1916, ii, 243), the charge of the central atom of a molecular configuration plays an essential part in determining its acid and basic properties. The acidity and basicity of the various molecules formed by the elements of any series of the periodic table show a graduated charge, proving acidity to be a definite function of the natural electric charge of an element. Further, a comparison of the first and second series in the periodic table shows the distance between the central atom and the hydrogen ions to be a factor (cf. Kossel, *loc. cit.*), the elements in the first series with smaller atomic volume forming hydrated ions of greater acidity than those in the second.

The solvent influences the acid-basic equilibrium (*a*) through its dielectric constant and (*b*) through its acid-basic properties. The electrostatic effect tends to make acids with two or more positive charges more strongly ionising in solvents of low dielectric constant than in water. On account of the hydration of the hydrogen ion, scheme (1) is more correctly represented as A $(acid)_1 + H_2O$ $(base)_2 \rightleftharpoons$ B $(base)_1 + H_3O^{\cdot}$ $(acid)_2$, where the hydrogen ion cannot exist in the presence of other molecules. The ionising tendency is thus to be measured by the product of an acid and a basic constant. The slight ionisation in pure solvents such as hydrogen chloride or water and the strong ionisation in a mixture of the two is then explained. L. S. THEOBALD.

Electropy. IX. L. KARCZAG (Biochem. Z., 1926, **170**, 337—343).—A reply to Bálint (this vol., 125) concerning the relationship of hydrogen-ion concentration and electropy (cf. A., 1924, i, 688).

P. W. CLUTTERBUCK.

Thermodynamics of non-isothermal systems. E. D. EASTMAN (J. Amer. Chem. Soc., 1926, **48**, 1482—1493).—Theoretical. Non-isothermal equilibrium within a homogeneous or heterogeneous system, in which the irreversible effects are known or are negligibly small, may be established through a series of heat reservoirs differing infinitesimally in temperature. If S_r is the entropy of the reservoirs and S_s that of the system, then $\delta S_r + \delta S_s = 0$; with the aid of the first law, δS_r and δS_s are evaluated for individual systems, and in this way expressions representing the equilibrium conditions of these systems are obtained. Applications are made to thermal endosmosis, osmotic temperature (which is shown to be thermodynamically without significance), thermocells, electric and non-electric thermocouples, etc.

S. K. TWEEDY.

Properties of ammonium nitrate. I. Metastable inversion. II. System ammonium nitrate–ammonium chloride. III. System ammonium nitrate–ammonium sulphate. N. L. BOWEN (J. Physical Chem., 1926, **30**, 721—725, 726—735, 736—737; cf. Early and Lowry, J.C.S., 1919, **115**, 1387; Wallerant, Bull. Soc. Min. Franç., 1905, **28**, 311).—I. The transformations of crystalline ammonium nitrate have been followed by direct microscopical observation. A metastable inversion corresponding with the change orthorhombic (IV) $\rightleftharpoons$ tetragonal (II) occurs at approximately 50°. The temperature given by Behn (Proc. Roy. Soc., 1908, **80**, 449), viz., 45°, is too low. The transformation, in spite of the metastability of both forms at 50°, is more readily observed than that of most of the stable inversions. Extrapolation of Bridgman's values (Proc. Amer. Acad. Arts, 1916, **51**, 605) for the change II $\rightleftharpoons$ IV at high pressure gives 50·5° for the inversion temperature at atmospheric pressure.

II. The complete equilibrium diagram for this system has been obtained by direct observations under the microscope, whereby the various crystalline phases can be identified through their optical properties and the phase changes in the system can be observed actually in progress. The results of Perman (J.C.S., 1922, **121**, 2473) are confirmed, but, in addition, a series of solid solutions has been found. All mixtures from pure ammonium nitrate up to 8% by weight of ammonium chloride crystallise to a homogeneous mix-crystal phase of isometric symmetry. As a result of the existence of these solid solutions, the eutectic is not reached until the limits of solid solution are passed, each member of the series beginning to melt at a successively higher temperature as the pure nitrate is approached. The inversion intervals have also been observed. The inversion isometric (I) $\rightarrow$ tetragonal (II) changes from 125·5° for pure ammonium nitrate to 109° for the solid solution containing 3·5% of ammonium chloride. At the same temperature, the curve of unmixing of the solid solutions is met and the mixing and unmixing of the solid solutions along this curve are described. Solid solutions of ammonium chloride in the other modifications of the nitrate are not formed.

III. Direct observation of the phase-changes shows that in agreement with Perman and Howells (J.C.S.,

1923, **123**, 2128) the rising liquidus in the system ammonium nitrate–ammonium sulphate is due to solid solution, and not to the limiting position of the eutectic as suggested by Freeth (A., 1925, ii, 669).

L. S. THEOBALD.

Thermodynamic potential difference between two liquid phases. S. VOSNESENSKI (J. Russ. Phys. Chem. Soc., 1926, **57**, 475—485).—See A., 1925, ii, 673.

Thermal dissociation of calcium and magnesium carbonates. H. L. J. BÄCKSTRÖM (Z. physikal. Chem., 1926, **121**, 289—298).—An investigation of the thermal dissociation of calcium carbonate by a method similar to that of Andrussov (A., 1925, ii, 803) gave results differing from those of the latter author but agreeing with those of Johnston (A., 1910, ii, 831). It is considered that Andrussov's temperature measurements were inaccurate.

Of published data concerning the thermal dissociation of magnesium carbonate, those of Marc and Šimek (A., 1913, ii, 708) are probably the most trustworthy.

L. F. GILBERT.

Thermal decomposition of methane. II. R. C. CANTELO (J. Physical Chem., 1926, **30**, 899—901; cf. A., 1924, ii, 840).—The equilibrium $CH_4 \rightleftharpoons C+2H_2$ is considered in reference to the results of Bone and Coward (J.C.S., 1908, **93**, 1197).

L. S. THEOBALD.

Basic copper sulphate at 100°. J. M. BELL and G. M. MURPHY (J. Amer. Chem. Soc., 1926, **48**, 1500—1502).—An investigation of the ternary system copper oxide–sulphur trioxide–water at 100° indicates that basic copper sulphate has the composition $4CuO,SO_3,4H_2O$ at this temperature (cf. Britton, this vol., 246). At least 6 hrs. are necessary for the attainment of equilibrium between the components at 100°.

S. K. TWEEDY.

Eutectic point lowering in binary mixtures. E. KORDES (Z. anorg. Chem., 1926, **154**, 93—125).—A mechanical mixture of two components, which form no mixed crystals or compounds, frequently begins to melt at a temperature below the m. p. of either pure component. This is probably due to the destruction of the crystal structure by diffusion at high temperatures. When the two components are binary electrolytes, the m. p. of the eutectic is related to those of the two components by equations of the form $\log (I_b-I_e)/I_a=c_1 \log I_b/I_a-c_2$, in which I_a, I_b, and I_e are the absolute m. p. of the higher-melting and lower-melting components and of the eutectic, respectively, and c_1 and c_2 are constants. The composition of the eutectic is given by equations of the form $I_e/I_a=c_3 \log$ (mol.% a)$+c_4$, in which c_3 and c_4 are constants. Binary electrolytes fall into three classes in which neither, one, or both of the components are associated, and these are distinguished by different values of the constants c_1, c_2, c_3, and c_4. In the first class when $I_a=I_b$, $I_e/I_a=0{\cdot}78$ and the eutectic contains 50 mol.% of each component; as I_b falls compared with I_a, I_e approaches I_b and equals it when $I_b/I_a=0{\cdot}45$. Similar equations hold for systems of two ternary electrolytes, but the ratio I_e/I_a is somewhat higher. Since few binary systems of metals are known in which neither compounds nor mixed crystals are formed, partial systems with congruent m. p. and no mixed crystal formation are considered, *e.g.*, the three partial systems of the system $A–A_2B–AB_2–B$. Equations similar to the above are applicable to such systems, and also to systems of non-electrolytes other than metals. The eutectic point lowering is greatest for binary electrolytes, less for ternary electrolytes, and least for non-electrolytes, whereas the lowering of the f. p. of dilute solutions is greater for ternary than for binary electrolytes. When a mixture of two substances is heated, fusion begins when the mobility of the constituents of the lattice of the higher-melting component is sufficient to allow penetration by the other component with consequent destruction of the crystal structure. When the ratio of the m. p. of the two components is less than 0·5—0·6, this does not occur below the m. p. of the lower-melting component, and no eutectic is formed. The intermediate position of ternary electrolytes relative to binary electrolytes and non-electrolytes is in agreement with their crystal structure as determined by *X*-ray examination.

A. GEAKE.

System stannic oxide–water. A. GUTBIER, G. F. HÜTTIG, and H. DÖBLING (Ber., 1926, **59**, [*B*], 1232—1246).—The pressure–temperature curves for the system give no indication of the existence of definite hydrates. Ageing of the specimens [part of which are those used by Mecklenburg (A., 1910, ii, 41; 1912, ii, 355)] is accompanied by weaker retention of water. At higher temperatures, the pressure increases relatively rapidly at first, but there is a subsequent slow increase. It is probable that the ultimate state towards which the system tends is water and anhydrous stannic oxide; this accords with the fact that hydrated stannic oxide does not occur naturally. The reversibility of the system is incomplete. *X*-Ray measurements show that fresh preparations give no interference figures, but gradually acquire the lattice of cassiterite. In conjunction with adsorption experiments and determinations of specific heat and density, the observations show that there is no region in which a stable stoicheiometric chemical compound of stannic oxide and water is capable of existence. The so-called "stannic acids" cannot be regarded as individuals subject to the laws of definite proportions. The assumption of such compounds is not necessary for the explanation of solubility and adsorption effects in systems such as stannic oxide–water or aluminium oxide–water.

H. WREN.

Dependence of vapour pressure of desminite on water content and temperature. L. CHROBAK (Bull. Int. Acad. Polonaise, 1925, *A*, 333—345; cf. Tammann, A., 1898, ii, 208; Löwenstein, A., 1909, ii, 736).—The fully-hydrated mineral has the composition $CaO,Al_2O_3,6SiO_2,7H_2O$, part of the calcium being usually replaced by sodium, and in a lesser degree by potassium. Vapour pressures in relation to water content and temperature have been measured, using specimens ranging from the almost anhydrous substance to the fully hydrated form. The results show that dehydration and hydration are not entirely reversible. The isobars and isotherms indicate that there are at least two stages in the hydration process, the first of which apparently involves the formation of

a tetrahydrate. The measurements appear, however, to support the formula $CaAl_2Si_2O_8,H_8Si_4O_{12},H_2O,2aq$ suggested by Tschermak (A., 1921, ii, 703), 4 mols. of water being combined with silica. The remaining water is present as water of crystallisation and as adsorbed water. It is, however, impossible to decide whether there are 2 mols. of the former and 1 mol. of the latter or *vice versa*. J. S. CARTER.

Transition points of salt hydrates in non-aqueous solvents. W. W. LUCASSE and J. M. HARRIS, jun. (J. Physical Chem., 1926, **30**, 930—938).—The transition points of certain salts have been determined from the resistance–temperature curves of solutions of the salts in alcohol, the point of intersection of the two curves being calculated from the difference in the slopes of the curves above and below the transition temperature. For the system $CaCl_2,6H_2O \rightleftharpoons CaCl_2,4H_2O(\beta)+2H_2O$, the transition temperatures in three diluted solutions were 29·2°, 29·2°, and 29·1°, respectively, and in a solution saturated at the ordinary temperature, 29·8°, indicating that the unstable β-tetrahydrate is formed in the less concentrated solutions. The temperatures obtained for other systems are as follows: $LiNO_3,3H_2O \rightleftharpoons LiNO_3,0{\cdot}5H_2O+2{\cdot}5H_2O$, 29·2° and 29·8°; $Ba(C_2H_3O_2)_2,H_2O \rightleftharpoons Ba(C_2H_3O_2)_2+H_2O$, 42·4° and 40·3°; and $CaBr_2,6H_2O \rightleftharpoons CaBr_2,4H_2O+2H_2O$, 34·0°. No light is thrown on the problem of complete and partial dissociation. L. S. THEOBALD.

Ternary system iron–chromium–carbon. A. VON VEGESACK (Z. anorg. Chem., 1926, **154**, 30—60).—Iron and chromium form a continuous series of mixed crystals. The m. p. is depressed when chromium is added to iron to a minimum of 1490° with 28% of chromium, and then rises to that of chromium, which is above 1700°. The lower values previously found for chromium are probably due to the presence of carbon arising from carbon monoxide penetrating the walls of the crucibles. The best material for the crucible is silica for the alloys rich in iron and "pythagoras" for those rich in chromium. The carbon content of the alloys after fusion was always less than 0·1%. To obtain homogeneous mixtures from the constituents it is necessary to heat at 100° higher than the m. p. of the higher-melting component; when this is impossible, vigorous stirring and possibly a second fusion are necessary. The transformation point of γ- to α-iron is lowered by the addition of chromium; it is also less well-defined and cannot be observed when the alloy contains 20% of chromium. The microscopic structure of alloys containing less than 30% of chromium depends on their heat treatment, and this is probably due to the transformation of the iron being slow. When the chromium content is above 30%, the alloys consist principally of large polyhedra, but small needles and grains are also observed which probably arise from impurities; the structure is independent of the heat treatment. In the binary system chromium–carbon, the m. p. of the eutectic Cr–Cr_5C_2 is 1543°, and this probably has been recorded as the m. p. of chromium. Within the concentration range Fe–Fe_3C–Cr_5C_2–Cr, the solid phases separating out are mixed crystals of iron and chromium which may also contain a little carbon, rhombic cementite which contains little or no chromium, and mixed crystals of the carbides Cr_5C_2 and Fe_3C, which are probably hexagonal. Each of these solid phases exists in bivariant equilibrium with the liquid phase, which is represented by a surface in the temperature–concentration diagram. The positions of these surfaces are established, and also of the three lines where they intersect, and where two solid phases are in equilibrium with the liquid. The data for the invariant point are chromium 8%, carbon 3·6%, iron 88·4%, and 1090° (cooling) or 1150° (heating). A. GEAKE.

Ternary system silver bromide–potassium bromide–water. R. H. LAMBERT (J. Physical Chem., 1926, **30**, 973—979).—The composition of solutions saturated with silver and potassium bromides has been determined between −13° and 100°, using the method of Feigl (A., 1918, ii, 227). These results, together with those of other workers for the three corresponding binary systems, have been used to define the ternary system. *X*-Ray analysis confirmed Hellvig's conclusion (A., 1900, ii, 723) that no compound or double salt of the two bromides exists in precipitates from the aqueous solution. L. S. THEOBALD.

System sodium iodide–acetone–water. R. MACY and E. W. THOMAS (J. Amer. Chem. Soc., 1926, **48**, 1547—1550).—The solubility of sodium iodide in acetone has been determined from −34° to the b. p. of the saturated solution. The composition of the only compound isolated in this temperature range is $NaI,3COMe_2$. The solubility of this compound decreases with fall of temperature, whereas sodium iodide (the stable solid phase above 25·7°) is less soluble at higher than at lower temperatures. The 25° isotherm of the ternary system sodium iodide–acetone–water has been determined. M. CARLTON.

Equilibria between metals and salts in the molten state. V. Equilibrium between tin and lead and tin chloride and lead chloride. R. LORENZ, W. FRAENKEL, and M. GANZ (Z. anorg. Chem., 1926, **153**, 281—288).—The equilibrium $Sn+PbCl_2 \rightleftharpoons Pb+SnCl_2$ between 500° and 600° is depicted graphically. Calculation of the reaction constant by application of the law of mass action gives a "constant" which first diminishes and then increases with the lead chloride content. Lorenz's modified formula for the law of mass action (A., 1924, ii, 484) gives a fairly steady reaction constant (0·44—0·63).

Addition of potassium chloride displaces the equilibrium $SnCl_2+Pb \rightleftharpoons PbCl_2+Sn$ to the left until the proportions are 1·5 mols. of potassium chloride to 1 mol. of lead chloride, when further addition of potassium chloride produces no effect. Sodium chloride has less effect than potassium chloride, the maximum being with equimolecular proportions.

Experiments with antimony or bismuth and lead chloride show that neither antimony nor bismuth occurs in the salt phase. M. CARLTON.

Equilibria in the reduction of cuprous chloride and lead chloride by hydrogen. N. PARRAVANO and G. MALQUORI (Gazzetta, 1926, **56**, 3—13).—The reactions of cuprous and lead chlorides with hydrogen

between 300° and 500° and at pressures below atmospheric have been studied in a specially designed apparatus. The reversibility of the system $RCl_2+H_2 \rightleftharpoons R+2HCl$ has been directly established. A considerable time (a day or so) may be required, however, to reach equilibrium, and the reaction is more rapid in the former direction. The data are in agreement with the mass action law, and the equilibrium constants conform fairly well to the equation $\log Q/RT+\log p+\log K=C$. The equilibrium constants and the thermal data are also in fair concordance with those obtained or deduced by other means.

S. B. TALLANTYRE.

Thermal dissociation of some chloroaurates. N. PARRAVANO and G. MALQUORI (Gazzetta, 1926, **56**, 13—19; cf. A., 1919, ii, 291, 395).—The vapour pressures developed by heating silver, potassium, and cæsium chloroaurates at 100—400° have been measured. In the first stage of dissociation the equilibrium corresponds with the equation $RAuCl_4 \rightleftharpoons RAuCl_2+Cl_2$. The dependence of pressure on temperature is given for silver chloroaurate by $\log p=0{\cdot}01171t-0{\cdot}550$; potassium chloroaurate $\log p=0{\cdot}01122t-1{\cdot}773$; cæsium chloroaurate $\log p=0{\cdot}00956t-1{\cdot}770$. By calculation, the temperatures at which the pressure is 1 atm. are found to be 294°, 415°, and 486°, respectively. If this temperature (Abs.) is T, then Q/T is found to conform to the rule of Matignon. The establishment of the equilibrium is very slow, in some cases several days being required. Although the removal of small quantities of chlorine does not affect the dissociation pressure, the withdrawal of large quantities is accompanied by a change of pressure, and the existence of solid solutions in the decomposition residue is inferred.

S. B. TALLANTYRE.

Equilibria in systems in which the phases are separated by a semi-permeable membrane. XIV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1916, **29**, 359—370).—A continuation of previous work (cf. this vol., 578). The properties of isotonic curves in ternary systems in which separation into two liquids occurs are discussed.

M. S. BURR.

Thermal properties of different forms of selenium. P. MONDAIN-MONVAL (Compt. rend., 1926, **182**, 1465—1468).—The heats of transformation and specific heats of different forms of selenium have been determined. The heat of transformation of vitreous selenium to "metallic" selenium at 130° is 13·5 cal./g.; it increases with rise of temperature, and at the m. p., 217°, becomes identical with the latent heat of fusion=16·4 cal./g. The heat of transformation of red crystalline selenium to "metallic" selenium at 150° is 2·2 cal./g. The mean specific heat of "metallic" selenium between 15° and 217° is 0·084, and between 15° and 75°, 0·078; that of red crystalline selenium between 15° and 75° is 0·082, and of liquid selenium above 217° is 0·118.

W. HUME-ROTHERY.

Heat of solution of sulphur dioxide. A. G. STILES and W. A. FELSING (J. Amer. Chem. Soc., 1926, **48**, 1543—1547).—The heat of dissolution of sulphur dioxide has been measured. The relation obtained between $-\Delta H$(Cal./mol.) and N(mols. of water/mols. of sulphurous acid) is given by $-\Delta H=4911{\cdot}6+1105{\cdot}26\log N$. The average deviation between the calculated and observed results is 0·2%, but in most cases an accuracy of 1 in 400 at 25° is claimed. The rate of change of total heat of solution per mol. of sulphur dioxide at any concentration point is given by $d(-\Delta H)/dN=479{\cdot}92(1/N)$.

M. CARLTON.

Heats of combustion of homologous and isomeric dicarboxylic acids and their anhydrides. H. HARTMAN (Diss., Delft, 1925, 1—126).—On adaptation of the ethyl cyanoacetate synthesis of Bone and Sprankling to bromodiethylacetic acid, the product is β-methyl-α-ethylglutaric acid instead of the anticipated αα-diethylsuccinic acid. *ααββ-Triethylsuccinic acid*, m. p. 118°, was obtained by saponification of *ethyl αβ-dicyano-ααββ-triethylpropionate*, b. p. 184°/29 mm., 138°/2 mm. Heats of combustion were determined (i) for acids of the oxalic series from C_2 to C_{13}, (ii) for methyl-, ethyl-, and phenyl-substituted succinic acids, and (iii) for anhydrides of the latter. In the oxalic series the observed alternation between acids with an odd or even number of carbon atoms is ascribed to differences of crystal structure; oxalic and malonic acids are anomalous. Normal dicarboxylic acids have a lower heat of combustion than the isomeric alkylsuccinic acids, of which the *anti*-acids give the highest, and the unsymmetrical acids the lowest values. In the dialkylsuccinic anhydrides, the heat of combustion is greater when the alkyl groups are in closer proximity. With the exception of that of *r*-αβ-diethylsuccinic acid, all the heats of combustion follow Stohmann's rule. The heat of hydration of succinic anhydride decreases regularly with successive introduction of methyl groups. Those of the methyl and the *as*-diethyl derivatives, however, show little change. The liquid ethyl derivatives follow the same order as the solid methyl derivatives. Solid tetraethylsuccinic anhydride has practically the same heat of hydration as the tetramethyl derivative.

CHEMICAL ABSTRACTS.

Heats of adsorption and the problem of promoter action. C. F. FRYLING (J. Physical Chem., 1926, **30**, 818—829; cf. Foresti, A., 1925, ii, 692; Beebe and Taylor, A., 1924, ii, 159).—The heats of adsorption of hydrogen on simple nickel catalysts and on nickel catalysts promoted by cerium and thorium nitrates have been measured at 0° by the method of Beebe and Taylor (*loc. cit.*). The nickel oxide was reduced by hydrogen at 300°, but no highly adsorptive catalysts of the type prepared by Foresti (*loc. cit.*) or by Schmidt (this vol., 134) were obtained. Heat treatment of an unpromoted catalyst reduces the adsorptive capacity and the total integral heat of adsorption (cf. Beebe and Taylor, *loc. cit.*), but in the case of a promoted catalyst only a slight decrease in the last-named occurred. The curve heat of adsorption–volume adsorbed for promoted nickel shows a maximum which is attributed to the production of atomic hydrogen by the active atoms of the nickel surface. On this assumption, together with Taylor's theory of the catalytic surface (this vol.,

365), promoter action and the phenomena encountered in this study are discussed.

L. S. THEOBALD.

[Electrical] conductivity and viscosity of pure sodium and potassium hydroxides. K. ARNDT and G. PLOETZ (Z. physikal. Chem., 1926, **121**, 439—455).—The electrical conductivity of fused potassium hydroxide has been determined between 400° and 600° by a method similar to that employed for sodium hydroxide (A., 1925, ii, 127). As with sodium hydroxide, the value for the pure substance was obtained by extrapolating data for potassium hydroxide containing varying amounts of potassium carbonate. Tables are given showing the effect of silica and lime on the conductivities of both sodium and potassium hydroxides. The densities and viscosities of the fused hydroxides containing known amounts of chloride, carbonate, silica, and lime have also been determined and used in the same way. A special apparatus for measuring the viscosity by the capillary flow method is described. L. F. GILBERT.

Effect of hexahydroxybenzene, tetrahydroxy-*p*-benzoquinone, and triquinoyl on the conductivity of boric acid. J. BÖESEKEN and J. C. MEUWISSEN (Rec. trav. chim., 1926, **45**, 496—498; cf. A., 1915, ii, 667).—The conductivities of diacetyl, hexahydroxybenzene, tetrahydroxy-*p*-benzoquinone, and triquinoyl have been determined in aqueous solutions and in 0·5*M* solutions of boric acid. The conductivity of a 0·25*M* solution of diacetyl 2 min. after preparation is $27{\cdot}8\times10^{-6}$, and increases to $69{\cdot}5\times10^{-6}$ after 70 hrs. In contradiction to the previous statement (*loc. cit.*), the conductivity of a mixture of diacetyl and boric acid is greater than the sum of that of the two components; when freshly prepared, this increase appears to be due chiefly to the diacetyl itself, but on keeping, the effect of the α-hydroxy*iso*butyric acid formed by hydrolysis is apparent. The conductivities of 0·01, 0·005, and 0·0025*M* solutions of triquinoyl are 1394, 821, and 540×10^{-6}, respectively, the high values probably being due to the formation of a hydroxy*cyclo*pentatetronecarboxylic acid by hydrolysis. With boric acid, a marked increase in conductivity is produced. Both hexahydroxybenzene and tetrahydroxy-*p*-benzoquinone have a similar effect, that of the former being the greater, but the actual figures have no significance owing to the action of air and water on these substances. W. HUME-ROTHERY.

Electrical conductivity in benzene solutions. S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1925, **57**, 276—282).—See this vol., 29.

Electrode capacities and resistance of electrolytes for a wide range of frequencies. B. B. BANERJI (Trans. Faraday Soc., 1926, **21**, 111—133).—See this vol., 246.

Polarisation capacity of platinised platinum electrodes in aqueous solutions of potassium ferro- and ferri-cyanide. K. BECKER (Z. Elektrochem., 1926, **32**, 305—311).—A summary of previous researches on polarisation capacity is given. The polarisation capacity of platinised platinum electrodes in solutions of potassium ferro- and ferri-cyanide and its dependence on the concentration, the concentration ratio ferro-/ferri-, and the vibration number up to $n=150{,}000$ have been investigated. The polarisation capacity in the region of the rapid vibrations is constant and independent of the composition of the electrolyte. With the most rapid vibrations, a small increase in the capacity was observed. With small total concentrations, the capacity is independent of the vibration number. Concentrated solutions obey the limiting law $C\sqrt{n}=\text{const.}$ (where C is the capacity and n the vibration number). The conditions under which this law holds are reached at different total concentrations for different ratios of ferro-/ferri-cyanide. The influence of hydrogen adsorbed on the electrode has also been investigated.

N. H. HARTSHORNE.

Electrolysis of molten alloys. XI. Sodium-mercury alloys. R. KREMANN, H. KRIEGHAMMER, and P. GRUBER-REHENBURG (Monatsh., 1926, **46**, 515—529; cf. A., 1925, ii, 132; this vol., 477).—Alloys containing 4—6% of sodium behave abnormally on electrolysis, the concentration of sodium accumulating being higher near each electrode than in the bulk of the liquid. Observations were impossible with alloys of about 10% sodium content. With alloys containing 13—32% of sodium, the sodium migrates towards the cathode during electrolysis, the highest percentage excess of sodium observed being 13% with a current density of 6 amp./mm.^{2} This effect increases continuously with increasing concentration of sodium, although the known compounds Na_3Hg_2, Na_5Hg_3, and Na_3Hg occur within the range examined, and maxima in the effect might have been expected at compositions corresponding with these compounds.

G. M. BENNETT.

Electrolysis of molten alloys. XII. Bismuth–tin alloys. R. KREMANN, H. KRIEGHAMMER, and A. TRÖSTER (Monatsh., 1926, **46**, 531—539).—Electrolysis of fused bismuth–tin alloys results in the accumulation of the better-conducting tin at the cathode, the effect being large, since the difference in conducting power of the two metals is extreme. The full electrolytic effect at 170—300° is attained after 18—24 hrs. The maximum effect of a 29% excess of tin is found with an alloy containing 25 atoms % of bismuth. The previously reported observation (A., 1925, ii, 312) that this maximum occurred with 50 atoms % of bismuth was due to an insufficient time (4 hrs.) of electrolysis. The new result is assumed to indicate the presence in the liquid alloy of intermetallic compounds containing more tin than the equimolecular compound. G. M. BENNETT.

Electrolysis of molten alloys. XIII. Tin–cadmium alloys. R. KREMANN and O. BAUKOVAC (Monatsh., 1926, **46**, 541—546).—When tin–cadmium alloys are subjected to a current at 300°, equilibrium is reached in 4 hrs., cadmium, which is the better conductor, accumulating near the cathode. The effect is small (6% with 10 amp./mm.^{2}), since the difference in conductance of the two metals is slight. Observations with alloys of varying composition show that the effect has a sharp maximum at 50 atomic % of

tin, and changes symmetrically on either side of this point. G. M. BENNETT.

Electrolysis of molten alloys. XIV. Alloys of aluminium with magnesium, antimony, zinc, and silver. R. KREMANN and J. DELLACHER (Monatsh., 1926, **46**, 547—553).—Observations with the alloys of aluminium with magnesium, antimony, and zinc are impossible owing to the oxidation of one of the constituents of the alloy and interruption of the current. When an aluminium–silver alloy is electrolysed at 900°, aluminium appears in excess near the cathode and silver near the anode, the effect increasing to 12·2% excess of silver with a current density of 10 amp./mm.^{2} This value is a large one for an alloy at so high a temperature. The maximum effect is found with an alloy of 50 atoms % of silver. The transfer of silver towards the anode is opposed to the usual rule of the better-conducting metal moving towards the cathode, since the conducting powers are silver 1·45, aluminium 0·43; but the result is accounted for if the determining factor is the order of the elements with respect to their energies of ionisation. This is generally the same as their order of conducting power, but aluminium lies between silver and sodium in energy of ionisation, although it lies far below silver in conducting power.
G. M. BENNETT.

Electrolysis of molten alloys. XV. Metal sulphides and phosphides. R. KREMANN and O. BAUKOVAC (Monatsh., 1926, **46**, 555—557).—Electrolysis of fused ferrous or cuprous sulphides or of mixtures of cuprous and lead sulphides is impossible owing to the liberation of gas bubbles or of free sulphur. A fused iron–phosphorus alloy was electrolysed in a magnesite capillary at 1400° for 2·25 hrs. with a current density of 6·6 amp./mm.^{2}, but no variation in composition could be detected: higher current densities caused interruption of the current. In view of the high temperature of the experiment, a much higher current density might well be necessary to produce a measurable effect. G. M. BENNETT.

Electrolysis of molten alloys. XVI. Alloys of silver with tin, antimony, bismuth, and lead. R. KREMANN and K. BAYER (Monatsh., 1926, **46**, 649—659).—Electrolysis for 6 hrs. of alloys of silver with tin, antimony, and bismuth under the conditions previously used by Kremann and Benda (A., 1925, ii, 679) show a smaller, but definite migration of the silver towards the cathode and of the other metal towards the anode. With a silver–tin alloy (25 atoms % of silver), differences of composition of 2% were observed for current densities varying from 3 to 10 amp./mm.^{2}; with a silver–bismuth alloy (50 atoms % of silver) the small effect increases with increase of current density, reaching a maximum of 2·7% at 8·7 amp./mm.^{2}; with a silver–antimony alloy (50 atoms % of silver) the effect increases with increase in current density, reaching 2·47% at 8·33 amp./mm.^{2}, but shows no approach to a maximum value. Electrolysis of a silver–lead alloy (50 atoms % of silver) confirmed the higher values for the migration effect previously obtained by Kremann and Benda (*loc. cit.*), but, contrary to their observations, the effect remained constant between the values 6 and 12 amp./mm.^{2} for the current density. J. W. BAKER.

Passage of current in solid salts. P. VAILLANT (Compt. rend., 1926, **182**, 1335—1337; cf. A., 1925, ii, 40, 165).—The conductivities of several salts have been determined at the f. p. of tin, lead, and zinc, and the rate of decrease of the conductivity with time, which is greater the higher the temperature, examined. The results show a better agreement with the formula $\log c=a+bt$, where c is the conductivity and a and b are constants (Benrath and Wainoff, A., 1911, ii, 847; Rautenfeld, Ann. Physik, 1923, [iv], **72**, 617) than with that of Joffe (*ibid.*, 1923, [iv], **72**, 617) and Seelen (A., 1925, ii, 185), where $\log c=a-b(273+t)$. F. G. SOPER.

Separation of the dicarboxylic amino-acids from certain protein hydrolysates by electrical transport. G. L. FOSTER and C. L. A. SCHMIDT (J. Amer. Chem. Soc., 1926, **48**, 1709—1714; cf. A., 1923, i, 963).—When protein hydrolysates are introduced into the centre compartment of a three-compartment cell, the p_H of the electrolyte in which is maintained at 5·5, and electrolysed, the basic amino-acids migrate to the cathode, the dicarboxylic acids (including pyrrolidone-2-carboxylic acid) migrate to the anode, whilst the amphoteric acids remain in the centre compartment. The method is applied to the preparation of arginine and lysine from hydrolysed gelatin. F. G. WILLSON.

Significance of hydration and adsorption in the mechanism of the production of *E.M.F.* N. ISGARISCHEV (Z. Elektrochem., 1926, **32**, 281—286).—The Nernst equation for electrode potentials presupposes the existence of perfectly free ions, whereas modern research tends more and more to show that only hydrated ions exist. The Nernst equation also fails to explain the irregular results obtained when a cation foreign to the electrode metal is present. A theory is developed which is based on Fajans' theory of the hydration and solution of solid substances. Applied, for example, to the case of an insoluble metal like zinc dipping in a solution, it postulates that the water dipole is electrically adsorbed on the zinc surface, its negative pole being in contact with the metal and thus lessening the attraction between the zinc and its valency electrons. In this case, however, the energy of hydration is insufficient to overcome the attraction completely and thus ionise the zinc and it is only when the system is combined with an electropositive metal such as copper to form an ordinary galvanic cell that the electrons are detached, since they can then move from their position of high tension to one of lower tension, viz., to the copper. The resulting electrical energy is thus influenced by two factors, the energy of hydration and the electron tension. Expressed mathematically, the theory results in a combination of the Nernst equation and the empirical adsorption equation of Freundlich. The theory is applied to explain the influence of foreign ions, the action of gas electrodes, and to polarisation. N. H. HARTSHORNE.

Electro-affinity of hydrogen. G. Joos and G. F. Hüttig (Z. Elektrochem., 1926, **32**, 294—295).—An addition to a previous paper (cf. this vol., 686). Calculation of the electro-affinity for hydrogen by another method now gives 33 cal., which agrees with the previous result within the margin of error.

N. H. Hartshorne.

Electrode potential of thallium. L. M. Vollstein (J. Russ. Phys. Chem. Soc., 1925, **57**, 265—275).—By the rotating electrode method, the electrode potential of thallium is found to be 0·6181 volt. The voltage of the half-element Tl|TlCl (saturated) has the value 0·7782 immediately after assembly, and the value 0·7813 after rotation. The potential of the thallium electrode is lowered by oxidising agents, and it is advisable to use the method of rotating electrodes for investigating the electrode potentials of all readily oxidisable metals.

T. H. Pope.

***E.M.F.* of calcium electrodes.** C. Drucker and F. Luft (Z. physikal. Chem., 1926, **121**, 307—329).—The *E.M.F.* of cells of the types Ca_xHg|$CaCl_2$|3*N*-KCl|*N*-KCl,HgCl|Hg and Ca|CaI_2|Ca_xHg have been determined, the latter cell having pyridine as liquid medium. From these data, the normal potential, $_0\varepsilon_h$, of calcium is calculated to be −2·76 volts, whereas the value deduced from thermal data lies between −2·8 and −3·1 volts. Further information regarding the ionisation of calcium chloride at low concentrations has been obtained by determining the anion transport numbers in the concentration range 0·0014 to 0·016*M* and by measurements of the *E.M.F.* of cells of the type Hg|HgCl,$CaCl_2(c_1)$|$CaCl_2(c_2)$,HgCl|Hg. The anion transport numbers have a minimum value at about 0·01*M*, from which it is inferred that the complex anion, $CaCl_3^-$, and the primary cation, $CaCl^+$, are both present. With increasing dilution, the relative importance of the positive ion increases (cf. A., 1913, ii, 1015).

L. F. Gilbert.

Potential of the iron electrode. W. H. Hampton (J. Physical Chem., 1926, **30**, 980—991; cf. Richards and Behr, Carnegie Inst. Pub. No. 61).—The potential of several varieties of iron has been measured in the cell Fe|$FeCl_2$(aq.),HgCl|Hg, in which there was no liquid junction. An amalgam prepared by the electrolysis of ferrous sulphate using a mercury cathode gave 0·8090 volt as the best equilibrium value in 0·1*M*-ferrous chloride, whilst finely-divided iron, prepared by the reduction of ferric oxide, gave the value 0·8088 volt. The potentials of annealed iron in water were lower by 0·05 volt, but no true equilibrium value was observed. The difference of potential between finely-divided iron and the annealed form in a solution of ferrous chloride in a fused, eutectic mixture of lithium and potassium chlorides showed little or no difference to exist between the activity of each form. The difference when water is present is attributed to the passivity of compact iron in contact with water.

The most probable value of the normal electrode potential, calculated from the results, is 0·4413 volt (correct to 0·003 volt), and this is supported by measurements made on the equilibrium represented by the scheme $Fe+2TlCl=Fe^{\cdot\cdot}+2Cl'+2Tl$.

L. S. Theobald.

Potential of fluorine from the decomposition potentials of fused fluorides. B. Neumann (Z. Elektrochem., 1926, **32**, 274—276).—A reply to the criticisms by Ruff and Busch (this vol., 129) of an earlier communication of the author (with Richter) (A., 1925, ii, 1164), together with a brief rejoinder by Ruff.

N. H. Hartshorne.

Electrometric study of the allotropic forms of mercuric sulphide. M. Bourgeaud (Compt. rend., 1926, **182**, 1619—1621).—Black mercuric sulphide is converted into the stable red modification by treatment with aqueous solutions of polysulphides. The dependence of the rate of transformation on temperature, concentration of ammonium sulphide, and changes in the ratio of hydrogen sulphide to ammonia in the ammonium sulphide used has been investigated by actual measurements at 18° and 25° of the cells: Hg|Hg_2Cl_2,sat.KCl|sat.KCl|$(NH_4)_2S$,HgS_{black}|Hg and Hg | HgS_{black},$(NH_4)_2S$ | sat.KCl | $(NH_4)_2S$,HgS_{red} | Hg. A mechanism of the transformation is suggested. The *E.M.F.* of the cell Hg|Hg_2Cl_2,sat.KCl|sat.KCl|*M*-$(NH_4)_2S$,HgS_{red}|Hg at 18° is 0·7934 volt.

J. S. Carter.

Electrokinetic behaviour and electrode potential. F. L. Usher (J. Physical Chem., 1926, **30**, 954—963).—Measurements of the contact potential and of the electrocapillary behaviour of mercury in solutions (0·001*N* to *N*) of the chlorides of lithium, potassium, and ammonium, of hydrochloric acid, potassium hydroxide, and sodium citrate have been made. The results indicate the absence of any direct connexion between electrode potential and electrokinetic behaviour in the case of this metal (cf. Garrison, A., 1923, ii, 115). When the potentials of mercury in solutions of the chlorides with and without addition of hydrazine are compared, it appears that mercurous ions are produced at the metal surface and are present at the interface in practically the same concentration as if the solutions had been saturated with calomel.

Electro-osmotic experiments on the influence of potassium chloride on the surface energy of a diaphragm indicate an initial adsorption of that ion which enhances the original charge. This effect is greatly reduced when a strongly adsorbed ion bearing the same charge as the surface is present.

L. S. Theobald.

Streaming potentials. H. Lachs and J. Kronman (Bull. Int. Acad. Polonaise, 1925, *A*, 289—301; cf. Kruyt, A., 1918, ii, 289; Freundlich and Rona, Sitzungsber. Preuss. Akad. Wiss., 1920, **20**, 397; Freundlich and Ettisch, A., 1925, ii, 873).—Using a method similar to that of Freundlich and Rona, streaming potentials have been examined with a view to determine their reproducibility and stability. It is found that with tubes of glass or silica the initial values of the streaming potentials, under apparently identical conditions, can only be reproduced with an accuracy of about 14%. Furthermore, the value for a given arrangement is not constant, but varies considerably with time. Although quantitative measurements are impossible, the experimental numbers show, in harmony with the results of the authors cited, that glass and silica receive a negative charge from the streaming of water and that the magnitude of the

charge is reduced by the addition of electrolytes according to the concentration, valency, and adsorbability of the cations. In presence of aluminium and thorium salts, a reversal of sign occurs.

J. S. CARTER.

Influence of *X*-rays on bioelectric potential differences. A. LIECHTI (Biochem. Z., 1926, **171**, 240—255).—*X*-Rays have no effect on the *P.D.* between 0·002*M*- and concentrated hydrochloric acid separated by potassium chloride–agar; between 0·002*M*-hydrochloric acid and 0·002*M*-sodium hydroxide separated by glass or ferrocyanide membranes; or between 0·0005*M*-hydrochloric acid and 0·0005*M*-hydrochloric acid+gelatin separated by a collodion membrane. The *P.D.* at the interface between solutions of sodium chloride and dimethylaniline hydrochloride or sodium oleate in guaiacol or *o*-toluidine is, however, increased by the action of *X*-rays.

E. C. SMITH.

Influence of gelatin on the potential and discharge potential of zinc in zinc sulphate solution. E. RABALD (Z. Elektrochem., 1926, **32**, 289—294).—The author has been unable to reproduce the polarisation maximum at 0·025% of gelatin found by Isgarischev and Titov (A., 1921, ii, 620) in the electrolysis of zinc sulphate with zinc electrodes in presence of gelatin, but has found a maximum at 0·005%. The existence of zinc–gelatin complexes postulated by these authors would not therefore seem to have been fully proved. The measurements of the present author show that the factors influencing the polarisation value are more complicated than was assumed by Isgarischev and Titov. N. H. HARTSHORNE.

Hydrogen overvoltage at a mercury cathode and its bearing on current theories. A. L. MCAULAY and F. P. BOWDEN (Phil. Mag., 1926, [vii], **1**, 1282—1285).—Experiments have shown that the overvoltage at a mercury cathode with a mixed electrolyte containing acid and a metallic salt is independent of the current and that the current carried by the hydrogen ions is the same in all cases. Under overvoltage conditions, hydrogen and the metal are both deposited at a potential which is characteristic of hydrogen and independent of the reversible potential of the metal. Of various theories which have been advanced to explain overvoltage, it is suggested that a combination of that requiring an active film of hydrogen or hydride the high free energy of which provides part of the overvoltage, with that in which a further over-potential is necessary for the desorption of the film, will explain all the observed facts. A. E. MITCHELL.

Cathodic deposition of metals. III. Electrochemical and *X*-ray investigations on lead precipitates. P. K. FRÖHLICH, G. L. CLARK, and R. A. ABORN (Z. Elektrochem., 1926, **32**, 295—305).—Lead precipitates deposited cathodically from acetate, nitrate, perchlorate, fluoborate, and fluosilicate solutions, both in the presence and absence of free acid and of gelatin, have been investigated by means of *X*-rays, and the relation between the crystal structure and the electrochemical conditions during deposition has been studied. From a practical point of view, the deposit from the perchlorate solution in the presence of excess of acid and gelatin is the best for a given current density; it shows the minimum grain size and is free from dendrites. The results support the present views on the influence of various factors on the structure of electrolytically deposited metals, with the exception that, in contrast to iron, nickel, and other metals, lead shows an increased preferential orientation with increasing current density. The grain size increases with the amount of deposit, and the preferential orientation is smaller in the outer than in the inner layers. Experiments with iron and platinum cathodes, with and without a wax coating, have led to the confirmation of the earlier observations of Clark and Fröhlich on the deposition of nickel on aluminium and platinum. The current density–potential curves show that with lead the resistance to cathodic crystal formation is small. Gelatin retards the crystal growth and hinders the even distribution of the metal over the whole surface of the electrode. N. H. HARTSHORNE.

Electrodeposition of radium-*D* and -*E*. J. P. MCHUTCHISON (J. Physical Chem., 1926, **30**, 925—929; cf. this vol., 655; von Hevesy, A., 1912, ii, 414).—The deposition of radium-*D* and -*E* from neutral aqueous solutions on metal plates takes place irrespectively of whether the latter are more electropositive or electronegative than bismuth or lead, and the ratio radium-*D* to radium-*E* deposited decreases with increasing electronegative character of the metal concerned. Radium-*E* is extracted almost pure by aluminium and nickel from boiling, neutral solutions of the two isotopes. The half-life period of radium-*E* has been redetermined as 4·87 days, which confirms the value of 4·85 days given by Thaller (Wien. Ber., 1912, **121**, 1611). L. S. THEOBALD.

Electrolytic formation of ammonium persulphate. O. A. ESSIN (Z. Elektrochem., 1926, **32**, 267—269).—The influence of the concentration of sulphate and of persulphate on the current yield in the electrolytic preparation of ammonium persulphate has been studied. The current yield is independent of the current density between 1 and 16 amp./cm.^{2} It is also independent of temperature between 10° and 30°, provided the solution is kept saturated with sulphate, as was found by Levi (A., 1903, ii, 474). Within the range of anodic current densities and temperatures given above and with a saturated solution, the current yield is given by $100c_1/(c_1+c_2)\%$, where c_1 and c_2 are the concentrations of the sulphate and persulphate, respectively.

N. H. HARTSHORNE.

Catalysis in electrochemistry. V. M. PERSON (J. Russ. Phys. Chem. Soc., 1925, **57**, 189—205).—Intermediate products containing oxygen are said to accelerate the reaction taking place in primary batteries and in the lead accumulator and to raise the *E.M.F.* T. H. POPE.

Comparison between unimolecular and bimolecular gaseous reactions. Thermal decomposition of gaseous acetaldehyde. C. N. HINSHELWOOD and W. K. HUTCHISON (Proc. Roy. Soc., 1925, **A**, **111**, 380—385).—At about 500°, acetaldehyde decom-

poses thus: $CH_3 \cdot CHO = CH_4 + CO$. The reaction is bimolecular and under the conditions of the experiment practically homogeneous. The rate of reaction can be calculated from the equation $k = 5 \cdot 5 \times 10^{10} \sqrt{T} \cdot e^{-45,500/RT}$, k being expressed in g.-mols. per litre per sec. The heat of activation is 45,500 cal. for 2 g.-mols., and the rate of reaction can be calculated from kinetic considerations. In the decomposition of acetone, which is unimolecular (J.C.S., 1924, **125**, 393), the reaction is not necessarily dependent on collisions, whereas in the bimolecular reaction at present investigated there is almost the exact relation between heat of activation, number of collisions, and rate of reaction predicted by theory.

W. THOMAS.

Extinction of methane flames by diluent gases. H. F. COWARD and F. J. HARTWELL (J.C.S., 1926, 1522—1532).—The influence of carbon dioxide, nitrogen, argon, and helium on the limits of inflammability of methane in air has been determined. The relative extinctive effects of the first three gases are mainly determined by their relative heat capacities. The more extinctive effect of helium as compared with argon is, however, ascribed to the high thermal conductivity of helium. Of all mixtures of methane and oxygen, that represented by the proportions $CH_4 + 2O_2$ is the last to become non-inflammable as inert gases are added. The "lags" on ignition and the dilution limits of the mixtures seem to be dependent on the same factors. W. THOMAS.

Walden inversion. X. Reaction between water and the phenylchloroacetate and phenylbromoacetate ions. A. M. WARD (J.C.S., 1926, 1184—1195).—A quantitative test has been made of the view that displacement racemisation is the result of two simultaneous reactions $l\text{-CHPhCl}\cdot CO_2' + H_2O \longrightarrow (k_1)\ l\text{-CHPh(OH)}\cdot CO_2'$ and $\longrightarrow (k_2)\ d\text{-CHPh(OH)}\cdot CO_2'$. The sign of the product depends on the relative values of k_1 and k_2. The divergences of the values of the velocity coefficient from the titration and optical experiments are due to catalytic racemisation which also takes place. The above mechanism is also better in accord with the results in the case of phenylbromoacetate than that suggested by McKenzie and Walker (J.C.S., 1915, **105**, 1685). The effect of the solvent on the sign of the product obtained in such displacement reactions is discussed in connexion with the view that two simultaneous reactions proceed during the process. W. THOMAS.

Velocities of the reactions between ethyl iodide and the sodium salts of various substituted phenols in ethyl-alcoholic solution. L. J. GOLDSWORTHY (J.C.S., 1926, 1254—1256).—The reactions are bimolecular, but of a special type, the velocity coefficient being smaller the greater the initial concentrations, in accordance with the equation $k_v = k + a \log V$, where V is the volume containing 1 g.-mol. of the alkyl halide and sodium phenoxide. The following are the mean values obtained ($k \times 10^5$) for 42·5° and 0·5N-sodium salts and ethyl iodide: phenol 702, *p*-cresol 918, *m*-cresol 810, *o*-cresol 726, *p*-chlorophenol 393, *o*-chlorophenol 334, *m*-chlorophenol 278, 2 : 4-dichlorophenol 196. Except in the case of sodium *o*-tolyloxide the reactivities are in the inverse order of the ionisation constants of the corresponding phenols. W. THOMAS.

Irreversible endothermic chemical processes. A. E. ARBUSOV (Z. physikal. Chem., 1926, **121**, 209—220).—The hydrolysis of the acetals of a number of aliphatic ketones in alcoholic solution has been studied. The reaction, which proceeds rapidly in the presence of dilute acids but comparatively slowly in the presence of alkalis, appears to go to completion, and is accompanied by the absorption of heat. 4·51 Cal. are absorbed during the hydrolysis of 1 g.-mol. of the acetal of acetone. A suitable lecture experiment illustrating qualitatively these phenomena is described. L. F. GILBERT.

Hydrolysis of substituted benzyl chlorides and the theory of induced alternate polarities. S. C. J. OLIVIER and G. BERGER (Rec. trav. chim., 1926, **45**, 452—457; cf. A., 1923, i, 908; this vol., 511).—The relative velocities of hydrolysis of substituted benzyl chlorides previously described (*loc. cit.*) are not in agreement with the theory of induced alternate polarities, and the discrepancy cannot be ascribed to steric hindrance. The discrepancies chiefly concern the *ortho*-substituted compounds, and this is possibly due to the direct chemical influence of neighbouring groups. W. HUME-ROTHERY.

Basis for the physiological activity of -onium compounds. VI. Rates of hydrolysis of certain esters of choline and its analogues. R. R. RENSHAW and N. BACON (J. Amer. Chem. Soc., 1926, **48**, 1726—1732).—*Acetylcholine bromide*, m. p. 143°, and *acetoxymethyltrimethylammonium bromide*, m. p. 159°, are obtained by condensing liquid trimethylamine with β-bromoethyl acetate and bromomethyl acetate, respectively. β-Bromoethyl nitrate affords similarly *β-nitro-oxyethyltrimethylammonium bromide*, m. p. 187°. The following (unimolecular) hydrolysis constants were determined in solution of p_H 7·8: chloroacetylcholine bromide, 0·5—0·6; acetoxymethyldimethylsulphonium bromide, 0·1; acetoxymethyltrimethylammonium bromide, 0·04; acetylcholine bromide, $0 \cdot 8 \times 10^{-3}$; and β-nitro-oxyethyltrimethylammonium bromide, immeasurably small. In the case of the last-named substance, the muscarine action is very prolonged, whilst that of all the remaining substances is about equal and very evanescent, indicating that the rate of hydrolysis is not, in all cases, the determining factor in either the extent or the persistence of the physiological action of these compounds. F. G. WILLSON.

Kinetics of the precipitation of copper from solutions of its salts by metallic zinc. A. GALECKI and T. ORLOVSKI (Bull. Int. Acad. Polonaise, 1925, *A*, 303—332).—See this vol., 364.

Influence of rate of stirring on reaction velocity. F. C. HUBER and E. E. REID.—See B., 1926, 519.

Rapid corrosion of metals by acids within capillaries. U. R. EVANS (J. Amer. Chem. Soc., 1926, **48**, 1601—1602).—Localised corrosion under the conditions of experiment described by McCulloch

(A., 1925, ii, 879) is interpreted by the author as being mainly due to differential aëration and not to capillary action. Experimental evidence is given in support of this. M. CARLTON.

Rapid corrosion of metals within capillaries. L. MCCULLOCH (J. Amer. Chem. Soc., 1926, **48**, 1603—1604).—An explanatory reply to Evans (preceding abstract). M. CARLTON.

Corrosion of steels in the atmosphere. W. G. WHITMAN and E. L. CHAPPELL.—See B., 1926, 545.

Catalysis. J. BÖESEKEN (Rec. trav. chim., 1926, **45**, 458—474; cf. A., 1921, ii, 500).—The author's theory of dislocation in catalysis (*loc. cit.*) is discussed in detail with regard to the following reactions: (1) Friedel and Crafts' reaction; (2) the transformation of white phosphorus to red in the presence of different substances; (3) the polymerisation of chloral; (4) the decomposition of heptachloropropane; (5) some photochemical reactions of benzophenone. Catalysis is the result of activation of the molecule and not of the atom. The majority of catalysts are atoms (in the case of metal catalysts), or ions of molecules, which are readily ionised or which possess residual valencies, *e.g.*, sulphuric acid, ferric chloride, aluminium chloride, pyridine, etc. These may be described as "open" systems, whilst the majority of organic substances, even unsaturated compounds, are "closed." When the two are brought into contact, the closed system is partly opened. Negative catalysts may act by closing the open system of the positive catalyst; *e.g.*, water closes the residual valencies of aluminium chloride and so acts as a negative catalyst in Friedel and Crafts' reaction.
W. HUME-ROTHERY.

Oxidation of oxalic acid by iodic acid in aqueous solution. S. TODA (Biochem. Z., 1926, **171**, 231—239).—At least 90% of the oxidation of oxalic acid by iodic acid when the reagents are not specially purified is brought about by the catalytic action of iron, 10^{-5} mg. of which in 4 c.c. of a solution of the purified reagents can be detected by reason of its catalytic action. At least 90% of the inhibitory action of hydrocyanic acid is due to the fixation of iron, but the remaining 10% is not referable to any known reaction. Solutions of iodic acid and oxalic acid completely free from the heavy metals are probably non-reactive, since the reaction is completely inhibited by hydrocyanic acid, the effect being reversible. The activity of the iron is probably due to the formation of complex compounds with iodic and oxalic acids, and not to its presence in the ionic form. E. C. SMITH.

Mechanism of oxidative processes. X. Oxidative action of iodic acid and its restriction. XI. Catalytic dehydrogenation. H. WIELAND and F. G. FISCHER (Ber., 1926, **59**, [*B*], 1171—1180; 1180—1191; cf. A., 1925, ii, 1171).—X. The interaction of iodic and oxalic acids to form iodine, carbon dioxide, and water is accelerated by ferric chloride or bromide, but not by ferric ammonium sulphate, iron iodate, iron iodide, or ferrous ammonium sulphate. Acceleration is attributable to the halogen ion, since it is also produced by hydrochloric acid, whereas sulphuric acid is inactive. Hydrocyanic acid in sufficient concentration completely inhibits the reaction; inhibition is not affected by ferric salts, but is partly overcome by hydrochloric acid. Since the presence of catalytically active material in the original substances could not be detected, the restrictive action of hydrocyanic acid is negatively catalytic. An equilibrium is assumed between the bulk of the iodic acid molecules and a few which are particularly mobile, and hence reactive, and the effect of the hydrocyanic acid is explained by formation with the latter of an unstable complex which dissociates with production of sluggish iodic acid. Acceleration by chlorine ions is due to liberation of chlorine, which oxidises oxalic acid, whereas partial restoration of activity by hydrochloric acid in solutions which contain hydrocyanic acid is caused by production of cyanogen chloride.

A similar case of restriction of a reaction in which a catalysed change does not appear to be repressed by the presence of minimal amounts of a restrictive substance is found in the effect of phenols on the autoxidation of benzaldehyde. This change is scarcely affected by the addition of ferric salts, and the accelerating effect of the latter on systems restricted by quinol is due solely to oxidation of the phenol to benzoquinone.

In homogeneous solution, hydrogen peroxide decomposes in the presence of iodic acid, whereas the latter substance is recovered unchanged; the action is explained by the intermediate formation of periodic acid. The change is greatly accelerated by hydrochloric acid and is not restricted by hydrocyanic acid, which, however, partly neutralises the accelerating influence of the halogen acid.

XI. The primary formation of hydrogen peroxide during the oxidation of hydrogen at a platinum or palladium contact is firmly established as well as the activation of hydrogen in the action of palladium-black on hydrazobenzene or 1 : 4-dihydronaphthalene. Failure to isolate hydrogen peroxide as primary product of the dehydration of alcohol, formic acid, acetic acid, quinol, or hydrazobenzene in presence of platinum-black is not a proof of its non-formation, since greater quantities than could be theoretically produced would be completely decomposed during the period of action, in part catalytically, in part as hydrogen acceptors. Similar experiments are recorded with benzoyl peroxide. The detection of the formation of hydrogen peroxide during biological oxidations is rendered exceptionally difficult by the presence of catalases and peroxydases. Preparations from *Lactarius vellereus*, freed as completely as possible from catalase by repeated solution in water followed by fractional precipitation with alcohol, accelerate the oxidation of quinol, pyrocatechol, pyrogallol, guaiacol, or anthraquinol, and give hydrogen peroxide in 50% yield or in almost 100% yield if the effect of residual catalase is negatived by addition of hydrogen cyanide. These preparations are remarkably stable towards rise of temperature, and in their activity resemble closely solutions of calcium glycollate and manganous acetate.

The evolution of hydrogen from aqueous solution of chromous and certain complex cobaltous salts,

regarded by Traube and Lange (this vol., 257) as a direct decomposition of water, is interpreted according to the scheme $Cr(OH)_2 \longrightarrow Cr(:O)\cdot OH+H$. Traube and Lange's failure to detect formic acid as product of the oxygen-free oxidation of carbon monoxide is not a proof of its non-formation, since its decomposition at the active contact surface may occur much more rapidly than its slow diffusion into the solution. H. WREN.

Interaction of hydrogen and nitrous oxide on the surface of gold. W. K. HUTCHISON and C. N. HINSHELWOOD (J.C.S., 1926, 1556—1559). —The reaction of these two gases examined at 704° and 880° is of the type where the two gases are adsorbed independently of one another. The rate of reaction tends to a limiting value as the pressure of each gas is increased, the maximum in the case of nitrous oxide being at 300 mm. and in the case of hydrogen at 500 mm. The rate was measured by the change of pressure: $N_2O+H_2=N_2+H_2O$ (liquid). W. THOMAS.

Catalytic oxidation of carbon monoxide. II. Adsorption of carbon dioxide, carbon monoxide, and oxygen by the catalysts, manganese dioxide, cupric oxide, and mixtures of these oxides. W. M. HOSKINS and W. C. BRAY (J. Amer. Chem. Soc., 1926, **48**, 1454—1474).—The adsorption isotherms at 20° and the rates of total adsorption at 20° and 76° (cf. Benton, A., 1923, ii, 382, 383) of the above gases in the oxides named were determined. The adsorptive capacity changes fairly regularly in passing from manganese dioxide through the mixtures to copper oxide; in the case of carbon dioxide and oxygen, this change is a decrease, and in the case of carbon monoxide, an increase. Catalytic activity is not related to total adsorptive capacity. The rate of interaction with carbon monoxide and the initial rate of reoxidation are greater for mixtures than for individual oxides. Manganese dioxide oxidises carbon monoxide almost completely to the dioxide, the total adsorption coinciding closely with that of carbon dioxide. Copper oxide, however, retains large quantities of carbon monoxide and the total adsorption becomes much greater than that for carbon dioxide. The former reaction and the initial stages of the latter probably consist of the rapid adsorption of small quantities of carbon monoxide followed by electronic rearrangement. In the mixed oxides, the rate of electronic rearrangement is increased. S. K. TWEEDY.

Reactions of the alcohols over zinc oxide catalysts. H. ADKINS and W. A. LAZIER (J. Amer. Chem. Soc., 1926, **48**, 1671—1677; cf. A., 1925, i, 878).—The decomposition of ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and *sec.*-butyl alcohol, in contact with zinc oxide catalysts prepared (*a*) from zinc sulphate by precipitation, (*b*) by a dry process, and (*c*) by hydrolysis of zinc *iso*propoxide, between 330° and 450°, has been examined. The ratio of dehydration to dehydrogenation is relatively independent of the structure of the alcohol, as compared with the effect of the catalyst surface. With primary alcohols, the ratio of dehydration to dehydrogenation is practically independent of the temperature. With secondary alcohols, the ratio is dependent on the temperature, but the extent of the change in this ratio depends on the catalyst, and may even change in direction with change of catalyst. Generally, catalyst (*a*) is best for dehydration, whilst (*b*) is best for dehydrogenation. It is concluded that the spatial arrangement of the catalyst surface is of primary importance in determining the relative proportions of the decomposition products. F. G. WILLSON.

Electrochemical formulation of the irreversible reduction and oxidation of organic compounds. J. B. CONANT (Chem. Reviews, 1926, **3**, 1—40).

Nitric acid. II. Behaviour of nitrous acid at the anode. A. KLEMENC and P. GROSS (Z. anorg. Chem., 1926, **153**, 332—338).—Nitrite solutions can be oxidised using platinum and magnetite electrodes; lower nitrogen–oxygen compounds can be oxidised to concentrated nitric acid. Measurements were made using nitrite–nitrate mixtures which were rendered either alkaline with sodium carbonate or weakly acid by saturation with carbon dioxide. The method used was that of Haber and Russ (A., 1904, ii, 309). The anodes were of smooth platinum foil; two methods of measurement were employed: (i) a slow method in which equilibrium was established before readings were made, (ii) a rapid method where readings were taken immediately the circuit was closed. Linear current-density–potential curves were obtained.

The equation, $\varepsilon=a+b\log(i/c)$, where a and b are characteristic constants of the current density–potential curve, i is the current density, and c the concentration of the depolariser, is deduced.

The values of the constants a and b, particularly of the latter, differ in acid and alkaline solutions. The calculated value of $(a/b)_{acid}-(a/b)_{alk}$ is 6·3; the observed value is 6·5. M. CARLTON.

Periodic phenomena at anodes of copper and silver. E. S. HEDGES (J.C.S., 1926, 1533—1546). —Periodic variations in current strength and in the *P.D.* between the electrodes accompanying the anodic solution of copper in solutions of hydrogen chloride (investigated in detail), ammonium chloride, sodium chloride, copper chloride, and potassium cyanide and of silver in solutions of potassium cyanide, sulphuric acid, ammoniacal ammonium sulphate, and ammonium chloride have been observed. Periodic film formation over the anode occurs between certain limiting current densities, the critical current density being a linear function of the concentration of the electrolyte. The phenomenon is attributed to the metastability of the oxide film between the critical current density, at which it is formed, and a certain higher value above which it is stable. The frequency of the periods is unaffected by catalytic poisons, but increases with rising temperature and concentration and decreasing current density. S. K. TWEEDY.

Electrochemical oxidation and peroxides. F. FICHTER (Chem. Weekblad, 1925, **23**, 302—310).—A *résumé* and discussion of recent work. Electrolytic

oxidation generally proceeds further than ordinary chemical oxidation, but similar results can be obtained by chemical means. Thus the action of fluorine on a saturated solution of potassium acetate yields pure ethane, and the electrochemical synthesis may be regarded as merely due to the effect of oxygen at high potential, an unstable diacyl peroxide being formed in both cases. S. I. LEVY.

Mechanism of the photochemical reaction between hydrogen and chlorine. III. Mean life of activity in illuminated chlorine. A. L. MARSHALL (J. Physical Chem., 1926, **30**, 757—762; cf. A., 1925, ii, 883).—The work of Bodenstein and Taylor (A., 1916, ii, 463) has been repeated, using an improved technique. Pure dry chlorine was passed into hydrogen 3×10^{-4} sec. after intense illumination by a quartz mercury arc, but no reaction was detected. Wet chlorine gave a similar result. A mathematical analysis based on the Nernst atomic mechanism predicted a large reaction. It follows that either this mechanism is incorrect or that the glass walls of the capillary used catalyse the recombination of the chlorine atoms produced by the illumination.

L. S. THEOBALD.

Yield of photochemical reactions with complex light. II. M. PADOA and N. VITA (Gazzetta, 1926, **56**, 164—174; cf. A., 1924, ii, 322).—The interaction of hydrogen and chlorine proceeds better under the influence of white light than under the separate influences of the constituent monochromatic radiations. The same is the case with direct-printing photographic paper only if, of the separate radiations, those of lesser frequency act on the paper first; if the colours of greater frequency act first, the result is greater than with white light.

The latent impression either of a photographic plate, whether sensitised or not, or of silver bromide paper is far more intense when effected by white light than by the coloured lights separately, if relatively long exposures are made with filtered lights. With shorter exposures, the extent of the action is the greater for the separate coloured lights, provided that those of the greater frequency act first.

T. H. POPE.

Substances which affect photographic plates in the dark. G. L. KEENAN (Chem. Reviews, 1926, **3**, 95—111).

Relation between time and intensity in photographic exposure. III. L. A. JONES, E. HUSE, and V. C. HALL.—See B., 1926, 566.

Studies with the microbalance. IV. Photochemical decomposition of silver iodide. E. J. HARTUNG (J.C.S., 1926, 1349—1354).—The decomposition was studied in various gases, using silver as absorbent for iodine. After 2 months' insolation, decomposition had taken place to the extent of 94·0% in oxygen, 88·5% in nitrogen, and 91·6% in hydrogen, the products being silver and iodine. To promote the change, it is necessary to have thin films, low gas pressure, and efficient absorption of iodine. No evidence of the formation of subiodides or periodides was obtained (cf. A., 1925, ii, 57; this vol., 34).

W. THOMAS.

Photolysis of acetaldehyde and of acetone. E. J. BOWEN and H. G. WATTS (J.C.S., 1926, 1607—1612).—A comparison has been made of the number of molecules chemically changed and the number of molecules activated. In the case of acetaldehyde vapour two photochemical changes take place: (photolysis) $CH_3\cdot CHO=CH_4+CO$; (polymerisation) $3CH_3\cdot CHO \rightarrow$ paraldehyde + metaldehyde. With unsaturated vapour, more molecules are polymerised than photolysed. The results show that two molecules are chemically activated for each quantum absorbed. In the case of acetone two molecules are decomposed for each quantum absorbed. The energy in the light absorbed was directly measured by an oxalic acid–uranyl sulphate solution. W. THOMAS.

Photochemical effect of chlorophyll and its significance for carbon dioxide assimilation. K. NOACK (Z. Botanik, 1925, **17**, 68 pp.; from Chem. Zentr., 1926, I, 699—700).—Illuminated eosin in aqueous solution oxidises benzidine to a violet colouring matter, with benzidine-blue as an intermediate stage. The reaction is catalysed by manganese salts and is faster in organic solvents. The same reaction is performed only by fluorescent solutions of chlorophyll. The photo-oxidative effect is destroyed when, as in phæophytin, magnesium is replaced by copper, yielding a non-fluorescent colouring matter. Carotin and xanthophyll are bleached in the presence of fluorescent chlorophyll and themselves exert a protective effect on chlorophyll. Benzidine and neutral sodium sulphite also protect chlorophyll from photo-oxidation. Non-fluorescent is more stable to light than fluorescent chlorophyll. These reactions can also be confirmed in chloroplasts of *Elodea* and *Fontinalis* which have been freed from enzymes. Leaves without chlorophyll or in which the chlorophyll has been changed to the non-fluorescent copper chlorophyll do not give the photo-reaction with benzidine. Chloroplasts which do not contain lipins are as rapidly bleached in light as normal chloroplasts. The consumption of oxygen increases in linear relationship with the oxygen content of the atmosphere. When carbon dioxide assimilation is inhibited, the photo-reaction is confined to the chlorophyll itself. The death of green plant organs in carbon dioxide-free air occurs because the rôle of oxygen acceptor is taken by chlorophyll and protoplasm. In the photochemical oxidation of sodium carbonate (? sulphite) by illuminated eosin, the same result is obtained with intermittent illumination with periods of 1/200 sec. as with continuous illumination. G. W. ROBINSON.

Krypton and xenon content of the air. E. RABINOWITSCH (Z. angew. Chem., 1926, **39**, 737—738).—A critical review of the work of other investigators. Taking into account the vapour pressure of liquid krypton and xenon at $-195°$ and their solubility in liquid oxygen, it appears that, in all the processes used so far for fractionating these gases from the air, a recovery of only 10% of the krypton and 1% of the xenon is effected. The most probable figures for the content of these gases in the air are those of Moureu (J.C.S., 1923, **123**

1305), viz., 1×10^{-4} vol.-% of krypton and 1×10^{-5} vol.-% of xenon. A. R. POWELL.

Anhydrous borates of lithium, cadmium, lead, and manganese. C. MAZZETTI and F. DE CARLI (Gazzetta, 1926, **56**, 19—28; cf. A., 1904, ii, 259, 610, 614, 654).—By means of lengthy fusion experiments and a study of the devitrifying points of various mixtures, using Tammann's method (cf. A., 1914, ii, 545) to induce crystallisation, the existence of the following series of acid *borates*, the greater number of which have not been previously described, is inferred; PbO,B_2O_3; $PbO,2B_2O_3$; $2PbO,5B_2O_3$; $PbO,3B_2O_3$; Li_2O,B_2O_3; $Li_2O,2B_2O_3$; $Li_2O,3B_2O_3$; $Li_2O,4B_2O_3$; $Li_2O,5B_2O_3$; CdO,B_2O_3; $CdO,2B_2O_3$; MnO,B_2O_3; $MnO,2B_2O_3$; $MnO,3B_2O_3$. Their existence has been confirmed by microscopical examination of the aggregate which forms in the devitrification, but the smallness of the individual crystals precluded complete crystallographic examination. By polarised light, however, the products were optically anisotropic, and also birefringent, and in many cases the observation of interference figures indicated crystals of a biaxial nature.

S. B. TALLANTYRE.

Polysulphides of sodium and potassium. C. Z. DRAVES and H. V. TARTAR (J. Amer. Chem. Soc., 1926, **48**, 1527—1529).—Sodium dropped into a boiling, dilute solution of excess of sulphur in toluene reacts to form sodium trisulphide (cf. Thomas and Rule, J.C.S., 1917, **111**, 1063). Potassium reacts analogously to form the pentasulphide.

S. K. TWEEDY.

Hydrogen absorption by sodium and calcium. B. KAMIEŃSKI (Bull. Int. Acad. Polonaise, 1926, *A*, 109—128).—Pure sodium commences to absorb hydrogen appreciably at 100—110°, and more rapidly as the temperature is raised. A mixture of sodium hydride and sodium is formed, having the m. p. of sodium (cf. Troost and Hautefeuille, A., 1874, 767). Sodium hydride shows the behaviour of a salt. Calcium hydride, prepared by direct union of the elements in an electric furnace, has a heat of formation of $42{,}383 \pm 296$ cal. The m. p. of calcium hydride is 816·15°. The mean atomic frequency of calcium and lithium hydrides at the m. p., calculated from Lindemann's formula, is greater than for the corresponding halides, the order being $H > F > Cl > Br > I$. The conductivity of calcium hydride increases 20 times at the m. p., which, together with other facts, indicates that the compound has the character of a salt in which the negatively-charged hydrogen ion appears. The hydrolysis of boroethane is readily explained on this basis by supposing that six negative ions neutralise six positive hydrogen ions (from water) with the formation of free hydrogen. C. H. D. CLARK.

Double chlorides of cæsium and tervalent thallium. G. MALQUORI (Gazzetta, 1926, **56**, 37—41; cf. A., 1900, ii, 597, 655).—The system $TlCl_3$–$CsCl$–H_2O has been studied at 15°, starting with the salt $3CsCl,2TlCl_3$, which is readily obtained by treating a solution of cæsium chloride with excess of thallic chloride. From a ternary diagram, it is deduced that at 15° only the following double thallic chlorides exist: $2TlCl_3,3CsCl$; $TlCl_3,2CsCl,2H_2O$; $TlCl_3,3CsCl,H_2O$; $TlCl_3,3CsCl$. The solubility of thallic chloride at 15° is 65·17 g. in 100 g. of solution. Contrary to some previous statements, only the compound $2TlCl_3,3CsCl$ is soluble, but its solubility decreases very rapidly by the addition of thallic chloride. The other double salts are insoluble in water, which decomposes them rapidly with formation of the compound $2TlCl_3,3CsCl$. The insolubility of these double salts renders possible their use in the determination of thallium.

S. B. TALLANTYRE.

Doubtful existence of aurous oxide. W. B. POLLARD (J.C.S., 1926, 1347—1349).—No evidence of the existence of aurous oxide could be obtained. The so-called aurous oxide is probably a mixture of gold and auric oxide ($4Au+Au_2O_3$) analogous to purple of Cassius. W. THOMAS.

Hydrogen. V. Compounds of hydrogen with calcium. G. F. HÜTTIG and F. BRODKORB (Z. anorg. Chem., 1926, **153**, 309—318).—When calcium (98·5%) is heated in pure hydrogen, there is no combination below 380°, but between 380° and 450° a brisk reaction occurs. On further raising the temperature, reaction recommences at 550° and is very vigorous at 600°. Analysis of the product corresponds with $CaH_{1.94}$. Absorption of hydrogen in two steps is due to previous treatment and surface of the calcium. At 20°, calcium hydride shows a measurable hydrogen pressure, steadily increasing with time, the increase continuing after 9 days. The formula CaH_2 expresses an ideal limit which is never completely reached. By removal of hydrogen from calcium hydride, the substance slowly separates into a portion richer and a portion poorer in hydrogen, the richer approximating most closely to CaH_2. The poorer portion cannot contain metallic calcium, but a compound of calcium with hydrogen which is fairly stable, as the decomposition pressure of the preparation shows. Experiments at 200° and 240° show a general increase in the rate of decomposition. Above 550°, sublimation of calcium etc. interferes. Hydrides of barium and strontium may be assumed to behave similarly. The internal energy of calcium hydride is calculated to be 229 Cal. M. CARLTON.

Constitution of bleaching powder. H. DITZ and B. NEUMANN.—See B., 1926, 537.

Ammonates of metallic sulphates. F. EPHRAIM (Ber., 1926, **59**, [*B*], 1219—1231).—Cadmium sulphate and ammonia yield the *compounds* $CdSO_4,6NH_3$, $CdSO_4,5NH_3$, $CdSO_4,2NH_3$, and $CdSO_4,NH_3$, the temperatures of incipient decomposition being 61°, 84·5°, 197°, and 253°, respectively. Copper sulphate yields $CuSO_4,5NH_3$; $CuSO_4,4NH_3$; $CuSO_4,2NH_3$; $CuSO_4,NH_3$, the tetrammonate being formed at 96° and the diammonate at 166°. Copper sulphate trihydrate appears to give the compound $CuSO_4,3H_2O,5NH_3$. Zinc sulphate yields the *substances* $ZnSO_4,5NH_3$; $ZnSO_4,4NH_3$; $ZnSO_4,3NH_3$; $ZnSO_4,2NH_3$; $ZnSO_4,NH_3$, and $2ZnSO_4,NH_3$, the temperatures of decomposition being 34—45°, 109—119°, 179—181°, 244°, 348°, and 403—407°, respect-

ively. Nickel sulphate gives the *compounds* $NiSO_4,6NH_3$; $NiSO_4,4NH_3$; $NiSO_4,2NH_3$; (?) $NiSO_4,NH_3$, and $2NiSO_4,NH_3$, the temperatures of decomposition being 135—137°, 177·5°, (?) 325°, 335°, and above 380°. Cobalt sulphate absorbs ammonia relatively slowly, giving the *substances* $CoSO_4,6NH_3$; $CoSO_4,4NH_3$; $CoSO_4,3NH_3$; $CoSO_4,2NH_3$, and $2CoSO_4,NH_3$, with temperatures of decomposition 106—116°, 132—135°, 135—254°, 254—257°, and above 320°, respectively. From ferrous sulphate, the following *compounds* are derived: $FeSO_4,6NH_3$; $FeSO_4,4NH_3$; $FeSO_4,3NH_3$; $FeSO_4,2NH_3$, and $FeSO_4,NH_3$, the temperatures being mainly 87—91°, 110°, 120—123°, 221—222°, and 300—400°. The *substances* $MnSO_4,6NH_3$; $MnSO_4,5NH_3$; $MnSO_4,2NH_3$, and $2MnSO_4,NH_3$ decompose at 53°, 70·5°, 201°, and 276°, respectively. $SnSO_4,4NH_3$; $2SnSO_4,5NH_3$; $2SnSO_4,3NH_3$, and $SnSO_4,NH_3$ lose ammonia at 40·5—42°, 142°, 168—172°, and above 190°. The *compound* $HgSO_4,4NH_3$ is converted at 74° into $HgSO_4,2NH_3$. Beryllium sulphate gives the *compound* $BeSO_4,2NH_3$, passing through a series of solid solutions into $BeSO_4,NH_3$. Silver sulphate combines with 4 mols. of ammonia per mol. of salt. Bismuth sulphate gives a continuous series of solid solutions with 0—9 mols. of ammonia, further quantities of which are added below 0°. Ferric sulphate gives similar solid solutions the composition of which at 0° corresponds with 13 mols. of ammonia; *compounds* $Fe_2(SO_4)_3,6NH_3$ and $Fe_2(SO_4)_3,4NH_3$ are described. Addition of ammonia is not effected by the sulphates of barium, strontium, calcium, lead, sodium, potassium, rubidium, cæsium, and univalent thallium, and only at very low temperatures by those of magnesium, aluminium, and lithium. H. WREN.

Barium aluminates. System Al_2O_3–BaO–H_2O at 20°. G. MALQUORI (Gazzetta, 1926, **56**, 51—55; cf. A., 1911, ii, 725).—From a study of the solubility curves and the composition of the solid phase in the system Al_2O_3–BaO–H_2O at 20°, only two barium aluminates could be isolated, viz., the compounds $2BaO,Al_2O_3,5H_2O$, stable in solutions containing from 3·5 to 2·1% of barium oxide, and $BaO,Al_2O_3,6H_2O$, stable in concentrations of from 2·1 to 1·2% of barium oxide. Several compounds described in the literature were not obtained. The former compound is rapidly decomposed by water into the latter, which is also decomposed by a large excess of water into barium hydroxide and gelatinous aluminium hydroxide. The mode of reaction of the aluminium hydroxide with the barium hydroxide varies according to the manner of its preparation. The best process is to add specially precipitated aluminium hydroxide little by little to a calculated quantity of barium hydroxide solution, and boil until no further dissolution is effected. By evaporation under reduced pressure, crystals of the dibarium aluminate pentahydrate were obtained. S. B. TALLANTYRE.

Conversion of mercurous into mercuric chloride [on keeping]. E. RABALD (Arch. Pharm., 1926, **264**, 366—368).—The statement (cf. Gmelin-Kraut, "Handbuch der anorgan. Chemie," 1914, **5**, ii, 635) that when calomel is preserved, as tablets containing sugar, it is slowly converted into mercuric chloride has been doubted by Vive and Budde (Apoth.-Ztg., **20**, 408) and is now shown to be untrue. Colorimetric comparison of the mercuric sulphide precipitates obtained showed that in 3-year-old tablets containing lactose no more mercuric chloride was present than in freshly-prepared tablets. W. A. SILVESTER.

Double chromates of rare-earth metals with the alkali metals. II. Lanthanum and ammonium. G. CAROBBI (Gazzetta, 1926, **56**, 76—81; cf. A., 1924, ii, 261, 414, 763).—A study of the system $La_2(CrO_4)_3$–$(NH_4)_2CrO_4$–H_2O at 25°. From solutions of lanthanum and ammonium chromates at 25° only the chromate of the composition $La_2(CrO_4)_3,3(NH_4)_2CrO_4,5H_2O$ is deposited, and not a compound similar to that obtained with potassium sulphate, *i.e.*, $K_2CrO_4,La_2(CrO_4)_3,6H_2O$. In air, no evolution of ammonia takes place. The study of the system is complicated by the alteration which ammonium chromate undergoes in solution, forming dichromate. When ammonium chromate is in excess, ammonium dichromate crystallises out, and when the lanthanum chromate is in excess, the salt of the composition $La_2(CrO_4)_3,8H_2O$ separates. Crystals of the normal ammonium chromate were never seen, even under the microscope, where it should be readily distinguishable. S. B. TALLANTYRE.

Zirconium, thorium, and hydrogen. A. SIEVERTS and E. ROELL (Z. anorg. Chem., 1926, **153**, 289—308).—Powdered zirconium reacts vigorously in hydrogen above 700° and on cooling in hydrogen at atmospheric pressure a black powder is obtained, which is not affected by the air and contains 1·76 atoms of hydrogen to 1 atom of zirconium. Below 700°, no equilibrium between zirconium and hydrogen was attained. Isobars show a rapid reduction in hydrogen absorption above 900°; isotherms at 800° resemble those of the cerium metals; at 1100°, the amount of hydrogen absorbed by zirconium is nearly proportional to the square root of the hydrogen pressure.

Thorium absorbs hydrogen vigorously at 400°; on cooling the product in hydrogen, a black substance is obtained which often reacts with the air. The maximum value obtained for Th : H is 1 : 3. Isobars show a rapid decrease in hydrogen absorption above 900°; the 800° isotherm resembles that for zirconium.

Experiments on hydrogen pressure etc. indicate that the hydrides of zirconium and thorium are not stoicheiometric compounds of the metal and hydrogen, but solid solutions in which they resemble those of cerium.

Pauses in the reaction between zirconium, thorium, and hydrogen are frequently observed. Observations at 1100° on hydrogen absorption of zirconium give unexpectedly high absorption values which cannot be explained. M. CARLTON.

Rare earths. XXIII. Element No. 61. I. Concentration and isolation in the impure state. J. A. HARRIS and B. S. HOPKINS (J. Amer. Chem. Soc., 1926, **48**, 1585—1594).—The rare earths of the cerium group are fractionally crystallised as the double magnesium nitrates. This concentrates element 61

between neodymium and samarium, both of which have very broad absorption bands masking any bands peculiar to element 61 which may occur. These fractions, moreover, contain too small an amount of this element for its detection by *X*-ray analysis. Fractionation of the bromates separates element 61 from neodymium by interposing terbium and from samarium by interposing gadolinium. Gadolinium has no absorption bands and terbium only one in this region, so that faint bands at 6700 and 5905 Å. and stronger bands at 5830, 5816, and 4520 Å. are probably due to element 61. Bands at 4893, 4411, and 4177 Å. usually assigned to samarium are stronger than would be expected. M. CARLTON.

[Non-]existence of the suboxides of lead and thallium. F. AUFENAST and H. TERREY (J.C.S., 1926, 1546–1549).—No indications were obtained of the existence of suboxides of lead or thallium. The heats of dissolution of the products obtained by the reduction of thallous oxide and litharge in acetic acid correspond with those given by a mixture of the metal and its monoxide. W. THOMAS.

Reactions in the solid state between lead dioxide and other oxides. F. DE CARLI (Gazzetta, 1926, **56**, 55—58; cf. A., 1924, ii, 758).—The thermal changes taking place during the dissociation of lead dioxide when heated up to 1000° show the occurrence of three points, corresponding with endothermic transformations, viz., at 320—350°, about 570°, and at 875°. The same thermal experiments have been performed with admixtures of various oxides added in molecular proportions. Lead dioxide has a notable tendency to react with most metallic oxides at a relatively low temperature, *i.e.*, 200—300°. The alkaline-earth oxides, cuprous, stannous, zinc, and ferrous oxides form plumbates, but arsenious, antimonious, and chromic oxides give arsenates, antimonates, and chromates, respectively. The quantity of heat developed is greater than that absorbed in the reaction $PbO_2=PbO+O$. The thermal effects during the valency changes of the various oxides, when passing from a lower to a higher state of valency, by absorption of the oxygen from the lead dioxide, are also discussed. S. B. TALLANTYRE.

Behaviour of heavy metal sulphides towards heavy metal salts in the presence of alcohol. L. ROSENTHALER (Pharm. Zentr., 1926, **67**, 417—420).—Alcoholic suspensions of heavy metal sulphides react with alcoholic solutions of other heavy metal salts in the same way as the corresponding aqueous suspensions with aqueous solutions; thus lead, cadmium, or zinc sulphide precipitates silver, copper, and mercury sulphides from alcoholic solutions of their salts. Zinc sulphide, however, does not precipitate lead sulphide from lead salts in alcohol.

A. R. POWELL.

Synthetic pyromorphites, vanadinites, and mimetites, in which the lead is partly substituted by metals of the lanthanum series. G. CAROBBI and S. RESTAINO (Gazzetta, 1926, **56**, 59—68; cf. A., 1922, ii, 765; Carobbi, Rend. Accad. Sci. Fis. Mat. Napoli, 1925, **31**, 1; this vol., 14).—A study of the compounds $3Pb_3(XO_4)_2,PbCl_2$ (where X=P, V, or As) to examine the isomorphic relationships existing between the lead compounds and some rare-earth metals, and a comparison with the natural minerals containing similar rare earths. The existence of pyromorphite, vanadinite, and mimetite containing elements of the cerium group, as substituents isomorphous with the lead, is demonstrated, but only small quantities of the lanthanum metals can replace the lead in the pyromorphite group. About 14% of the phosphate of the rare metal can combine with pyromorphite, and for vanadinite this limit is still lower. No chlorovanadinite containing more than about 8% of lanthanum vanadate could be prepared. The following new synthetic minerals, with their content of rare earth, are described: ceriferous pyromorphite with 13·45% of cerium phosphate, lanthaniferous pyromorphite with 6·34% of lanthanum phosphate, neodymiferous pyromorphite with 14·04% of neodymium phosphate; ceriferous vanadinite with 7·89% of cerium vanadate, lanthaniferous vanadinite with 8·39% of lanthanum vanadate, praseodymiferous vanadinite with 3·34% of praseodymium phosphate; ceriferous mimetite with 17·92% of cerium arsenate.

S. B. TALLANTYRE.

Direct synthesis of nitrous oxide. D. L. CHAPMAN, R. A. GOODMAN, and R. T. SHEPHERD (J.C.S., 1926, 1404—1409).—Nitrous oxide has been synthesised by passing an electric discharge through nitrogen at a low pressure contained in a tube of fused silica the union wall of which had been previously saturated with oxygen by passing a discharge through the tube filled with the gas. The nitrous oxide was isolated as it was formed by condensing it in a U-tube surrounded with liquid air. Mixtures of oxygen and nitrogen produce nitrogen peroxide even when the partial pressure of the oxygen is only one tenth that of the nitrogen. W. THOMAS.

Nitrosylsulphuric acid. I. G. A. ELLIOTT, L. L. KLEIST, F. J. WILKINS, and H. W. WEBB [in part with R. PEPPERELL] (J.C.S., 1926, 1219—1232).—The action of acid chlorides on nitrosylsulphuric acid was examined. Benzoyl chloride gave dibenzoylsulphuric acid, and acetyl chloride gave acetylsulphuric acid. The action of ethyl alcohol and ether was also examined. Efforts were made to prepare the anhydride from the acid, the solubility of which in sulphuric acid was determined. The authors conclude that the crystalline acid probably has the formula $OH\cdot SO_2\cdot O\cdot NO$, but that the liquid probably contains the nitrosyl form and also $O_2S<^{O}_{O}>N\cdot OH$. No evidence was obtained in favour of the nitro-structure $OH\cdot SO_2\cdot NO_2$. W. THOMAS.

Additive compounds of ammonium perchlorate and ammonia. C. MAZZETTI and F. DE CARLI (Gazzetta, 1926, **56**, 29—33; cf. Kendall and Davidson, A., 1920, ii, 490).—Ammonium perchlorate, ammonium persulphate, and ammonium benzenesulphonate liquefy when exposed to an atmosphere of ammonia at the ordinary temperature. A saturated solution of ammonium perchlorate with pure ammonia contained 72·5% of the salt at 10°. With an apparatus similar to that described by Baume (cf. J. Chim. Phys., 1914, **12**, 217) the authors find that with ammonium perchlorate a eutectic mixture is formed

at −97° containing 51% of ammonia. The existence of the *compounds* $NH_4ClO_4,6NH_3$ and $NH_4ClO_4,4NH_3$ is inferred. S. B. TALLANTYRE.

Action of phosphorus on salts of silver and other metals. O. J. WALKER (J.C.S., 1926, 1370—1381).—Deposits of metallic appearance were obtained when sticks of phosphorus were placed in acid or neutral solutions of the following metals: gold, platinum, silver, mercury, and copper. In ammoniacal solution, salts of lead, nickel, thallium, tin, cobalt, cadmium, and zinc also gave deposits. In the case of silver and copper solutions, the first process is the formation of a black phosphide on the surface of the phosphorus, the phosphide then reacting with the metallic salt giving a deposit of the metal. The following equations quantitatively represent the two stages, M and X representing equivalents of the negative and positive salt radicals: 1. (*a*) $2P+3H_2O=PH_3+H_3PO_3$; (*b*) $PH_3+3MX=PM_3+3HX$. 2. $PM_3+5MX+4H_2O=8M+5HX+H_3PO_4$. Reaction 2 is responsible for the phenomena of an electrochemical nature. W. THOMAS.

Double decomposition between the halides of phosphorus, tin, arsenic, antimony, lead, bismuth, silicon, titanium, zirconium, and thorium. T. KARANTASSIS (Compt. rend., 1926, **182**, 1391—1393; cf. this vol., 487).—Phosphorus tri-iodide undergoes double decomposition with stannic chloride, antimony trichloride, antimony pentachloride, arsenic trichloride, bismuth chloride, and lead chloride; the corresponding reverse reactions will not take place. No reaction takes place between phosphorus tri-iodide and the tetrachlorides of silicon or zirconium. Phosphorus pentachloride and antimony tri-iodide react with liberation of iodine, and the formation of phosphorus trichloride and the substance $SbCl_5,PCl_5$; the reaction is probably represented by the equation $7PCl_5+2SbI_3=5PCl_3+6I+2SbCl_5,PCl_5$. Phosphorus trichloride and titanium tetraiodide undergo double decomposition; the reverse reaction will not take place even in sealed tubes at 200°. No reaction takes place between thorium tetrachloride and stannic iodide. These and the previous results lead to the following general rules: (1) the iodides of the tervalent metalloids of low at. wt. undergo double decomposition with the bromides or chlorides of elements of higher at. wt. (2) The iodides of carbon, silicon, titanium, zirconium, thorium, germanium, and celtium undergo double decomposition with the chlorides of tervalent metalloids, but do not react with stannic chloride.
W. HUME-ROTHERY.

Compounds of tervalent molybdenum. IV. Bromides. W. WARDLAW and A. J. I. HARDING (J.C.S., 1926, 1592—1596).—Solutions of tervalent molybdenum are obtained by the electrolytic reduction of the trioxide in hydrobromic acid solution. The oxybromide, $MoOBr,4H_2O$, was isolated. On the addition of alkali bromides, a *potassium* salt, $K_3[MoBr_6]$, and *potassium* (anhydrous), *cæsium*, ($5H_2O$) and *rubidium* salts of the type $[MoBr_5,H_2O]R_2$ were isolated, where the co-ordination number of molybdenum equals six. W. THOMAS.

Green colour of tungsten oxide. J. A. M. VAN LIEMPT (Chem. News, 1926, **132**, 357; cf. A., 1922, ii, 73).—Yellow tungsten oxide becomes greenish if traces of the pentoxide W_2O_5 (blue) are formed by reduction. This occurs on igniting the trioxide, on account of the reducing burner gases and also alkali salts. Of the latter, sodium is the most active, after which rank lithium, rubidium, and potassium.
W. THOMAS.

Chromammines. II. Hydroxopentammine-chromic salts and electrical conductivities of chromammines. H. J. S. KING (J.C.S., 1925, **127**, 2100—2109; cf. A., 1924, i, 1060).—Alkaline solutions obtained by the action of moist silver oxide on chloropentammine-chromic or aquopentammine-chromic chloride show anomalous behaviour with acids. The conductivities of aquopentammine-chromic and hydroxopentammine-chromic ions at zero concentration are 174·3 and 73·3 mhos at 0°, giving 489·3 and 283 mhos for limiting conductivities of the hydroxides. The value obtained by extrapolation for the chromammine alkaline solution was 283·9, confirming the view that it contained only hydroxo-pentammine-chromic hydroxide (cf. value of 296 obtained by extrapolation of the data of Lamb and Yngve, A., 1922, ii, 217).

Aquopentammine-chromic oxalate, *picrate*, and 2 : 4-*dinitrophenoxide*, also *aquopentammine-cobaltic* 2 : 4-*dinitrophenoxide* and *picrate* have been prepared (cf. Morgan and King, J.C.S., 1922, **121**, 1723). All partly decompose on heating at 100° for 3 hrs.

Hydroxopentammine-chromic sulphate, *nitrate*, *chloride*, *bromide*, *iodide*, *chromate*, and *oxalate* give solutions, only very slightly alkaline to litmus, which do not liberate ammonia from ammonium salts in the cold. The tendency to form aquo-salts is less pronounced than with the corresponding cobaltammines. The co-ordinated hydroxyl group cannot be acetylated or carbonated. These substances evolve ammonia and are unstable even in the dark, but can be kept indefinitely in an atmosphere of ammonia.

Evidence is adduced to show that these salts are hydroxo- and not hydrated aquo-salts.

The $\lambda-C^{1/3}$ graph (cf. Porter, A., 1920, ii, 151) is rectilinear for many salts for the concentration range $v=32$ to $v=1024$, and therefore it is concluded that deviations are due to polymerisation, hydration, and hydrolysis. Where this graph is rectilinear, extrapolation by means of the $1/\lambda-(C\lambda)^{n-1}$ graph gives concordant values for the mobility of the complex ion; different values are obtained where the graph is curved, but at infinite dilution the rectilinear $\lambda-C^{1/3}$ graph gives too high values. The hexammines give a curved graph, but extrapolation gives concordant results from different salts of the same ion.

The conductivity of these salts at different concentrations has been obtained and the mobility of the hydroxopentammine-, chloropentammine-, and aquopentammine-chromic and -cobaltic ions and hexammine-chromic ions calculated. The diminution in mobility produced by replacing one ammonia molecule of the hexammine by water is 5·7 in the chromammine and 5·3 in the cobaltammine series.

The mobility divided by the square of the valency, Λ/Q^2, is approximately constant, showing that the mobility is proportional to the square of the ionic charge. Mean values of Λ/Q^2 for uni-, bi-, and ter-valent ions are 18·0, 18·8, and 19 at 0° and 36·2, 34, and 37·4 at 25°. For metallic cations, Λ/Q is constant. M. CARLTON.

Formation of mother-of-pearl. P. B. GANGULY (J.C.S., 1926, 1381—1385).—The nature of the deposit of calcium carbonate from an aqueous solution of calcium hydrogen carbonate in the presence of gelatin depends on the initial concentration of the hydrogen carbonate and the ratio of gelatin to the calcium hydrogen carbonate. For each concentration of the hydrogen carbonate there is a range of gelatin concentrations which yield translucent layers showing the iridescent colours characteristic of mother-of-pearl. The structure of mother-of-pearl is discussed. W. THOMAS.

Preparation of silicon tetrachloride [from silica]. P. P. BUDNIKOV and E. SCHILOV (Z. angew. Chem., 1926, **39**, 765).—Silicon tetrachloride is formed by the action of carbonyl chloride on precipitated silica at 900—1000°. In the presence of sugar charcoal, 50—62% of the silica is acted on in 1 hr., without carbon only 23—31%. Finely-ground sand under similar conditions yields only traces of silicon tetrachloride. A. R. POWELL.

Analysis of gases from rocks by microchemical methods. N. METTA (An. Inst. Geol. Romaniei, 1925, **10**, 85—119).—The analysis of gas is made at constant volume in a volumeter of previously determined capacity and placed in communication with a MacLeod manometer modified to show 0·001 mm. Operating under an initial pressure of 3·5—4 mm., determinations may be made with 0·001 of the volume required by the ordinary methods of gas analysis. The construction and calibration and use of the apparatus are described. CHEMICAL ABSTRACTS.

Determination of small quantities of hydrogen in gaseous mixtures. P. LEBEAU and P. MARMASSE.—See B., 1926, 538.

Apparatus for the electrometric determination of hydrogen-ion concentration. H. LÜERS (Biochem. Z., 1926, **171**, 119—125). E. C. SMITH.

Measurements with the quinhydrone electrode. W. ACKERMANN (Collegium, 1926, 208—211).—The low hydrogen-ion concentration with the quinhydrone electrode and the use of a plain platinum electrode instead of a platinised electrode avoid the danger of reduction of the solute, so that the p_H of some solutions which cannot be determined by the hydrogen electrode can be measured by this electrode. The tendency for the quinol to oxidise in alkaline solution is a disadvantage, and the quinol, itself a weak acid, affects the hydrogen-ion concentration in non-buffered alkaline solutions. Hence solutions of p_H 8—9 can be measured by the quinhydrone electrode only after buffering. If insufficient quinhydrone is used, concordant values will not be obtained. There are many solutions for which the quinhydrone electrode is more suitable than the hydrogen electrode. D. WOODROFFE.

Iodometric titration of acids. I. M. KOLTHOFF (Chem. Weekblad, 1926, **23**, 260—261).—Weak acids can be titrated by addition of potassium iodide, potassium iodate, and a known excess of thiosulphate, so long as the dissociation constant is not below 1×10^{-6}. The mixture is kept for 15—30 min., and the excess of thiosulphate titrated with iodine solution. The hydrogen-ion concentration after the titration is about 7. S. I. LEVY.

Standardisation of hydrochloric acid with potassium iodate as compared with borax and sodium carbonate as standard substances. I. M. KOLTHOFF (J. Amer. Chem. Soc., 1926, **48**, 1447—1454).—Sodium carbonate, borax, and potassium iodate, used under appropriate conditions, are equally good substances for the standardisation of hydrochloric acid. Sodium carbonate is least suitable because of its hygroscopic nature and the uncertainty of its end-point with dimethyl-yellow indicator when excess of carbon dioxide is present. Borax, having a high mol. wt., and giving accurate end-points with methyl-red and dimethyl-yellow, is the most suitable standard. The titrations recorded confirm the value 10·82 for the at. wt. of boron (cf. Briscoe and Robinson, A., 1925, ii, 346); fused borax does not lose sodium oxide as stated by Briscoe, Robinson, and Stephenson (*ibid.*, 619). S. K. TWEEDY.

Colour of "yatrenum" in aqueous solutions of different hydrogen-ion concentration, and possible application of the material as an indicator. H. W. VAN URK (Pharm. Weekblad., 1926, **63**, 685—687).—The preparation consists of "2-iodo-1-oxyquinoline-4-sulphonic acid" [? 5-iodo-8-hydroxyquinoline-7-sulphonic acid], mixed with 20% of sodium hydrogen carbonate, and its aqueous solution is strongly coloured between p_H 8 and 1. The maximum intensity is at p_H 4, and the colour variations and disappearances permit of its use, with buffer solutions, as an indicator. S. I. LEVY.

Chemical reactions and volumetric titrations in Wood light. R. MELLET and A. BISCHOFF (Compt. rend., 1926, **182**, 1616—1619; cf. B., 1926, 49).—Solutions of acids or bases (ammonia excepted) may be titrated quantitatively in Wood light, using quinine as fluorescent indicator, there being marked changes in the nature of the fluorescence over the p_H ranges 1—2, 5—6, and 9—10, respectively. The method is particularly suitable when the solution to be titrated is turbid or coloured. J. S. CARTER.

Loebich's method for the determination of perchloric acid. F. FICHTER (Z. anal. Chem., 1926, **68**, 298—299; cf. Loebich, this vol., 489).—A claim for priority (cf. Fichter and Jenny, A., 1923, ii, 245). A. R. POWELL.

Microchemical determination of nitrates. F. ROGOZIŃSKI (Bull. Int. Acad. Polonaise, 1926, *A*, 129—132).—The procedure of Ulsch (A., 1891, 617, 960) for determining nitrates by reduction with iron has been satisfactorily modified for use under microchemical conditions. A 0·2% solution of the nitrate

(1—2 c.c.) is treated with 100 mg. of pure iron powder and 0·2 c.c. of sulphuric acid (*d* 1·35), and heated for 5 min. in small bulbs until reduction is complete. The solution is distilled with 2·5 c.c. of sodium hydroxide solution for 5 min., and the distillate titrated with 0·01*N*-sulphuric acid, using methyl-red as indicator. The maximum mean error was less than −1%. C. H. D. CLARK.

Variability of the titre of thiosulphate solutions. C. MAYR (Z. anal. Chem., 1926, **68**, 274—283).—Prolonged passage of a current of pure air or of pure carbon dioxide or of a mixture of both through thiosulphate solutions prepared from freshly-boiled water causes no change in the titre, but exposure of the same solutions to ordinary air soon results in the deposition of sulphur, and first a slight increase, then a more rapid decrease in the titre. This has been proved to be due to inoculation of the solution with sulphur bacteria derived from the air; in the presence of carbon dioxide, the bacteria thrive to a limited extent and cause first the decomposition of the thiosulphate into sulphur and sulphite, and then the oxidation of the sulphite to sulphate. Immersion of a piece of bright copper wire in a sterilised thiosulphate solution results in a similar decomposition, which is more rapid the higher the temperature. A. R. POWELL.

Calcium hypophosphite as a substitute for Bettendorf's reagent in qualitative tests for arsenic. E. DEUSSEN (Arch. Pharm., 1926, **264**, 355—360; cf. Rupp and Muschiol, A., 1923, ii, 335).—A distinct brown coloration is shown when between 0·01 and 0·02 mg. of arsenic is present in 1 g. or 1 c.c. of many medicinal preparations, and special methods for applying the test to a number of others (iron, bismuth, and antimony medicinals) are described. W. A. SILVESTER.

Determination of traces of carbon monoxide. H. DAVIES and H. HARTLEY.—See B., 1926, 537.

Identification reaction for sodium. N. SCHOORL (Pharm. Weekblad, 1926, **63**, 555—560).—The best conditions for the oxalate test consist in adding to 0·5 g. of the solid to be examined about 2·5 c.c. of a solution of 1 part of potassium oxalate in 4 parts of water, and shaking; a fine suspension of sodium oxalate crystals forms in the liquid, and may be identified under the microscope. The only common sodium compound which will not respond to this test is borax. Potassium pyroantimonate under similar conditions gives even better results than the oxalate, being positive for all sodium salts and negative for all potassium salts in neutral solution. S. I. LEVY.

Application of the thermal dissociation of ammonium halides in quantitative analysis. L. MOSER and S. MARIAN (Ber., 1926, **59**, [*B*], 1335—1344).—Ammonium iodide, bromide, and chloride in order of decreasing activity are generally superior to moist or dry hydrogen chloride in analytical practice (cf. Hantzsch, A., 1925, ii, 359; Hofmann, *ibid.*, 685). The action depends on the thermal dissociation of the salts into ammonia and halogen acid, which themselves are partly dissociated into hydrogen and nitrogen or hydrogen and halogen. The superiority of the bromide and iodide is due to the greater extent of the dissociation of hydrogen bromide and iodide than of hydrogen chloride under equivalent conditions.

Complete reduction of potassium perchlorate to chloride cannot be effected by repeated evaporation with hydrochloric acid (*d* 1·19), treatment with moist hydrogen chloride at 450°, or with dry hydrogen chloride at 350—400°. After two or three treatments with ammonium chloride at 350—400° in the presence of platinum, reduction is complete, but not after ten to twelve operations in the absence of the metal. With ammonium bromide at 500° in the absence of platinum, formation of potassium halide is quantitative after one or two treatments, with ammonium iodide at 400° after three operations. Quantitative conversion of alkali sulphate into chloride cannot be effected by dry hydrogen chloride at 350—450°, but is achieved by ten treatments with ammonium chloride at 350° in the absence of platinum or three to six operations in the presence of the metal; with ammonium bromide, the reaction is quantitative after four operations, with ammonium iodide after two to four treatments. In practice, the use of a mixture of ammonium bromide (4 parts) and ammonium iodide (1 part) is recommended. Similar treatment suffices for lithium sulphate. Alkali nitrate is quantitatively converted into chloride by a single treatment with ammonium chloride. The conversion of alkali arsenate into chloride requires 4—6 hrs.' treatment with gaseous hydrogen chloride at 350°, whereas one or two operations with ammonium chloride suffice. Magnesium pyroarsenate cannot be completely converted into halide by ammonium chloride, whilst with ammonium bromide the operation is rendered difficult by the production of magnesium arsenide; one to three operations with ammonium iodide at 400° are, however, sufficient. H. WREN.

Precipitation of cadmium sulphide from aqueous solutions of cadmium chloride in the presence of hydrochloric acid and other chlorides. S. KRISHNAMURTI (J.C.S., 1926, 1549—1555).—The critical concentration of hydrochloric acid increases very rapidly with increase of cadmium chloride concentration for the lower concentrations, whilst for higher concentrations the variation is slight. The critical concentration of acid also increases rapidly with the time of passing in the hydrogen sulphide. The cadmium chloride–hydrochloric acid "precipitation" curve has been considered from the point of view of ionic activity, and conclusions are confirmed by *E.M.F.* measurements. The neutral chlorides increase the hydrogen-ion activity. Supersaturation or induction delay in the appearance of the precipitate was revealed. W. THOMAS.

Colorimetric determination of very small quantities of mercury. A. STOCK and E. POHLAND (Z. angew. Chem., 1926, **39**, 791—792).—The mercury obtained by freezing or by deposition on copper as previously described (this vol., 703) is dissolved in 2 c.c. of chlorine water, the excess of chlorine expelled by means of a current of air, and the solution treated with 4 drops of a saturated solution of diphenyl-

carbazide in alcohol. The pink colour produced is compared with that given under similar conditions with freshly-prepared neutral solutions of mercuric chloride. The colour is visible when 2 c.c. of solution contain only 0·0005 mg. of mercury.

A. R. POWELL.

Cobalt aluminate. test for aluminium. C. OTTO (J. Amer. Chem. Soc., 1926, **48**, 1604—1605).—In testing for aluminium the precipitate is treated with a drop of sulphuric acid before ignition on a platinum wire. The delicacy of the test is not affected by this, but manipulation is easier; the precipitate no longer decrepitates when heated.

M. CARLTON.

Determination of aluminium oxide in aluminium metal. W. H. WITHEY and H. E. MILLAR.—See B., 1926, 546.

Colorimetric determination of molybdenum. A. D. FUNCK (Z. anal. Chem., 1926, **68**, 283—286).—Solutions of molybdic acid in excess of sodium hydroxide are coloured brownish-red by hydrogen peroxide, the depth of the colour being proportional to the amount of molybdenum present and dependent to a certain extent also on the amount of hydrogen peroxide added. Ammonium salts interfere and must be previously removed by boiling with sodium hydroxide. The method is not suitable for the determination of very small quantities of molybdenum, but may be used for the rapid determination of the element in molybdenite, ferromolybdenum, and commercial molybdenum salts. As a standard, a solution of 1 g. of molybdic acid dissolved in 1 litre of water containing 2 g. of sodium hydroxide is used, 2 c.c. of a concentrated hydrogen peroxide solution being added to the standard and test solution. The colour produced slowly fades on keeping so that comparison should be made immediately the peroxide is added. A. R. POWELL.

Rapid determination of small quantities of palladium. F. C. ROBINSON.—See B., 1926, 546.

Fluorescope. H. MARCELET.—See B., 1926, 527.

Hydrogen sulphide generator. H. G. DENHAM and J. PACKER (J.C.S., 1926, 1344—1346; cf. *ibid.*, 1920, **117**, 527).—The gas is produced by the action of hydrochloric acid on iron sulphide in an electrically heated tube. The apparatus, which is automatic, is figured in the original. W. THOMAS.

Fine-pored filters and a new ultra-filter. R. ZSIGMONDY (Biochem. Z., 1926, **171**, 198—203).—A preliminary communication concerning a membrane suitable for use with organic solvents.

E. C. SMITH.

Apparatus for automatically washing precipitates. M. D. HADJIEV (Z. angew. Chem., 1926, **39**, 792—793).—A constant-level water-bath or glass stock-bottle is provided with a long, swinging jet, the lower end of which is connected with the larger wheel of a double pulley, to the smaller wheel of which is attached an adjustable arm carrying the funnel. By placing weights in a small pan attached to the washing jet a balance is obtained so that as the water runs out of the funnel the latter rises and the jet falls, thus allowing more water to run into the funnel, which then slowly falls as it fills, whilst the jet rises and thus regulates the water supply.

A. R. POWELL.

Boiling rod to prevent bumping. D. L. SCOLES (J. Amer. Chem. Soc., 1926, **48**, 1605—1606).—A glass tube is sealed at one end and slightly blown out; it is then reheated at the tip, and a small, bell-shaped depression formed in the end. The device is suitable for quantitative work and functions satisfactorily even when a precipitate is present.

M. CARLTON.

Laboratory latex. HSI-CHING CHEN (J. Physical Chem., 1926, **30**, 713—715).—An emulsion of 1 part of camphor, 4 parts of water, 2 of sodium oleate, and 1·5 of acetaldehyde gives most of the reactions of a caoutchouc latex. The usual methods of coagulating caoutchouc were successfully applied to the emulsion, yielding camphor. L. S. THEOBALD.

Danger of mercury vapour. A. SCHMIDT (Z. angew. Chem., 1926, **39**, 786), G. PINKUS (*ibid.*, 787—788), H. REIHLEN (*ibid.*, 788), F. GRADENWITZ (*ibid.*, 788—789), L. WOLFF (*ibid.*, 789—790), A. STOCK (*ibid.*, 790—791).—A discussion of Stock's paper (this vol., 707). Schmidt, Reihlen, and Wolff cite further evidence in support of Stock's assertion that prolonged exposure to the vapour of mercury at the ordinary temperature leads to chronic poisoning, whereas Pinkus and Gradenwitz bring forward evidence to the contrary.

In reply, Stock has investigated the loss of mercury from old amalgam teeth fillings and found a loss of 150 mg. of mercury when one was kept in a vacuum at 30° for 3 days and a loss of 1·3 mg. from another under the same conditions. A. R. POWELL.

Sensitivity of selenium cells. A. O. RANKINE (Nature, 1926, **118**, 13).

Observations by Arabian alchemists and doctors on mercury poisoning. J. RUSKA (Z. angew. Chem., 1926, **39**, 790).—The poisonous nature of mercury and its salts was known to Al Qazwīnī, Avicenna, and Gābir ibn Ḥajjān. A. R. POWELL.

Mineralogical Chemistry.

Graphical representation of rock analyses. F. BECKE (Tsch. Min. Petr. Mitt., 1926, **37**, 27—56).—The relative proportions of various constituents can be expressed by a point in a geometrical figure, for two components a line, for three a triangle, and for four by a point in a tetrahedron (" concentration tetrahedron "). The last can be conveniently represented by projections on different planes. L. J. SPENCER.

Chemical classification of the mica group. II. Basic micas. A. F. HALLIMOND (Min. Mag., 1926, **21**, 25—33).—The molecular ratios of published

analyses of biotite and phlogopite are calculated and plotted on the same lines as in the previous paper (A., 1925, ii, 819). They represent a series of mixtures extending from phlogopite, $K_2O,6RO,R_2O_3,6SiO_2,2H_2O$, towards biotite, $K_2O,4RO,3R_2O_3,6SiO_2,2H_2O$.

L. J. SPENCER.

Aerolith discovered in the department of the Côte-d'Or. Classification and nomenclature of the chondrites. A. LACROIX (Compt. rend., 1926, **182**, 1498—1501).—An arbitrary method of classification of chondrites into three possible sub-groups is suggested. Thus, in pyroxenic chondrites iron is present only as metal or as sulphide, and calcium partly as sulphide (oldhamite), with a minimum quantity of nickel. Pyroxeno-peridotic chondrites contain less metallic iron proportionally as the silicates are more ferruginous. The peridotic chondrites consist of orthosilicates, and not yet having been observed among the chondrites, are purely theoretical. A sample may be assigned to its group by the estimation of its metallic iron content from direct observation of its polished surface. Sideric and sideriferous chondrites are those containing most and least metallic iron, respectively, and the latter are again subdivided into megasideriferous, oligosideriferous, and cryptosideriferous. The amphoterites fall in the latter groupings. The meteorite described is a pyroxenoperidotic megasideriferous chondrite, the crystallisation of the sulphur being prolonged beyond that of the metal. The silicate portion contained bronzite, clinobronzite, and olivine, and the polished surface showed a number of simple and compound, but chiefly pyroxenic chondres, some of which were broken.

J. GRANT.

Chemico-mineralogical studies on aluminosilicates. E. DITTLER (Tsch. Min. Petr. Mitt., 1926, **37**, 1—26).—Comparative experiments were made with anauxite and cimolite from Bilin, Bohemia (analyses, A., 1924, ii, 415), kaolin from Zettlitz, Saxony (anal. I, $Al_2O_3,2{\cdot}3SiO_2,1{\cdot}8H_2O$), nacrite from Freiberg, Saxony (anal. II, $Al_2O_3,2SiO_2,2H_2O$), and pink montmorillonite from Paris, Maine, U.S.A. (anal. III, $2Al_2O_3,7SiO_2,10H_2O$).

	SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	MgO.	CaO.	Na_2O+K_2O.	H_2O.	Total.
I.	50·23	36·12	1·22	—	trace	0·40	0·64	12·12	100·73
II.	47·97	38·05	0·01	—	—	—	—	14·11	100·17
III.	50·02	23·28	0·65	0·32	2·03	1·10	0·44	22·13	100·02

The results are recorded of the action of water, sodium hydroxide solution, and of dilute hydrochloric acid followed by sodium hydroxide solution. The amorphous cimolite is the most susceptible to change. Analyses are also given of fresh basalt and fresh augite from Bilin and of the same when altered ("cimolised") to a white, earthy material. Powdered augite when treated for two weeks with water or with sodium carbonate solution showed some alteration suggesting a commencing change to cimolite.

L. J. SPENCER.

Smithsonite from Rhodesia Broken Hill mines. E. D. MOUNTAIN (Min. Mag., 1926, **21**, 51—54).—Distinctly developed crystals of zinc carbonate are of rare occurrence, and the physical constants of this mineral are incompletely known Clear, colourless rhombohedra (111), measuring 7 mm. along the edge, gave the cleavage-angle rr 72° 21′, d 4·398, H 4—4½, n_ϵ 1·6212, n_ω 1·8485 (for sodium light; for other colours the original must be consulted). Analysis of the same sample of material on which these constants were determined gave: ZnO 63·18, FeO 0·58, MnO 0·01, CaO 0·27, MgO 0·45, CO_2 35·35, H_2O 0·04, total 99·88, corresponding with $ZnCO_3$ 97·34%. On ignition, the powder becomes orange-coloured (zinc oxide), and on cooling it retains a reddish-brown tint. Hydrochloric acid then leaves a residue of ferric oxide; but the original mineral is completely dissolved in hydrochloric acid, showing that the ferric oxide is produced during ignition.

L. J. SPENCER.

Cæsium compounds in products of the present-day activity of Vesuvius. F. ZAMBONINI and L. CONIGLIO (Atti R. Accad. Lincei, 1926, [vi], **3**, 521—524).—A fragment of lava, much altered by fumarole exhalations, found at the bottom of the crater of Vesuvius in November, 1924, contains copper, lead, titanium, iron, aluminium, calcium, magnesium, sodium, potassium, and cæsium, the last in amount greatly exceeding that previously found in volcanic sublimations or in minerals, with the sole exception of pollucite.

T. H. POPE.

Synthetic pyromorphites, vanadinites, and mimetites, in which the lead is partly substituted by metals of the lanthanum series. G. CAROBBI and S. RESTAINO.—See this vol., 811.

Organic Chemistry.

Manufacture of methane. SOC. D'ETUDES MINIÈRES ET IND.—See B., 1926, 524.

B. p. of some higher aliphatic *n*-hydrocarbons. F. FRANCIS and N. E. WOOD (J.C.S., 1926, 1420—1423).—The vapour-pressure curve for synthetic *n*-docosane coincides with that of a fraction obtained by distillation of paraffin wax, and this result agrees with the mol. wt. of this fraction as deduced by X-ray analysis. The b. p., at 15 mm., of four other fractions the mol. wts. of which had been deduced by the same method also coincide with those for tetracosane, hexacosane, octacosane, and nonacosane. The corrected b. p. of the hydrocarbons $C_{15}H_{32}$ to $C_{35}H_{72}$ are given in a table.

C. J. STILL.

Unsaponifiable matter from the oils of elasmobranch fish. I. Constitution of squalene (spinacene). I. M. HEILBRON, E. D. KAMM, and W. M. OWENS (J.C.S., 1926, 1630—1644).—Squalene, obtained from liver oils of elasmobranch fish, may be freed from a small quantity of an oxygenated impurity by treatment with phthalic anhydride at 130—140° or by decomposition of the hexahydro-

chloride. Squalene is concluded to be a dihydrotriterpene in which one half of the molecule has the carbon skeleton C_2·C·C·C·C·C(C)·C·C·C·C·C(C)·C·C· and to be a mixture of isomerides, one form of which might be represented as $CMe_2{:}CH{\cdot}CH_2{\cdot}[CH_2{\cdot}CMe{:}CH{\cdot}CH_2]_4{\cdot}CH_2{\cdot}CMe{:}CHMe$. Isomerisation of squalene to cyclic compounds is readily accomplished by means of formic acid. Distillation of squalene at atmospheric pressure gives a number of fractions; that of lowest b. p. contains an amylene, $CMe_2{:}CHMe$; a higher fraction yields a sesquiterpene, probably identical with bisabolene; higher fractions contain dicyclic diterpenes, which, on treatment with formic acid, pass into tricyclic isomerides. There is a close analogy between the products of decomposition of squalene and caoutchouc. Squalene is concluded to be identical with Chapman's spinacene (J.C.S., 1917, **111**, 56).

C. J. Still.

Bromotrinitromethane (IV) and acetbromoamide (I). E. Schmidt, W. von Knilling, and A. Ascherl (Ber., 1926, **59**, [*B*], 1279—1282).—Addition of hypobromous acid, its esters, or the mixed anhydride, Br·OAc, to olefinic double linkings can be effected by use of acetbromoamide in aqueous, alcoholic, or acetic acid solution. The reagent is frequently superior to bromotrinitromethane, since by-products are more readily removed. The following compounds are described: 2-bromo*cyclo*hexanol; 2-bromo*cyclo*hexyl methyl ether; 2-bromo*cyclo*hexyl acetate; trimethyl glycol bromohydrin, its *methyl ether*, b. p. 41—43°/10 mm., d_4^{20} 1·2474, n_D^{20} 1·4549, and *formate*, b. p. 57—59°/9 mm., d_4^{20} 1·3609, n_D^{20} 1·4612; *α-methyl-β-propyl glycol bromohydrin methyl ether*, b. p. 60—61°/9 mm., d_4^{20} 1·2057, n_D^{20} 1·4530; bromohydroxyhydrindene, m. p. 130°.

H. Wren.

Action of organo-magnesium compounds on αγ-dibromopropylene. A. Kirrmann (Compt. rend., 1926, **182**, 1629—1631; cf. A., 1925, i, 803, 1374).—Aliphatic organo-magnesium bromides react with αγ-dibromopropylene, giving the substituted γ-bromo-Δ^β-propylenes in very small yield. The main reaction consists in simultaneous replacement of both bromine atoms by alkyl groups. A series of hydrocarbons, which appears to include the type $(R{\cdot}CH{:}CH{\cdot}CH_2)_2$, is also obtained. The following are described: γ-bromoallylbenzene, b. p. 106—107°/12 mm., d_4^{18} 1·3418, n_D^{18} 1·5629; *octadiene*, b. p. 118—120°, d_4^{17} 0·748, n_D^{17} 1·4292; *hydrocarbon*, $C_{10}H_{18}$, b. p. 70—80°/12 mm., d_4^{20} 0·808, n_D^{20} 1·4618; *Δ^δ-nonene*, b. p. 144—146°, d_4^{18} 0·732, n_D^{18} 1·4212; *δε-dibromononane*, b. p. 119—120°/12 mm., d_4^{17} 1·410, n_D^{17} 1·4988; *hydrocarbon*, $C_{12}H_{22}$, b. p. 83—88°/13 mm., d_4^{18} 0·778, n_D^{18} 1·4470 (*tetrabromide*, b. p. 170—180°/2 mm.).

M. Clark.

Isomeric bromobutenes. Ethylenic stereoisomerism of α-bromo-Δ^α-butenes and β-bromo-Δ^β-butenes. M. Lépingle (Bull. Soc. chim., 1926, [iv], **39**, 741—762).—β-Bromo-Δ^α-butene and the two stereoisomeric α-bromo-Δ^α-butenes have been prepared by the action of sodium phenoxide in alcoholic solution on αβ-dibromobutane (cf. Reboul, A., 1892, 127), the mixture of Δ^α-bromobutenes being separated by means of their azeotropic mixtures with ethyl alcohol. *β-Bromo-Δ^α-butene* has b. p. 81·0°/760 mm., m. p. —133·4°, d_4^{15} 1·3209, $n_D^{18·7}$ 1·4523 (the azeotropic mixture with alcohol has b. p. 67·4—67·6°). Of the two *α-bromo-Δ^α-butenes*, the one, b. p. 86·1°, d_4^{15} 1·3265, $n_D^{18·5}$ 1·4523 (azeotropic mixture with alcohol, b. p. 69·6—69·8°), reacts about 8 times as rapidly with alcoholic potassium hydroxide, and is accordingly regarded as possessing the *cis*-structure; the *trans*-isomeride has b. p. 94·7°, m. p. —100·3°, d_4^{15} 1·3275, $n_D^{16·2}$ 1·4600 (azeotropic mixture with alcohol, b. p. 72·8—73°). The two stereoisomerides are rapidly converted by sunlight, halogens, or hydrogen halides into an equilibrium mixture containing approximately 40% of the *cis*-isomeride. These three Δ^α-bromobutenes are converted quantitatively into true acetylenes by alcoholic potassium hydroxide at 120—125°. With bromine in chloroform, β-bromo-Δ^α-butene yields *ααβ-tribromobutane*, b. p. 216·2°/760 mm., 94·6°/14 mm., d_4^{15} 2·1913, $n_D^{17·2}$ 1·5626, converted by zinc in alcoholic solution into the equilibrium mixture of α-bromo-Δ^α-butenes. The two latter similarly yield the same *αββ-tribromobutane*, b. p. 213·8°/760 mm., 90·1°/14 mm., d_4^{15} 2·1761, n_D^{16} 1·5624. The two β-bromo-Δ^β-butenes were similarly obtained from the mixture of βγ-dibromobutanes and separated by means of their azeotropic mixtures with ethyl alcohol. The isomeride having b. p. 93·9°/760 mm., m. p. —111·5°, d_4^{15} 1·3416, $n_D^{19·2}$ 1·4631 (azeotropic mixture with ethyl alcohol, b. p. 72·2—72·4°, is regarded as the *cis*-form, since it reacts with alcoholic potassium hydroxide much more slowly than the isomeride, b. p. 85·55°/760 mm., m. p. —114·65°, d_4^{15} 1·3323, $n_D^{16·3}$ 1·4602 (azeotropic mixture with ethyl alcohol, b. p. 69·0—69·2°). These configurations are the reverse of those suggested by Wislicenus and Schmidt (A., 1901, i, 1). Physical measurements on the equilibrium mixture confirm the composition given by Wislicenus. *ββγ-Tribromobutane* has b. p. 206·5°/760 mm., 86·0°/14 mm., m. p. 1·85°, d_4^{15} 2·1806, n_D^{17} 1·5628. With zinc in alcohol, the equilibrium mixture of α-bromo-Δ^α-butenes is regenerated. The "*cis*"-isomeride is also obtained pure by the action of alcoholic sodium phenoxide on the βγ-dibromobutane, b. p. 157·3°, but the experimental evidence is insufficient to verify Wislicenus' conclusions regarding the structures of the βγ-dibromobutanes. The addition of hydrogen bromide to crotonylene yields ββ-dibromobutane, in accordance with Pfeiffer's hypothesis (A., 1904, ii, 525).

R. Brightman.

Stereoisomeric forms of bis(trimethylethylene nitrosate). C. A. Taylor and W. H. Rinkenbach (J. Amer. Chem. Soc., 1926, **48**, 1684—1687).—Treatment of amylene with nitrogen peroxide affords bimolecular amylene nitrosate, m. p. 88·8° (decomp.) (cf. Wallach, A., 1891, 1004; Schmidt, A., 1903, i, 2). Oxides of nitrogen (from arsenious oxide and nitric acid) convert amylene, in glacial acetic acid solution, into a mixture of two forms of the bimolecular nitrosate, one of which crystallises in needles, m. p. 91° (decomp.), whilst the other forms pseudo-cubes, m. p. 93·5—94° (decomp.). The needle form is obtained by the action of nitric acid on a cooled mixture of amylene, glacial acetic acid, and amyl nitrite. Each form can be converted more or less

completely into the other by recrystallisation from ether or benzene. Both forms are optically inactive, and it is suggested that they are stereisomerides, the *syn*-structure, $\begin{matrix}CMe_2(ONO_2)\cdot CHMe\cdot N\\ CMe_2(ONO_2)\cdot CHMe\cdot N\end{matrix}\!\!:O$, being ascribed to the needles, and the *anti*-structure to the cubes. Both forms decompose slowly when kept in a desiccator over sulphuric acid, with evolution of gas and formation of an oily residue. F. G. WILLSON.

Reactions of the alcohols over zinc oxide catalysts. H. ADKINS and W. A. LAZIER.—See this vol., 807.

Manufacture of methyl alcohol and formaldehyde from methane. BAKELITE GES.M.B.H. and R. HESSEN.—See B., 1926, 565.

Production of butyl alcohol and acetone. D. A. LEGG.—See B., 1926, 562.

Dehydration of α-glycols. N. I. DOLGORUKOVA-DOBRIANSKA (J. Russ. Phys. Chem. Soc., 1925, **57**, 283—286).—The products obtained by heating αβ-dihydroxy-β-methylpropane with sulphuric acid or with fuming hydrobromic acid contained *iso*butaldehyde and the *acetal*, $CHPr^{\beta}<\begin{matrix}O\cdot CMe_2\\ O\cdot CH_2\end{matrix}$, b. p. 136—137°/752 mm., d_0^{20} 0·90661, which yields acetone and formic, acetic, and *iso*butyric acids when oxidised with permanganate; it is formed either from the original glycol and *iso*butaldehyde (formed by dehydration), $CHMe_2\cdot CHO+OH\cdot CMe_2\cdot CH_2\cdot OH=H_2O+C_8H_{16}O_2$, or by isomerisation of the intermediate ethereal compound, $CMe_2<\begin{matrix}O\cdot CH_2\\ CH_2\cdot O\end{matrix}>CMe_2$.

T. H. POPE.

Two stereoisomeric α-ethylene γ-glycols. C. PRÉVOST (Compt. rend., 1926, **182**, 1475—1477).—Bromination of crude $\Delta^{\alpha\gamma}$-pentadiene yields the *cis*- and *trans*-αδ-dibromo-Δ^{β}-pentenes (cf. this vol., 496). Acetylation of the impure forms gives the cis-*diacetate*, b. p. 104·5°/14 mm., d_0^{15} 1·0482, n_D^{15} 1·4430, the trans-*diacetate*, b. p. 115°/14 mm., d_4^{17} 1·0471, n_D^{17} 1·4410, and also Δ^{β}-*pentinenyl acetate*, b. p. 161°, and βγ-dibromo-Δ^{β}-pentene. From the diacetates are obtained the cis-*glycol*, b. p. 108·5°/14 mm., n_D^{17} 1·4633, d_4^{17} 1·0146, and the trans-*glycol*, b. p. 125·5°/14 mm., n_D^{17} 1·4730, d_4^{17} 1·0234, respectively. B. W. ANDERSON.

Action of trimethylglycerose on boric acid and on acetone in connexion with the configuration of the sugars. J. BÖESEKEN [with J. P. DOMMISSE] (Rec. trav. chim., 1926, **45**, 491—495).—By treatment with hydrogen peroxide in alkaline solution, mesityl oxide is converted into its oxide, b. p. 44—46°/15 mm., d_{21}^{21} 0·952, n_D^{21} 1·4221, which is hydrated by dilute sulphuric acid at the ordinary temperature, giving trimethylglycerose, b. p. 109°/19 mm., d_{21}^{21} 1·082, n_D^{21} 1·4442. It effects a large increase in the conductivity of boric acid. The acetone condensation *product* has b. p. 55°/8 mm., d_{21}^{21} 0·989, n_D^{21} 1·4200, and the formula $\begin{matrix}O\text{——}CMe\cdot O\\ |\qquad\quad |\\ CMe_2\cdot CH\text{—}O\end{matrix}>CMe_2$ is assigned to it. Probably the sugar also has a four-membered ring, with two hydroxyl groups on the same side of it. F. M. HAMER.

Configuration of inositol and of quercitol. J. BÖESEKEN and (MLLE.) A. JULIUS (Rec. trav. chim., 1926, **45**, 489—490).—Inositol does not increase the conductivity of boric acid or combine with acetone, confirming the supposition that the α-, γ-, and ε-hydroxyl groups are on the opposite side of the ring to the β-, δ-, and ζ-hydroxyl groups. *d*-Quercitol, $[\alpha]^{20}$ +24°, which probably has *cis*-vicinal hydroxyl groups, does not give these reactions either. F. M. HAMER.

Isomerisation of ethylene oxides. Saturation capacities and migratory powers of cyclic and acyclic radicals. M. TIFFENEAU and J. LÉVY (Bull. Soc. chim., 1926, [iv], **39**, 763—782; cf. this vol., 383).—In part a summary of work already published. The isomerisation of ethylene oxides on distillation involves, not only the rupture of the C·O linking, but also the migration of a radical or a hydrogen atom. It is concluded that the migratory power of the hydrogen atom is greater than that of the methyl or other acyclic groups. No general rule can be enunciated for the phenyl group; structural considerations may determine almost exclusive migration either of the phenyl group or of the hydrogen atom. The former predominates when the phenyl group is attached to a carbon atom with one or two acyclic radicals, whereas juxtaposition of cyclic radicals favours migration of the hydrogen atom. α-Phenyl-ββ-dimethylethylene oxide, obtained quantitatively by the action of perbenzoic acid on α-phenyl-β-methyl-Δ^{β}-propene in chloroform, isomerises at its b. p. to β-phenyl-β-methylpropanal. Similarly, the diethylene oxide derived from phenyldimethyl glycol, $O<\begin{matrix}CHPh\cdot CMe_2\\ CMe_2\cdot CHPh\end{matrix}>O$, yields β-phenyl-β-methylpropanal, and α-anisyl-ββ-dimethylethylene oxide, b. p. 150—160°/30 mm., d^0 1·042, affords β-anisyl-β-methylpropanal. The latter is also obtained by the action of 50% sulphuric acid on α-anisyl-β-methylpropane-αβ-diol. On the other hand, *α-phenyl-ββ-dibenzylethylene oxide*, b. p. 240—245°/36 mm., obtained by the action of perbenzoic acid on αγ-diphenyl-β-benzylpropan-β-ol, m. p. 29—30°, isomerises at 330° to αβδ-triphenylbutan-γ-one, migration of a benzyl group accompanying the rupture of the C·O linking on the less substituted carbon atom. Whilst αβ-diphenylethylene oxide on distillation yields benzaldehyde and stilbene, its methoxy-derivative, *α-phenyl-β-anisylethylene oxide*, m. p. 118—119°, obtained by oxidising α-phenyl-β-anisylethylene with perbenzoic acid, yields phenyl *p*-methoxybenzyl ketone, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot Ph$. Anisyl *iso*propyl ketone, b. p. 270—280°, α-anisyl-α-methylpropan-β-one, b. p. 140—150°/20 mm., obtained by the action of dry potassium hydroxide on the iodohydrin derivative of α-anisyl-β-methyl-Δ^{α}-propene, and αγ-diphenyl-β-benzylpropan-β-ol, b. p. 230—240°/30 mm., are also described. R. BRIGHTMAN.

Resolution of glycerol-α-phosphoric acid. II. P. KARRER and P. BENZ (Helv. Chim. Acta, 1926, **9**, 598—602; cf. this vol., 383).—The strychnine salt of glycerol-α-phosphoric acid after fractional crystal-

lisation from alcohol has m. p. 221°, $[\alpha]_D$ −21·99°. From this, through the barium and silver salts, was obtained the dimethyl ester of glycerol-α-phosphoric acid dimethyl ether, b. p. 122°/0·7 mm., which had $[\alpha]_D$ +2·38°, a value still lower than that of the antipode obtained from lecithin (this vol., 384). A repetition of the preparation of this dimethyl ester through the quinine salt gave the value $[\alpha]_D$ −1·78 (agreeing with that previously obtained), but the sodium salts regenerated from each active product were optically inactive, as also was the barium salt in the former case. Hence the value of $[\alpha]_D$ for the acids must be less than +0·2°, and the higher value of the crude salts of glycerol-α-phosphoric acid from lecithin must be due to other substances. This view is confirmed by the difference in the solubility of the barium salts in water. J. W. BAKER.

Nitrosylmercaptides and thionitrites. H. RHEINBOLDT (Ber., 1926, **59**, [*B*], 1311—1313; cf. Tasker and Jones, J.C.S., 1909, **95**, 1917).—Primary and secondary mercaptans and their salts form wine-red solutions with nitrosyl chloride which are stable at low temperatures, but evolve nitric oxide and yield disulphides at the atmospheric temperature: $2R{\cdot}SH + 2NOCl \longrightarrow 2HCl + 2R{\cdot}S{\cdot}NO$ and $2R{\cdot}S{\cdot}NO \longrightarrow 2NO + RS{\cdot}SR$. Tertiary mercaptans give relatively stable "thionitrites," $R_3C{\cdot}S{\cdot}NO$. Thiophenols assume an intermediate position, giving, like tertiary mercaptans, greenish-red primary products which decompose readily into disulphides. With simpler thiophenols, the isolation of thionitrites appears impossible, but pp′-*diphenylene dithionitrite* and *ditolylene dithionitrite* have been prepared. H. WREN.

Nitrosyl derivatives of bivalent sulphur. I. Nitrosylethylmercaptide. H. LECHER and W. SEIFKEN (Ber., 1926, **59**, [*B*], 1314—1321; cf. Tasker and Jones, J.C.S., 1909, **95**, 1917; Rheinboldt, preceding abstract).—The action of nitrosyl chloride on the mercury derivatives of ethyl- or phenyl-mercaptan does not afford a suitable means of preparing the corresponding thionitrites, since evolution of nitric oxide is complete and disulphides are produced at temperatures at which the pure thionitrite is stable. *Ethyl thionitrite*, Et·S·N·O, b. p. 19—20°/95 mm., is readily prepared by the addition of ethylmercaptan to ethyl nitrite at about −20°. In contrast to ethyl nitrite, it is remarkably stable towards aqueous acids and bases. It does not combine with olefines. At the atmospheric temperature in the absence of air, it is relatively stable, but between 70° and 130° it is rapidly and irreversibly decomposed into ethyl disulphide and nitric oxide. It readily undergoes autoxidation in air at 26°, yielding mainly ethyl disulphide and nitrogen peroxide; the initial product of the change appears to contain much ethanesulphonic acid. H. WREN.

Carbamide and guanidine derivatives of aliphatic sulphonic acids. IV. R. ANDREASCH (Monatsh., 1926, **46**, 639—647; cf. this vol., 277).—Monohalogen derivatives of the fatty acids readily react with potassium sulphite, and thus are obtained the *potassium* salts of ethyl sulphoacetate, m. p. 183°, and of ethyl α-sulphopropionate, m. p. 214°. Chlorosulphonic acid reacts with acetylguanidine acetate to yield sulphoacetylguanidine (two crystalline forms), and with propionylguanidine (*picrate*, m. p. 227°) to yield α-sulphopropionylguanidine. *Butyrylguanidine* [*hydrochloride*; *picrate*, m. p. 225° (decomp.)], and iso*butyrylguanidine* [*hydrochloride*, $+H_2O$; *picrate*, m. p. above 300° (decomp.); *chloroplatinate*, m. p. 203° (decomp.)], obtained by heating butyryl and *iso*butyryl chlorides, respectively, with guanidine hydrochloride in a sealed tube at 105—110°, similarly yield α-sulphobutyryl- and α-sulpho-*iso*butyrylguanidine (m. p. 325°, and not 168° as previously given), respectively. J. W. BAKER.

Cetyl xanthate. P. H. HERMANS (Rec. trav. chim., 1926, **45**, 499—500).—*Cetyl xanthate*, prepared by treating potassium hydroxide in molten cetyl alcohol with carbon disulphide, behaves like a soap. F. M. HAMER.

Producing dialkyl selenides and tellurides. C. A. HOCHWALT.—See B., 1926, 513.

Preparation of esters of formic acid. FARBW. VORM. MEISTER, LUCIUS, & BRÜNING.—See B., 1926, 513.

Manufacture of acetic anhydride and acetaldehyde from ethylidene diacetate. M. J. MARSHALL and G. S. SHAW.—See B., 1926, 513.

Resolution of α-bromo*iso*valeric acid into its optical isomerides. S. BERLINGOZZI and M. FURIA (Gazzetta, 1926, **56**, 82—88; cf. A., 1892, 427).—*r*-α-Bromo*iso*valeric acid is resolved by fractional crystallisation of the brucine salt. *d*-α-Bromo*iso*valeric acid has m. p. 43—44°, $[\alpha]_D^{20}$ +22·5° in benzene. Acylation of *l*-asparagine with α-bromo*iso*valeryl bromide yields α-bromo*iso*valeryl-*l*-asparagine, readily resolved by fractional crystallisation from water. d-α-*Bromoisovaleryl*-l-*asparagine* has m. p. 151° (decomp.) and $[\alpha]_D^{20}$ +8·6° for the sodium salt in water; l-α-*bromoisovalcryl*-l-*asparagine*, m. p. 172° (decomp.) and $[\alpha]_D^{20}$ −18·45° for the sodium salt in water. Both compounds differ in crystalline form and in solubility. S. B. TALLANTYRE.

Fatty acid derivatives. G. S. WHITBY (J.C.S., 1926, 1458—1465).—By interaction between the silver salts of fatty acids and appropriate halogen compounds a number of glycerides, acid anhydrides, and esters have been prepared. β-Acyldichlorohydrins are prepared by the action of acyl chlorides on α-dichlorohydrin or on epichlorohydrin, and readily react with these silver salts to give glycerides; several mixed glycerides thus prepared are described. The refractive indices of propionic, *n*-butyric, palmitic, and stearic anhydrides were determined and compared with those of the parent acids. Cetyl palmitate and cetyl stearate were obtained, in almost theoretical yield, from cetyl iodide and the corresponding silver salt, and cetyl stearate has been isolated from spermaceti. The physical constants of two homologous series of esters of palmitic and stearic acids are given. β-*Propionyl dichlorohydrin*, b. p. 208°, d_{20}^{20} 1·1222°, β-*palmityl dichlorohydrin*, m. p. 34·4°, n_D^{50} 1·4527; β-*stearyl dichlorohydrin*, m. p. 39·5°, n_D^{60} 1·4528; β-*butyrodipalmitin*, m. p. 43·6°, n_D^{60} 1·4431, and β-*palmitodibutyrin*, m. p. 18°, n_D^{20} 1·4530, are described. C. J. STILL.

China wood [tung] oil. K. H. BAUER.—See B., 1926, 551.

Salts of the rare earths with hydroxycarboxylic acids. II. Lactates. G. VANTSCH (*Z. anorg. Chem.*, 1926, **153**, 9—16.; cf. A., 1913, i, 247).—The lactates and benzilates of the rare earths are similar to the glycollates. The solubilities of the *lactates* in g.-mol. per litre of water at 20° are as follows: $La(C_3H_5O_3)_3,3H_2O$, $88{\cdot}2\times10^{-3}$; $Pr(C_3H_5O_3)_3,2{\cdot}5H_2O$, $54{\cdot}0\times10^{-3}$; $Nd(C_3H_5O_3)_3,2{\cdot}5H_2O$, $54{\cdot}2\times10^{-3}$; $Sm(C_3H_5O_3)_3,1{\cdot}5H_2O$, $25{\cdot}8\times10^{-3}$; $Gd(C_3H_5O_3)_3,1{\cdot}5H_2O$, $8{\cdot}5\times10^{-3}$; $Y(C_3H_5O_3)_3,2H_2O$, $2{\cdot}8\times10^{-3}$. Yttrium forms the least soluble lactate and glycollate; the solubilities of the other rare-earth lactates increase with decreasing atomic number, whereas the solubilities of the glycollates decrease in this order. The conductivities of the lactates, like those of the glycollates, are less than those of the corresponding acetates and phenylacetates, and it is concluded that they are internal complex salts. In aqueous solution they are partly split into the simple salts. A. GEAKE.

Crystallisation of metal lactates. F. C. KRAUSKOPF and A. S. CARTER (J. Amer. Chem. Soc., 1926, **48**, 1474—1481).—Solutions of barium lactate deposit the normal salt in crystalline form when heated for several days at 100° with excess of barium hydroxide; neutral solutions, or those containing free lactic acid, yield the salt as a vitreous solid. The presence of lactide anhydride inhibits crystallisation of metal lactates, possibly by acting as a protective colloid; excess of the base removes the lactide by hydrolysis and so promotes crystallisation. Metal lactates are more difficult to crystallise the more electropositive the metal. S. K. TWEEDY.

Oxidation of pyruvic acid by ceric ions. C. FROMAGEOT (Compt. rend., 1926, **182**, 1411—1413; cf. Henri and Fromageot, A., 1925, ii, 929; Fromageot, this vol., 687).—Solutions of the ketonic and enolic forms of pyruvic acid exhibit differences of behaviour on oxidation by means of ceric ions, the enolic form using more oxygen but undergoing slower oxidation than the ketonic form. Using the results obtained, oxidation of the tautomeric mixture enables the constituent proportions to be ascertained. H. J. EVANS.

Glutaconic acids. XIX. A consequence of mobility. J. PACKER and J. F. THORPE (J.C.S., 1926, 1199—1203).—The effect of tautomeric change on the configuration of the unsaturated forms of the glutaconic acids is dealt with, and the case of formation of an anhydride from a *trans*-form considered to depend on the mobility of the tautomeric system. The relative stability of the theoretically possible unsaturated forms is deduced from a study of the space-models and of the interconversion of the *cis*- and *trans*-forms by tautomeric change. The possibility of gaining further evidence of the existence or non-existence of the postulated "normal" forms from experiments on the optical resolution of various substituted glutaconic acids is suggested; a simple explanation of the effect of substitution on the mobility of the glutaconic system is given. C. J. STILL.

Salts of organic acids. II. Mercury derivatives of glutaconic acid. P. E. VERKADE (Rec. trav. chim., 1926, **45**, 475—488).—Reaction between glutaconic acid and mercuric acetate in aqueous solution gives a mixture of compounds

(I) $O<\begin{matrix}CO\\Hg\end{matrix}>CH\cdot CH{:}CH\cdot CO_2H,H_2O$ and

(II) $CH(OH)\left(CH<\begin{matrix}Hg\\CO\end{matrix}>O\right)_2$. On treating an alkaline solution of the mixture with hydrogen sulphide, β-hydroxyglutaric acid (diphenylhydrazide, m. p. 236—237°) and glutaconic acid are produced. The compounds dissolve in potassium bromide or chloride solution, giving solutions of

(III) $CO_2K\cdot CH(HgHal)\cdot CH{:}CH\cdot CO_2H$ and

(IV) $CO_2K\cdot CH(Hg\cdot Hal)\cdot CH(OH)\cdot CH(Hg\cdot Hal)\cdot CO_2K$,

but with potassium iodide give red *compounds* (III and IV); with excess of potassium iodide, these red compounds give colourless solutions, probably containing complex compounds of potassium iodide with the iodomercuric compounds. Potassium iodide also brings about fission of the carbon–mercury linking, and potassium hydroxide is liberated; equilibrium occurs, but, on titrating with acid, the reaction proceeds to completion. When the mixture of (I) and (II) is dissolved in dilute sulphuric or hydrochloric acid, glutaconic acid only is formed. F. M. HAMER.

Formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. VIII. Products derived from pimelic acid. Application of Bischoff's dynamic hypothesis. A. HASSELL and C. K. INGOLD (J.C.S., 1926, 1465—1471).—The action of alkalis on αα′-dibromopimelic esters resembles generally that in the shorter chain series, the differences being in good agreement with the strain hypothesis. The tendency to ring-formation in the pimelic series is considerably greater, and apparently no dihydroxypimelic acid is produced. Under various conditions, a considerable proportion of the material is converted into Δ¹-*cyclo*pentene-1 : 2-dicarboxylic acid, and the isomeric Δ²-cyclo*pentene*-1 : 2-*dicarboxylic acid*, m. p. 146—147°; the latter on exposure to bromine vapour forms 2 : 3-*dibromo*cyclo*pentane*-1 : 2-*dicarboxylic acid*, decomp. 165°. A small amount of cyclo*pentanol*-1 : 2-*dicarboxylic acid*, m. p. 159—160°, is also produced (*ethyl* ester, b. p. 168—171°/10—11 mm., *silver* salt, $C_7H_8O_5Ag_2$). With concentrated alkali, piperylenedicarboxylic acid is also obtained, and may possibly have been produced by isomerisation of an acid, $CH_2[CH{:}CH\cdot CO_2H]_2$, initially formed.

When methyl-alcoholic alkali is used, a new reaction, not found in the shorter chain series, occurs and *meso*- and *racemic* forms of αα′-dimethoxypimelic acid are produced in a non-crystalline condition. *αα′-Methoxypimelamide* (A-form) has m. p. 212°, and (B-form) m. p. 167°. C. J. STILL.

Formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. IX. Products derived from suberic and azelaic acids. F. R. GOSS and C. K. INGOLD (J.C.S., 1926, 1471—1477).—In addition to the known form of αα′-dibromosuberic acid, m. p. 172—

173°, a second form, m. p. 120—121°, has now been prepared. Either form of the acid when boiled with aqueous sodium carbonate (2*N*) gives *αα′-dihydroxysuberic acid*, m. p. 166—168°. When ethyl αα′-dibromosuberate, b. p. 230°/31 mm., is treated with methyl-alcoholic potassium hydroxide, it yields, as one of the products, suberocolic acid, m. p. 253°, which is shown to be an open-chain unsaturated acid; reduction of suberocolic acid gives A- and B-forms (m. p. 170° and 125°, respectively) of *dihydroxysuberocolic acid*. Other substances isolated from the products of hydrolysis are Δ^1- and Δ^2-*cyclo*hexene-1 : 2-dicarboxylic acids, and A- and B-forms of *αα′-dimethoxysuberic acid*, m. p. 145—146° and 117—118°, respectively.

In accordance with the general rules deduced in preceding work, the chief product of the action of methyl-alcoholic alkali on ethyl αα′-dibromoazelate is a mixture of *meso-* and r-*αα′-dimethoxyazelaic acids* (*ethyl* ester, b. p. 218—219°/30 mm.; *silver* salt, $C_{11}H_{18}O_6Ag_2$), from which *αα′-dimethoxyazelamide*, m. p. 164—165°, and an impure specimen of its stereoisomeride, m. p. 143—146°, were prepared. A mixture of *meso-* and racemic isomerides of *αα′-dihydroxyazelaic acid* (*ethyl* ester, b. p. 235—240°/16 mm.; *silver* salt, $C_9H_{14}O_6Ag_2$) was also isolated, as well as a small quantity of *α-ketoazelaic acid*, $CO_2H{\cdot}CO{\cdot}[CH_2]_6{\cdot}CO_2H$, m. p. 175°. C. J. Still.

Citromolybdic acid. P. Nyssens (Bull. Soc. chim. Belg., 1926, **35**, 132—135; cf. Honnelaitre, A., 1925, i, 509).—By the action of a hot solution of citric acid on excess of molybdenum trioxide, *citromolybdic acid*, $4C_6H_8O_7,12MoO_3,9H_2O$, is obtained (*sodium*, *potassium*, *calcium*, and *magnesium* salts). Its formation explains the value of adding citric acid in the rapid phosphomolybdate methods of determining phosphoric acid; excess of molybdenum trioxide is thereby dissolved. Excess of citromolybdic acid, however, prevents the formation of ammonium phosphomolybdate. The citric acid solution for the determination should not be heated above 93°, or it will be oxidised by the nitric acid present.

E. W. Wignall.

Constitution of pectin. C. F. Ahmann and H. D. Hooker (Missouri Agric. Exp. Sta. Res. Bull., 1925, **77**, 5—39; cf. B., 1926, 460).—Titration of pectic acid indicates 11 carboxyl groups, but more are probably present. The nucleus proposed for pectic acid is a dibasic acid, galacturonic–galactonic acid; at least six such nuclei are associated. The hydrolytic decomposition of pectin by cold, concentrated hydrochloric acid has been studied.

Chemical Abstracts.

Monomeric formaldehyde. M. Trautz and E. Ufer (J. pr. Chem., 1926, [ii], **113**, 105—136; cf. Kekulé, A., 1892, 1423).—The best method of preparing gaseous formaldehyde is a modification of that of Kekulé, in which paraformaldehyde is vaporised. The pure gas, which shows no marked deviation from the gas laws between 80° and 120° at atmospheric pressure, exhibits only a slight tendency to polymerise at 80—120°. Measurements of the velocity of polymerisation, which is greatly accelerated by moisture, show that the reaction is of a pseudo-unimolecular type. Well-dried formaldehyde polymerises very slowly. J. S. H. Davies.

Formaldehyde–sodium bisulphite and formaldehyde–sulphurous acid. Determination and properties. W. Ledbury and R. Taylor.—See B., 1926, 511.

Photolysis of acetaldehyde and acetone. E. J. Bowen and H. G. Watts.—See this vol., 808.

Unsaturated aldehydes from acetylenic alcohols. H. Rupe and E. Kambli (Helv. Chim. Acta, 1926, **9**, 672).—Tertiary acetylenic alcohols, CR′R(OH)·C:CH are converted, with 80% yields, on warming with acids (best with formic acid) into ethylenic aldehydes, CRR′:CH·CHO. Thus optically active 3-methyl-1-ethinyl*cyclo*hexan-1-ol yields 3-*methyl*cyclo*hexylideneacetaldehyde*, b. p. 85°/10 mm., $[\alpha]_D$ +133°, d_4^{20} 0·9433 (*semicarbazone*, m. p. 205°; *oxime*, m. p. 81°]. Other examples are given.

J. W. Baker.

Complex ferro-salts. W. Küster [with E. Erfle, E. von Roll, and K. Schiller] (Z. physiol. Chem., 1926, **155**, 157—185).—The blue acidic ferro-salt of nitrosopropionylacetylmethane (Kurtz, Chem. Zelle u. Gewebe, 1924, **12**, 16) has the formula $C_{18}H_{25}O_9N_3Fe$, and is considered to be hydrogen trinitrosopropionylacetylmethane ferroate. A similar structure is postulated for the cobaltoate of diacetylmethane (A., 1911, i, 619), $Na[Co(C_5H_7O_2)_3]$. Other exactly analogous complex ferroates are described. Dipropionylmethane, b. p. 172—173° (*copper* salt, m. p. 206°), yields a *nitroso*-derivative, m. p. 49°, which gives a complex *ferroate*, m. p. 142° (decomp.), and a *cobaltous* salt. Nitrosodiacetylmethane gives a *cobaltous* salt, m. p. 158°. Isolation of the complex ferroate is prevented by the ready solubility of its sodium and ammonium salts. Ethyl nitrosoacetoacetate gives a complex *ferroate* (*ammonium* salt) and a similar *cobaltoate*, $H[\{MeCO{\cdot}C(:NO){\cdot}CO_2Et\}_3Co]$ (*ammonium* salt). Replacement of the ketonic alkyl groups by alkoxy-groups diminishes the stability of the ferroate. Ethyl nitrosomalonate gives no ferroate. The free acid gives a *ferro*-salt of approximate constitution $(C_3O_5NFe)_2Fe,H_2O,0{\cdot}5EtOH$. Violuric acid gives a *ferrous* salt. Nitrosophenylmethylpyrazolone gives a *ferrous* salt, $(C_{10}H_8O_2N_3)_2Fe$, m. p. 231° (decomp.). Stable ferroates were not obtained from the nitroso-monoketones. Nitrosomethyl ethyl ketone gave a *compound* approximating to the constitution of an ammonium ferroate. The normal *cuprous* salt sinters at 175°. *Methyl benzyl ketone*, b. p. 210—212° (*phenylhydrazone*, m. p. 84°), gives a *nitroso*-derivative, m. p. 165°. Oxalylacetone gives a *ferrous* salt, m. p. 158°, whereas acetylacetone gives no ferrous salt. Ethoxalylacetmethylanilide (A., 1924, i, 542) yields a *nitroso*-derivative, m. p. 143°, giving a *ferrous* salt, m. p. above 280°. The blue ferro-salt from nitrosodimethyldihydroresorcinol (Haas, J.C.S., 1907, **91**, 1433) has the formula $C_{24}H_{31}O_9N_3Fe$ and is probably hydrogen trinitrosodimethyldihydroresorcinol ferroate. A possible structure is suggested for Blau's complex iron salts of α-dipyridine and

phenanthroline (A., 1899, i, 387). The complex salt from *o*-phenanthroline gives a *picrate*, $(C_{12}H_8N_2)_3Fe\cdot[C_6H_2(NO_2)_3O]_2$. The reaction of acetophenone with sodium nitroprusside in presence of sodium methoxide (Cambi, Atti R. Accad. Lincei, 1914, **22**, i, 373; **23**, i, 812) is shown to be of general applicability to β-diketones: $R\cdot CO\cdot CH_2\cdot CO\cdot R + Na_2[Fe(CN)_5NO] + 2MeONa \longrightarrow 2MeOH + Na_4[Fe(CN)_5ON{:}C(CO\cdot R)_2] \xrightarrow{H_2O} Na_3[Fe(CN)_5H_2O] + (R\cdot CO)_2C{:}N\cdot ONa$. Condensation *products* of this general type are obtained from dipropionylmethane, ethyl malonate, oxalylacetone, ethyl oxalacetate, and oxalyl methyl ketone. In the last-named case, treatment of the sodium salt with Mohr's salt yields the *salt* $(C_{13}H_{10}O_5N_6Fe)Fe(NH_4)_2$, whilst simple replacement yields the *ferrous* salt, $(C_{13}H_{10}O_5N_6Fe)Fe_2$. The constitution of the compound obtained from ethyl diketobutyrate dioxime and nickel nitrate (cf. Tschugaev, A., 1905, ii, 743) is formulated as the hydrogen nickcloate, $H_2\left[Ni\left(<\begin{matrix}ON{:}CMe\\ |\\ ON{:}C\cdot CO_2Et\end{matrix}\right)_2\right]$. Condensation of nitrosodipropionylmethane with ethyl acetoacetate, followed by treatment with zinc dust and acetic acid, yields ethyl 2-propionyl-5-methyl-3-ethylpyrrole-4-carboxylate, m. p. 148° (corresponding *acid*, m. p. 252°). Similar condensation of nitrosodipropionylmethane with dipropionylmethane yields 3 : 5-*dipropionyl*-2 : 4-*diethylpyrrole*, m. p. 128°. *Methylaniline methosulphate*, m. p. 146—147°, is obtained by the action of methyl sulphate on methylaniline. M. CLARK.

Catalytic and induced oxidation of some carbohydrates, uric acid, and inorganic substances. C. C. PALIT and N. R. DHAR (J. Physical Chem., 1926, **30**, 939—953; cf. A., 1925, i, 1041; Mittra and Dhar, *ibid.*, ii, 576).—In the presence of ferrous hydroxide or of sodium sulphite, many carbohydrates are oxidised by passing air through their solutions at the ordinary temperature either in the presence or absence of excess of alkali (cf. Spoehr, A., 1924, i, 836). With freshly-precipitated ferrous hydroxide, the descending order of oxidation in the absence of alkali is starch, maltose, lactose, lævulose, sucrose, arabinose, galactose, and dextrose, and with sodium sulphite the order is starch, lactose, galactose, sucrose, arabinose, and lævulose. In the former case, oxidation increases with increasing concentration of alkali, but in the latter the results become anomalous.

Uric acid is appreciably oxidised by air in the presence of alkali, and oxidation is increased by the addition of metallic hydroxides in the descending order: cupric, manganous, cobaltous (sodium sulphite), nickelous, cerous, and ferrous.

With sodium arsenite or arsenious acid, oxidation occurs only in the presence of hydroxides as catalysts. Sodium nitrite is oxidised by air in the presence of ferrous hydroxide only; other hydroxides even when freshly precipitated fail to catalyse the oxidation. There is no appreciable effect when air is passed through solutions of potassium oxalate containing reducing agents such as ferrous and cerous hydroxides or sodium sulphite.

L. S. THEOBALD.

Classification of the sugars. J. G. MALTBY (J.C.S., 1926, 1629—1630).—According to Hudson, a distinction between the α- and β-forms of sugars is based on their rotations and on Fischer's classification into the *d*- and *l*-series, but this distinction breaks down in the case of arabinose. It is suggested that this classification is erroneous, and that for the normal forms of the aldoses the configuration of the middle group of the oxide ring (γ group) is the deciding factor in the classification into the *d*- and *l*-series, and that, consequently, arabinose belongs to the *d*- instead of the *l*-series. C. J. STILL.

α- and β-forms of sugars and sugar derivatives. P. A. LEVENE and H. A. SOBOTKA (Science, 1926, **63**, 73—74).—A consideration of the applicability of Hudson's rule. A. A. ELDRIDGE.

Reactions between sugars and amines. II. Dextrose and amino-acids. H. VON EULER, E. BRUNIUS, and K. JOSEPHSON (Z. physiol. Chem., 1926, **155**, 259—269).—Cryoscopic determinations on mixtures of dextrose with glycine or alanine in aqueous solution indicate that after 18 hrs. at the ordinary temperature there is a considerable amount of association between the sugar and amino-acid. The reaction is slow and reversible, alkalinity favouring synthesis, acidity favouring hydrolysis. Previous treatment of the dextrose alone with alkali does not favour the synthesis. Both the reducing power and the amino-nitrogen are diminished after the mixture of dextrose and glycine, at p_H 9·5, has been kept for 18 hrs. From changes in the optical activity of this mixture on keeping, it is concluded that the compound of dextrose and glycine is lævorotatory. The compound reduces methylene-blue (Thunberg's technique). H. D. KAY.

Stable γ-dextrose. H. PRINGSHEIM and S. KOLODNY (Ber., 1926, **59**, [*B*], 1135—1140).—β-Glucosan is converted by cold, concentrated hydrochloric acid into a mixture of normal dextrose and stable *γ-dextrose*, $[\alpha]_D^{20}$ +77·9° or 85·2° in water, from which the former is removed by fermentation. The new sugar reduces Fehling's solution feebly and forms traces of an osazone, possibly due to partial conversion into normal dextrose or to presence of impurity. It is readily converted by hot, dilute acids into normal dextrose. With acetic anhydride and pyridine, it affords *γ-glucose penta-acetate*, $[\alpha]_D^{20}$ +88° in chloroform. It is transformed by exhaustive methylation into *trimethyl-γ-glucose*, $[\alpha]_D^{20}$ +92·6° in water, which is converted by hot, dilute hydrochloric acid into normal βγδ-trimethylglucose. Stable γ-dextrose is regarded as containing the hexylene oxide ring and, in spite of its stability, the prefix "γ" is provisionally adopted. H. WREN.

Degradation of reducing bioses. I. Direct determination of the constitution of cellobiose. G. ZEMPLÉN (Ber., 1926, **59**, [*B*], 1254—1266).—Cellobiose octa-acetate dissolved in chloroform is treated with a cold solution of sodium methoxide in absolute methyl alcohol and the precipitated additive compound is hydrolysed by ice-cold water to ethyl acetate and cellobiose. The latter substance dissolved in water is gradually treated with an

alcoholic solution of hydroxylamine in such a manner that the sugar is not precipitated, and the resultant oxime is treated with acetic anhydride and fused sodium acetate, yielding thereby *octa-acetylcellobiononitrile*, m. p. 132°, $[\alpha]_D^{18\cdot5}$ +34·3° in chloroform (*octa-acetylcellobiose*anti*oxime* has m. p. 165°, $[\alpha]_D^{19}$ −7·9° in chloroform). The nitrile is hydrolysed in the manner described for cellobiose octa-acetate, whereby hydrocyanic acid is quantitatively removed, yielding *d*-gluco-*d*-arabinose in 80% yield. The new sugar is transformed by acetic anhydride and sodium acetate into *hepta-acetylglucoarabinose* A, m. p. 196°, $[\alpha]_D^{18}$ −16·95° in chloroform, *hepta-acetylglucoarabinose* B, m. p. 157—161°, $[\alpha]_D^{16}$ −50·24° in chloroform, and *hepta-acetylglucoarabinose* C, m. p. 105·5—106°, $[\alpha]_D^{16}$ +12·0° in chloroform. All three compounds yield the same glucoarabinose, $[\alpha]_D$ −94·24° to −102·3° in water, and the same *glucoarabinosephenylosazone*, m. p. about 214° (decomp.). Application of Hudson's rules renders it probable that the products *B* and *C* are related to one another as α- and β-forms, but the existence of the *A* variety appears novel. Free glucoarabinose is a colourless syrup, hydrolysed by acids to dextrose and *d*-arabinose. It is readily converted into the corresponding oxime, but the conversion of the latter into hepta-acetylglucoarabononitrile is accompanied by considerable resinification. Treatment of the nitrile with sodium methoxide affords *d*-glucoerythrose, which is incapable of forming an osazone, thus establishing the formula

$$\begin{array}{l} CH(OH)\cdot[CH\cdot OH]_2\cdot CH\text{——}O\text{——}CH\cdot[CH\cdot OH]_3\cdot CH\cdot CH_2\cdot OH \\ \quad\quad\quad\

that the product is free from crystalline structure and its solution in chloroform is optically clear when viewed with the ultramicroscope. Under these conditions, the product is an amorphous powder soluble in organic media, the solutions being dextrorotatory, and consists of a mixture of acetates. The constituents of the mixture have been identified by deacetylation, followed by methylation; the chief products are derived from anhydrotriglucose (35%), triglucose (15%), a diglucose (20%), and dextrins (6%). The diglucose is presumably an *iso*cellobiose. It is concluded that at least one third of the cellulose aggregate is derived from anhydroglucose, and constitutional formulæ for the cellulose molecule, modified by the inclusion of the amylene-oxide ring, are presented and discussed. C. J. STILL.

Action of oxygen on alkali-cellulose. W. WELTZIEN and G. ZUM TOBEL (Papier-Fabr., 1926, **24**, 413—414).—Cotton or artificial silk swollen with sodium hydroxide absorbs gaseous oxygen at the ordinary temperature, and more rapidly at higher temperatures. Thus bleached cotton-wool when mercerised with 10% sodium hydroxide solution, pressed to three times the initial weight, and exposed to oxygen at 60°, absorbed volumes corresponding with 0·5 mol. per $C_6H_{10}O_5$ in 10 days and with 1 mol. in 33 days, and the absorption continues further at a fairly constant rate. A. GEAKE.

Chemical analysis of cotton. XII. Hydrocellulose. C. BIRTWELL, D. A. CLIBBENS, and A. GEAKE.—See B., 1926, 529.

Lignin. II. Preparation of primary lignin. A. FRIEDRICH and B. BRÜDA (Monatsh., 1926, **46**, 597—610; cf. B., 1926, 151).—After the removal of moisture, resins, and gums, 90% of the primary lignin present (16—17%) in white beech wood can be extracted by two successive hydrolyses with 16% hydrochloric acid and extraction of the liquors with alcohol. A single hydrolysis or extraction by the method of Willstätter and Zechmeister (A., 1913, i, 955) yields a low value for the lignin content. Energetic hydrolysis of the residue with concentrated hydrochloric acid for 10 hrs., hydrogen chloride being passed through for the whole period, yields the remaining 10% of the lignin. The portion of the wood soluble in hydrochloric acid (cellulose, hemicellulose, pentoses, and ash) is 45%. If the wood is completely freed from resin (which has the same analytical data as lignin, and, like it, is not hydrolysed by concentrated hydrochloric acid), the lignin content corresponds directly with the percentage of methoxyl group present. J. W. BAKER.

Preparation of primary aliphatic amines by the reduction of phenylhydrazones and oximes of aldehydes and ketones. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **57**, 221—233).—The reduction of aliphatic phenylhydrazones and oximes by active aluminium proceeds similarly to that effected by sodium amalgam, the principal products of the reactions being the primary amines. The yields of amine obtained from the phenylhydrazones and aluminium are less than those given by sodium amalgam (cf. Tafel, A., 1886, 939). The aldoximes and ketoximes give lower yields of amines than the phenylhydrazones, but purer products are obtained. The phenylhydrazones of acetone, methyl ethyl ketone, methyl propyl ketone, valeraldehyde, *iso*valeraldehyde, and heptaldehyde, and the oximes of acetone, methyl ethyl ketone, and heptaldehyde were investigated in this way. T. H. POPE.

Reduction of aliphatic and aromatic aldazines and ketazines by aluminium amalgam. I. MACUREVITSCH (J. Russ. Phys. Chem. Soc., 1925, **57**, 234—250).—Various aldazines and ketazines have been reduced, usually in alcoholic solution, by means of aluminium amalgam in rather less than the theoretical quantity. Under these conditions, propaldazine gives propyl- and dipropyl-amines; *iso*butaldazine yields *iso*butyl- and, mainly, di*iso*butyl-amines, and probably a small proportion of *s*-di*iso*butylhydrazine; *iso*propylideneazine gives *iso*propyl- and di*iso*propyl-amines; diethylketazine yields *sec.*-*n*-amylamine; bismethylpropylazimethylene gives only β-aminopentane; dipropylketazine yields δ-aminoheptane; benzaldazine gives benzylamine, with possibly a small amount of the hydrazone; *phenylethylketazine*, m. p. 66—67° after softening at 62°, gives α-phenyl-*n*-propylamine and a neutral compound of unknown constitution. T. H. POPE.

Base strength of α-alkoxylamines. Effect of oxygen on the basicity of amines. T. D. STEWART and J. G. ASTON (J. Amer. Chem. Soc., 1926, **48**, 1642—1655).—*Methoxymethylmethyldiethylammonium iodide*, $CH_2(OMe)\cdot NMeEt_2I$, m. p. 116·5—117°, and *ethoxymethylmethyldiethylammonium iodide*, m. p. 83°, were obtained by the action of methyl iodide on the appropriate bases in ethereal solution (cf. Robinson, J.C.S., 1923, **123**, 532), and their rates of formation were measured. *Methyl diethylaminomethyl ether*, b. p. 116·5—117°/763·3 mm., was prepared from diethylamine, formaldehyde, and methyl alcohol (cf. McLeod and Robinson, J.C.S., 1921, **119**, 1470). The following basic dissociation constants were determined by comparing the fraction of the bases neutralised in alcoholic solution, at a given indicator end-point, with the fractions of benzylamine and methylaniline neutralised at the same end-point: methyl diethylaminomethyl ether, $3·6\times10^{-9}$; diethylaminomethyl ethyl ether, $1·8\times10^{-8}$; and diethylaminomethyl *iso*butyl ether, 4×10^{-7}. Di(diethylamino)methane is as strong a mono-acid base as is diethylamine. Since all other amine bases having basic dissociation constants in this range are either amphoteric or tautomeric substances, it is suggested that the above bases are also mixtures of tautomerides.

Diethylaminomethyl ethyl ether hydrochloride has m. p. 75—78°. F. G. WILLSON.

***dl*-α-Methylarginine.** H. STEIB (Z. physiol. Chem., 1926, **155**, 279—291).—δ-Benzoylornithine is converted successively into *δ-benzoyl-α-p-toluenesulphonylornithine*, m. p. 183°, and *δ-benzoyl-α-p-toluenesulphonyl-N-methylornithine*, m. p. 185°, which is transformed by barium hydroxide into *α-p-toluenesulphonyl-N-methylornithine*, m. p. 214—219° (*hydrochloride*, m. p. 224°). The latter substance with cyanamide or *S*-ethyl*iso*thiocarbamide hydrobromide

affords 2-*toluenesulphonyl*-N-*methylarginine*, decomp. 268°, and thence *dl*-α-methylarginine [2 : 4-*dinitro*-α-*naphthol*-7-*sulphonate*, decomp. 245—248°; *mononitrate*, m. p. 192°; additive *compound* with copper nitrate (+$2H_2O$), decomp. 228—229°]. α-Methylarginine is not hydrolysed by arginase. H. D. KAY.

α-Amino-ε-guanido-*n*-hexoic and ε-amino-α-guanido-*n*-hexoic acids. H. STEIB (Z. physiol. Chem., 1926, **155**, 292—305).—ε-Benzoyl-lysine is converted successively into ε-*benzoyl*-α-p-*toluenesulphonyl-lysine*, m. p. 197° (*sodium* and *barium* salts), α-p-*toluenesulphonyl-lysine*, α-p-*toluenesulphonamido*-ε-*guanidohexoic acid* (+$2H_2O$), m. p. 149°, decomp. 237°, and α-*amino*-ε-*guanido*-n-*hexoic acid* [*picrolonate*, decomp. 252°; *flavianate*; *basic copper nitrate* (+$\frac{1}{2}H_2O$), decomp. 230—231°; *mononitrate*, m. p. (+H_2O) 97° (anhydrous) 115—120°]. ε-*Benzamido*-α-*guanido*-n-*hexoic acid* (+$3H_2O$), m. p. 216°, prepared from ε-benzoyl-lysine, sodium hydroxide, and *S*-ethyl*iso*thiocarbamide hydrobromide, is converted by hydrochloric acid into δ-*aminobutylglycocyamidine dihydrochloride* (corresponding *picrolonate*). α-Amino-ε-guanido-*n*-hexoic acid is not hydrolysed by arginase. H. D. KAY.

Dioximes. XXIX. G. PONZIO and I. DE PAOLINI (Gazzetta, 1926, **56**, 247—256).—A product identical with the "furoxancarboxylic acid," $CO_2H\cdot C(=N\cdot O\cdot N=)CH>O$, of Wieland, Semper, and Gmelin (A., 1909, i, 609) is obtained by the action of nitrogen tetroxide on α-glyoximecarboxylic acid, $CO_2H\cdot C(:N\cdot OH)\cdot CH:N\cdot OH$ (primary dioximinopropionic acid, Söderbaum, A., 1892, 815). In accordance with previous work in this series (cf. Avogadro, A., 1924, i, 294), this product is regarded as the oxide of oximinocyanoacetic acid, $CO_2H\cdot C(:N\cdot OH)\cdot C:N:O$, or $CO_2H\cdot C(:N\cdot OH)\cdot C\leqslant^{O}_{N}$, which view is supported by the absence of additive properties towards water, bromine, or hydrogen chloride in ether. When pure it has m. p. 118° (decomp.); it gives no colour with ferric chloride or with copper acetate; its *silver* salt explodes on heating above 100°, and its *aniline* salt is decomposed by acid to anilinoglyoximecarboxylic acid (*iso*nitrosomalonanilideoxime, Wieland and Gmelin, A., 1908, i, 1013).

When a solution of sodium α-glyoximecarboxylate is treated with chlorine, dichloroglyoxime, m. p. 206°, with sublimation (cf. Steinkopf and Jürgens, A., 1911, i, 531), and when with bromine water, *dibromoglyoxime*, m. p. 216° (decomp.) (*diacetyl* derivative, m. p. 163°), also formed from glyoximedicarboxylic acid and bromine, are obtained.

The oxide of oximinocyanoacetic acid (also prepared by the action of nitric acid on α-glyoximecarboxylic acid, in which case *nitroglyoxime* remains in the mother-liquor) is converted by alkali into a *substance* which is not hydroxyglyoximecarboxylic acid, since it yields dibromoglyoxime with bromine. The substance on acidification gives an olive-green precipitate with copper acetate; with barium chloride it gives a yellow precipitate of $C_3H_2O_5N_2Ba$ (cf. Wieland, Semper, and Gmelin, *loc. cit.*).

β-Glyoximecarboxylic acid (secondary dioximinopropionic acid, Söderbaum, *loc. cit.*) does not react with nitrogen tetroxide. E. W. WIGNALL.

Manufacture of carbamide. BADISCHE ANILIN- & SODA-FABR.—See B., 1926, 513.

Hydrolysis of guanidine. J. BELL (J.C.S., 1926, 1213—1219).—At the ordinary temperature in *N*/8-solution, guanidine is partly hydrolysed to carbamide only, but in a boiling solution ammonium cyanate and carbonate are also formed by decomposition of carbamide in the strongly alkaline solution of guanidine. Some dissociation of guanidine occurs in a boiling *N*-solution, resulting in the formation of a small proportion (3%) of melamine. The rate of formation of carbamide at the ordinary temperature increases when sodium hydroxide is present, and this supports the view of Krall (J.C.S., 1915, **107**, 1396) that guanidine exists as an equilibrium mixture of two forms. A mechanism for the decomposition of the β-form is suggested. C. J. STILL.

Ethylenediguanidine. M. SCHENK and H. KIRCHHOF (Z. physiol. Chem., 1926, **155**, 306—313).—This *compound* has been prepared by the action of *S*-methyl*iso*thiocarbamide hydriodide on ethylenediamine. It forms a *dipicrate*, decomp. 284—285°, *dichloroaurate*, decomp. 285°, *chloroplatinate*, decomp. 255—258°, *dipicrolonate*, decomp. 284°, *dihydriodide*, m. p. 218—220° after softening, and a *dinitrate*, decomp. 252°. H. D. KAY.

Fission of imino-chlorides and -bromides. J. VON BRAUN and F. JOSTES (Ber., 1926, **59**, [*B*], 1091—1096).—*d*(+)-β-Methyladipic acid, b. p. 220—222°/18 mm., m. p. 85°, $[\alpha]_D^{20}$ +8·43°, is converted successively into the corresponding chloride, b. p. 127°/13 mm., d_4^{20} 1·217, $[\alpha]_D^{20}$ +1·40°, and *amide*, m. p. 191°, $[\alpha]_D^{22}$ +14·71° in water; the latter substance is more conveniently prepared by passing ammonia over the molten acid, into which it is re-converted by hydrolysis. It is transformed by bromine and sodium hydroxide into *d*(+)-αδ-diamino-β-methylbutane (benzoyl derivative, m. p. 154°, $[\alpha]_D^{22}$ +1·11° in pyridine; *hydrochloride*, m. p. 173°, $[\alpha]_D^{22}$ +5·58° in aqueous solution). The benzoylated amide is converted by successive treatment with phosphorus pentabromide and hydrochloric acid into d(+)-αδ-*dibromo*-β-*methylbutane*, b. p. 78—79°/12 mm., d_4^{17} 1·695, $[\alpha]_D^{17}$ +4·21°, which is transformed successively into d(−)-β-*methyladiponitrile*, b. p. 150°/10 mm., d_4^{22} 0·9573, $[\alpha]_D^{22}$ −5·65° in alcohol, and *d*(+)-β-methyladipic acid. Sodium phenoxide and *d*(+)-αδ-dibromo-β-methylbutane in alcoholic solution afford d(−)-αδ-*diphenoxy*-β-*methylbutane*, b. p. 200°/12 mm., $[\alpha]_D^{22}$ −24·78° in 96% alcohol. The benzoylated amide and phosphorus pentachloride afford benzonitrile and d(+)-αδ-*dichloro*-β-*methylbutane*, b. p. 50°/12 mm., d_4^{21} 1·103, $[\alpha]_D^{21}$ +9·73°, which affords *d*(−)-αδ-diphenoxy-β-methylbutane, $[\alpha]_D^{22}$ −24·67° in 96% alcohol. Reaction takes place, therefore, without configurative change if the asymmetric carbon atom is not directly attached to the nitrogen atom. H. WREN.

Preparation of cyanamide hydrochloride. L. A. PINCK and H. C. HETHERINGTON (Ind. Eng. Chem., 1926, **18**, 629—630).—To a solution of

hydrogen chloride (40%) in ethyl chloride (95%) is gradually added sufficient solid cyanamide to react with about 95% of the hydrochloric acid, the temperature being kept at 45° or less. The mixture is agitated for 5—10 min., filtered, washed to remove excess of hydrochloric acid, and the salt dried below 80°. By making up the volume of the liquor with alcoholic hydrogen chloride and repeating the cycle of operations, the yield may be made practically theoretical. The process may be continued until the percentage of water rises to about 10%.

D. G. HEWER.

Action of organo-magnesium compounds on nitriles. P. BRUYLANTS (Bull. Soc. chim. Belg., 1926, **35**, 139—154).—The action of organo-magnesium halides on *tert.*-α-aminonitriles of the type CN·CRR′·N< is similar to that with those of the type CN·CHR·N< (cf. A., 1924, i, 984); with MgR″X, there are obtained amines of the type CRR′R″·N<.

α-Dimethylamino-α-methylbutyronitrile yields with magnesium phenyl bromide β-*dimethylamino*-β-*phenylbutane*, b. p. 234—235°/776 mm., d_4^{20} 0·9275, n_D^{20} 1·5097 (*picrate*, m. p. 178°); with magnesium benzyl chloride, β-*dimethylamino*-β-*benzylbutane*, b. p. 258°/771 mm., d_4^{20} 0·9265, n_D^{20} 1·5152 (*chloroplatinate*, m. p. 194—195°); with magnesium ethyl bromide, γ-*dimethylamino*-γ-*methylpentane*, b. p. 146°/766 mm., d_4^{20} 0·7830, n_D^{20} 1·4306 (*chloroplatinate*, decomp. about 210°), and a smaller quantity of a *substance*, b. p. 171—175°/766 mm., probably γδ-di-(dimethylamino)-γδ-dimethylhexane.

α-*Piperidino*-α-*methylbutyronitrile*, b. p. 110—111°/15 mm., prepared by the action of piperidine on the cyanohydrin of methyl ethyl ketone, yields similarly β-*piperidino*-β-*phenylbutane*, b. p. 288—290°/760·5 mm., d_4^{20} 0·9611, n_D^{20} 1·5253 [*chloroplatinate*, m. p. about 205° (decomp.)]; β-*piperidino*-β-*benzylbutane*, b. p. 310°/760·5 mm., d_4^{20} 0·9613, n_D^{20} 1·5277 [*chloroplatinate*, m. p. 192° (decomp.)] and γ-*piperidino*-γ-*methylpentane*, b. p. 214°/752 mm., d_4^{20} 0·8614, n_D^{20} 1·4637.

The nitrile obtained, with large quantities of polymerisation products, by the interaction of acraldehyde, potassium cyanide, and dimethylamine, (?)αγ-*bisdimethylaminobutyronitrile*, b. p. 90—91°/10 mm., d_4^{20} 0·8876, n_D^{20} 1·4416, reacts with magnesium phenyl bromide to give αγ-*bisdimethylamino*-α-*phenylpropane*, b. p. 128·5°/10·5 mm., 259°/758 mm. [*chloroplatinate*, m. p. 245° (decomp.); *hydrochloride*, *ethiodide*]. From piperidine hydrochloride, potassium cyanide, and acraldehyde, α-*piperidino*-Δ$^{\beta}$-*butenonitrile*, b. p. 94°/10 mm., d_4^{20} 0·9813, n_D^{20} 1·4746, is obtained, which with magnesium phenyl bromide gives γ-*piperidino*-γ-*phenyl*-Δ$^{\alpha}$-*propene*, b. p. 271°/702 mm., d_4^{20} 0·9704, n_D^{20} 1·5305 (*chloroplatinate*, m. p. 176—178°).

Crotonaldehyde, potassium cyanide, and dimethylamine yielded a *substance*, b. p. 126—127°/10·5 mm., and α-*dimethylamino*-Δ$^{\beta}$-*pentenonitrile*, b. p. 64—65°/10·5 mm., d_4^{20} 0·8761. The latter reacts with a magnesium phenyl compound to give α-*dimethylamino*-α-*phenyl*-Δ$^{\beta}$-*butene*, b. p. 237°/758 mm., d_4^{20} 0·9135.

α-*Methylaminoisobutyronitrile*, b. p. 109°/250 mm., 144°/atmospheric pressure, reacts with magnesium ethyl bromide to give a *base*, possibly $2COMe_2,NH_2Me$ or $[CMe_2(OH)]_2NMe$, b. p. 68—72°, from which methylamine chloroplatinate and acetonesemicarbazone are obtained (cf. Götschmann, A., 1879, 1035).

E. W. WIGNALL.

Organic compounds of phosphorus. II. β-Phosphinopropionic acid and γ-phosphino-*n*-butyric acid. P. NYLÉN (Ber., 1926, **59**, [*B*], 1119—1128; cf. A., 1925, i, 1134).—*Ethyl* β-*phosphinopropionate*, $CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OEt)_2$, b. p. 149—150° (corr.)/10 mm., $d_4^{16\cdot7}$ 1·1021, is prepared in 35% yield by the successive addition of ethyl phosphite and ethyl β-iodopropionate to sodium ethoxide suspended in ether. It is converted by alcoholic ammonia into the corresponding C-*amide*, m. p. 61—62·5° (corr.), and is hydrolysed with difficulty to β-*phosphinopropionic acid*, m. p. 178—180° (corr.) [the *salt*, $CO_2Ag{\cdot}CH_2{\cdot}CH_2{\cdot}PO(OEt){\cdot}OAg$, is described]. The acid is converted by ethyl alcohol and hydrogen chloride into the C-*monoethyl* ester, m. p. 64·5—66° (corr.), the *zinc*, *manganese*, *calcium*, *silver*, and *copper* salts of which are described. The *disodium hydrogen*, normal *calcium* (+H_2O), normal *barium* (+$6H_2O$), *zinc* (+$3H_2O$), *manganous* (+$7H_2O$), *lead*, and *silver* salts of β-phosphinopropionic acid are described.

Sodium diethyl phosphite and γ-chlorobutyronitrile in ethereal solution afford the *diethyl* ester of γ-*phosphinobutyronitrile*, b. p. 163—164°/8 mm., d_4^{15} 1·0885, which is hydrolysed to γ-*phosphino*-n-*butyric acid*, m. p. 127—128·5° (corr.) after softening at 122°. The corresponding C-*monoethyl* ester, m. p. 76—77°, gives *sodium*, *zinc*, *manganese*, *copper*, *calcium*, *lead*, and *silver* salts. The normal *barium* (+$6H_2O$), *calcium*, *copper* (+$4H_2O$), *lead*, and *silver*, and the *manganous hydrogen* (+H_2O) and *zinc hydrogen* (+H_2O) salts of γ-phosphino-*n*-butyric acid are described.

H. WREN.

Salts of phosphatide bases. A. GRÜN and R. LIMPÄCHER (Ber., 1926, **59**, [*B*], 1345—1350).—*Choline hydrogen carbonate*, prepared by saturating a solution of choline in alcohol with carbon dioxide, is converted by dilute, aqueous phosphoric acid into *choline dihydrogen orthophosphate*. Successive treatment of αβ-distearin with phosphoric oxide and choline hydrogen carbonate affords *choline* αβ-*distearoylglycerolphosphate*, $(CO_2C_{17}H_{35})_2C_3H_5{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}NMe_3{\cdot}C_2H_4{\cdot}OH$, m. p. 187—187·5° after softening at 80—81°, which behaves as a monobasic acid in the presence of phenolphthalein and with chloroplatinic acid affords choline chloroplatinate.

Colamine [β-aminoethyl alcohol] can be titrated quantitatively in aqueous solution in the presence of methyl-orange, Congo-red, and lacmoid, but not of phthaleins. In alcohol or benzene–alcohol, it is neutral towards phenol- or thymol-phthalein, but behaves as monacid base towards lacmoid. *Colamine carbonate* (mixed with free colamine), *colamine dihydrogen orthophosphate*, and *colamine* αβ-*distearoylglycerolphosphate*, $(CO_2C_{17}H_{35})_2C_3H_5{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}NH_3{\cdot}C_2H_4{\cdot}OH$, m. p. 177·5° after softening at 81°, decomp. 179·5°, are described. The latter compound closely resembles

kephalin, but behaves as a dibasic instead of as a monobasic acid towards phenolphthalein.

H. WREN.

Synthesis of lecithins. I. A. GRÜN and R. LIMPÄCHER (Ber., 1926, **59**, [*B*], 1350—1360; cf. preceding abstract).—αβ-Distearin, heated somewhat above its m. p., is mixed successively with phosphoric oxide and dry choline hydrogen carbonate, whereby a mixture of cholinephosphoric acid, $C_2H_4{-}O\rangle PO{\cdot}OH$ (NMe$_3$·O), and the *endo* salt of *choline αβ-distearoylglycerol-α′-phosphate*, $C_2H_4{-}O\rangle PO{\cdot}O{\cdot}C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2$ (NMe$_3$·O), m. p. 187° after softening at 80·2—80·5° (corr.), is produced.

The latter compound differs from choline αβ-distearoylglycerolphosphate (preceding abstract) in that it is neutral towards phenolphthalein and, under definite conditions, affords the corresponding *chloroplatinate*, m. p. 162° (decomp.) after softening at 82—83°, and an additive *salt* with cadmium chloride, whereas the latter salt gives choline chloroplatinate. The synthetic lecithin readily absorbs water with reversible formation of choline αβ-distearoylglycerolphosphate. It is readily hydrolysed by hydrochloric acid to distearoylglycerolphosphoric acid and choline hydrochloride. Boiling barium hydroxide solution converts it into choline, stearic, distearoylglycerolphosphoric, glycerolphosphoric, and phosphoric acids. It swells in water, giving transparent solutions in the warm solvent except in the presence of free glycerides; electrolytes, particularly hydrochloric acid, cause coagulation. The synthetic lecithin resembles very closely a hydrolecithin obtained by catalytic hydrogenation of carefully-purified egg-lecithin.

H. WREN.

Organo-silicon compounds. R. R. WIDDOWSON (J.C.S., 1926, 958).—Repetition of some of Hart's experiments (Rep. Brit. Assoc., 1887, 661) fails to confirm the existence of "dichlorosilicoethylene dibromide," "trimethylenesilicon dichloride," "trimethylenesilicon oxide," and "di-*o*-diphenylenesilicium."

C. HOLLINS.

***n*-Butylbenzene.** R. R. READ and L. S. FOSTER (J. Amer. Chem. Soc., 1926, **48**, 1606—1607).—*n*-Butyl bromide and bromobenzene are mixed and added to metallic sodium under dry ether at such a rate that the temperature remains at 20° or lower. After two days the mixture is extracted with several portions of benzene and the combined extracts are fractionated twice through a Clarke–Rahrs column.

F. G. WILLSON.

Photo-chlorination of toluene. G. BOOK and J. EGGERT (Ber., 1926, **59**, [*B*], 1192—1193; cf. A., 1924, ii, 10; Bergel, this vol., 389).—At 100—105°, the energy of artificial illumination is not sufficiently great to have a marked influence on the chlorination of toluene, whereas at −80° the purely chemical change is so far repressed that reaction becomes almost exclusively photochemical. With a sufficiently powerful source of light and an ample supply of chlorine, the rate of photochemical change is of the same order as that of chemical change.

H. WREN.

Rule of the conservation of type of substitution in aromatic substances. I. Chlorination of 2-chloro-4-nitrotoluene. W. DAVIES and G. W. LEEPER (J.C.S., 1926, 1413—1419).—2-Chloro-4-nitrotoluene, chlorinated in the presence of antimony trichloride, yields more than 30% of 2 : 6-dichloro-4-nitrotoluene (Davies, *ibid.*, 1922, **121**, 806). By determining this compound as 2 : 6-*dichloro*-3 : 4-*dinitrotoluene*, m. p. 129—130°, it has now been found that the product of monochlorination of the 2-chloro-4-nitrotoluene contains 47·9% of the 2 : 6-dichloro-derivative and considerable quantities of substances other than nuclear-substituted dichloronitrotoluenes, this constituting an exception to the rule of conservation of substitution type.

Reduction of 2 : 6-dichloro-3 : 4-dinitrotoluene with zinc dust in dilute alcohol forms 1 : 3-*dichloro*-2-*methylbenzophenanthrazine*, m. p. 279—286° (corr.). When 2 : 6-dichloro-3 : 4-dinitrotoluene is heated under pressure with alcoholic ammonia, it yields 2 : 6-*dichloro*-4-*nitro*-m-*toluidine*, m. p. 136°, the identity of which is established by its conversion into 2 : 6-dichloro-4-nitrotoluene. 2 : 6-*Dichloro*-4-*nitroacet*-m-*toluidide* has m. p. 185°, the *benzoyl* derivative, m. p. 215°, and the *chloroacetyl* derivative, m. p. 170°.

C. J. STILL.

Reductive passivity of zinc dust in the alkaline reduction of nitro-compounds. V. ISMAILSKI and V. KOLPENSKI (Z. angew. Chem., 1926, **39**, 507—509).—In the reduction of nitro-compounds with zinc dust and alkali, the irregularities in the reaction, observed with some samples of zinc dust (almost complete cessation of reduction followed by a reaction of explosive violence), may be avoided by first warming the zinc dust with weak alkali or water. The reaction then proceeds quickly and smoothly. The irregularities are due to the assumption by the zinc of a state of reductive passivity, possibly due to the occlusion of a film of gas with formation of zinc hydride.

C. T. GIMINGHAM.

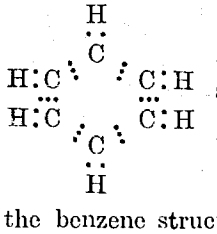
Unsymmetrically substituted dinitro- and diamino-derivatives in the stilbene and tolane series. II. Mode of addition of water to 3 : 4′-dinitro- and -diamino-tolanes. H. A. HARRISON (J.C.S., 1926, 1232—1239).—By bromination of 3 : 4′-dinitrostilbene two forms, α- (m. p. 234°) and β- (m. p. 214°), of 3 : 4′-*dinitrostilbene dibromide* are obtained, and from this, by the action of alcoholic potassium hydroxide, there is formed 3 : 4′-*dinitrotolane*, m. p. 173—174°, which on treatment with sulphuric acid yields 3-nitrophenyl 4-nitrobenzyl ketone. On the other hand, the *diacetyl* derivative (m. p. 226°) of 3 : 4′-*diaminotolane* (m. p. 124—125°), obtained by reduction of the dinitrotolane, yields 4-*acetamidophenyl* 3-*acetamidobenzyl ketone*, m. p. 204°, when treated with sulphuric acid. These results are in accord with polarity considerations. Other compounds described are: 3 : 4′-*diaminostilbene*, m. p. 156°, its *hydrochloride* and *diacetyl* derivative, m. p. 226—227°; 3 : 4′-*diaminodibenzyl*, m. p. 73—75°, *diacetyl* derivative, m. p. 177°, and *hydrochloride*.

C. J. STILL.

Directive influence of substituents in the benzene ring. V. Suggested relations between directive influence and thermal data. A. W. FRANCIS, D. H. ANDREWS, and J. JOHNSTON (J. Amer. Chem. Soc., 1926, **48**, 1624—1631; cf. A., 1925, i, 1399).—When liquid monosubstituted benzene derivatives are placed in the order of comparative directive influence of their substituents, a progressive decrease in m. p., b. p., and dielectric constant is observed through the "*ortho-para*" series OH, NH_2, Br, Cl, Me, and a similar increase through the "*meta*" series CHO, NO_2, SO_3H, CO_2H. The constants for benzene stand between those of toluene and benzaldehyde, and a similar order is observed when hydrogen is substituted for the phenyl group. The same sequence of m. p. and b. p. is also approximately observed amongst the corresponding derivatives of phenol, chlorobenzene, and benzoic acid. Whilst the m. p. of the *para* isomeride is in all cases the highest of the three, that of the *meta* isomeride is usually lowest when the directive influences of the two substituents are similar, whilst that of the *ortho* isomeride is usually lowest when the orienting influences of the two substituents are unlike. When the observations are extended to include derivatives containing substituents of less pronounced directive influence than those listed above, this generalisation holds in about two thirds of the cases. In the case of disubstituted benzene derivatives, the entropy of melting of the *meta* isomeride is usually higher than that of the *para* isomeride where the two substituents have unlike directive influences, whilst when these influences are similar, the *meta* isomeride has the smaller entropy of melting.

F. G. WILLSON.

Directive influence of substituents in the benzene ring. VI. A. W. FRANCIS (J. Amer. Chem. Soc., 1926, **48**, 1631—1642; cf. preceding abstract).—In extension of previous researches (cf. A., 1925, i, 1141), the competition of a large number of pairs of organic compounds for bromine from a bromide–bromate mixture in aqueous solution has been examined. The results indicate that the relative rates of successive bromination of amino- and phenolic compounds is in accord with the postulate of intermediate substitution of bromine in the side-chain; that the directive influences of several substituents in the same nucleus are usually cumulative; and that chlorine and bromine have exactly the same directive influence. A method has been devised for estimating numerical values for directive influences, the results of which are in accord with previous qualitative observations. In addition to its directive influence, a substituent may accelerate or retard the rate of substitution, regardless of its position, a phenomenon apparently related to the effect of such a substituent on the acidity of the compound. The data so far obtained can be explained by shifts, brought about by substitution, among the electrons associated with the benzene structure, as positioned in the annexed formula.



F. G. WILLSON.

Constitution of the condensation product of β-phenylhydroxylamine and acetone. F. H. BANFIELD and J. KENYON (J.C.S., 1926, 1612—1629; cf. Bamberger and Rudolf, A., 1907, i, 606; Beckmann and Scheiber, *ibid.*, 829; Scheiber and Wolf, *ibid.*, 1028).—Acetone and β-phenylhydroxylamine react slowly at the ordinary temperature to give a compound, $C_{18}H_{22}O_2N_2$, m. p. 136° (slight decomp.), which is regarded as *β-phenylhydroxylamino-β-methylpentan-δ-oneoxime N-phenyl ether* (I) or *β-phenylhydroxylamino-β-methylpentane-δ-phenylimine oxide* (II). It forms a *monoacetyl* derivative ($+1H_2O$, m. p. 99—101°, and anhyd., m. p. 105—106°), a *monobenzoyl* derivative ($+1H_2O$, m. p. 96—98°, and anhyd., m. p. 98—99°), a *potassium* derivative, which is quantitatively oxidised by air to the red compound (III), and a *monohydrochloride*, m. p. 62—64°. With dilute hydrochloric acid the condensation product gives *β-p-chloroanilino-β-methylpentan-δ-one*, b. p. 169—172°/11 mm. (*nitrosoamine*, m. p. 75—76°; *semicarbazone*, m. p. 125°), which is decomposed by heat into *p*-chloroaniline and mesityl oxide, and by acetic anhydride into *p*-chloroacetanilide and mesityl oxide, whilst with sodium and alcohol it gives sodium chloride and aniline, together with *p*-chloroaniline and methyl*iso*butylcarbinol; it has been synthesised from β-phenylhydroxylamine and mesityl oxide (*sodium* derivative of unstable intermediate product prepared). When treated with dilute hydrochloric acid, the condensation product (I or II) loses 1 mol. of β-phenylhydroxylamine; with hot, concentrated hydrochloric acid it yields mesityl oxide, *p*-chloroaniline, and azoxybenzene; with steam it gives azoxybenzene and mesityl oxide; with alcoholic zinc chloride it gives *p*-phenetidine, azoxybenzene, *p*-chloroaniline, aniline, and mesityl oxide; with dilute sulphuric acid it gives *p*-aminophenol, mesityl oxide, and azoxybenzene. It is reduced by sodium and alcohol to a secondary *base*, $C_{12}H_{19}ON$, b. p. 130—133°/2—4 mm., 160—163°/15 mm., d_4^{18} 1·0043, which is probably $NHPh{\cdot}CMe_2{\cdot}CH_2{\cdot}CHMe{\cdot}OH$ [*chloroplatinate*, m. p. 197—198° (decomp.); *nitrosoamine*, m. p. 44—48° (decomp.); *diacetyl* derivative, m. p. 104—105°]. When the condensation product is oxidised with ammoniacal silver oxide, it gives a 98% yield of a red *compound*, m. p. 88—90° (decomp.), which is believed to contain quadrivalent nitrogen, $O{:}NPh{\cdot}CMe_2{\cdot}CH_2{\cdot}CMe{<}\overset{O}{\underset{NPh}{|}}$ (III); the action of hydrogen chloride on its ethereal solution gives a *compound*, $C_{18}H_{21}O_2N_2,2HCl$, which is converted by water into the condensation product and nitrosobenzene, and the same products are formed from (III) by the action of heat, whilst hot, dilute mineral acids give rise to mesityl oxide; (III) may be quantitatively reduced to the original condensation product, whilst acylating agents yield derivatives of the latter. With phenylcarbimide the condensation product forms a *substance*, $C_{25}H_{27}O_3N_3$, m. p. 128—129° (decomp.). The electronic structure of (III) is discussed.

F. M. HAMER.

Anilidophenylglycine. Z. MOTYLEVSKI (Bull. Int. Acad. Polonaise, 1926, *A*, 93—101).—Chloroacetanilide, which may be prepared from

formanilide by treatment with chloroacetyl chloride, reacts with aniline in the presence of zinc chloride to give in good yield phenylglycineanilide, which forms a *hydrochloride*, m. p. 216°, a *hydrogen sulphate* ($1H_2O$), m. p. 194—195°, and a *nitrosoamine*, m. p. 145°. Sulphonation produces *phenylglycineanilide*-p-*sulphonic acid* (*sodium* salt, $+1H_2O$), whilst bromine in alcohol solution gives *bromophenylglycinebromoanilide*, m. p. 132—133°. Interaction of *p*-toluidine and chloroacetanilide in the presence of zinc chloride gives *phenylglycine*-p-*toluidide*, m. p. 161—162°.

M. CLARK.

Acetylation of diphenylamine derivatives with acetic anhydride and zinc chloride. F. KEHRMANN and E. BAUMGARTNER (Helv. Chim. Acta, 1926, **9**, 673—675).—Acetylation of diphenylamine derivatives which are not attacked by acetic anhydride and fused sodium acetate is readily effected by the use of acetic anhydride and zinc chloride (cf. Kehrmann, Oulevay, and Regis, A., 1914, i, 84). In this way are obtained *acetyl* derivatives of the following: o-*nitrodiphenylamine*, m. p. 134—135°; p-*nitrodiphenylamine*, m. p. 99—100° (also obtained by nitration of acetyldiphenylamine); 5-*chloro*-2-*nitrodiphenylamine*, m. p. 98°; 4 : 4′-dinitrodiphenylamine (cf. Stoermer and Hoffmann, A., 1899, i, 45); 2 : 4- and 2 : 4′-*dinitrodiphenylamine*, m. p. 151—152° and 129—130°, respectively; and hexanitrodiphenylamine.

J. W. BAKER.

Tenacity of organic residues. IV. J. VON BRAUN and R. MURJAHN (Ber., 1926, **59**, [*B*], 1202—1209).—The influence of branching in the hydrocarbon residue becomes less important as the absolute magnitude of the residue increases. It is improbable that steric relationships exercise any considerable effect (cf. von Auwers and Pfuhl, A., 1925, i, 1100).

n-Butylaniline, b. p. 119—120°/12 mm. (cf. Reilly and Hickinbottom, J.C.S., 1917, **111**, 1026), conveniently prepared from *n*-butyl bromide, formanilide, and potassium hydroxide, yields a hydrochloride, m. p. 114°, and p-*toluenesulphonyl* derivative, m. p. 54°. The *hydrochloride*, m. p. 192°, and p-*toluenesulphonyl* derivative, m. p. 120°, of *iso*butylaniline, b. p. 110°/10 mm., are described. n-*Butyl*iso*butylaniline*, b. p. 142°/11 mm., and cyanogen bromide give mainly *n*-butyl bromide and *phenyl*iso*butylcyanamide*, b. p. 163°/11 mm., which is hydrolysed to almost homogeneous *iso*butylaniline. *n*-Amylaniline, b. p. 130°/11 mm. (*hydrochloride*, m. p. 120°; p-*toluenesulphonyl* derivative, m. p. 76—77°), and *iso*amylaniline (*hydrochloride*, m. p. 151°; p-*toluenesulphonyl* derivative, m. p. 81—82°) are described. n-*Amyl*iso*amylaniline*, b. p. 161°/11 mm., and cyanogen bromide give a mixture of *n*-amyl and *iso*amyl bromide and *phenylamylcyanamide*, b. p. 167°/12 mm., which is hydrolysed to a mixture of *n*-amyl- and *iso*amyl-aniline. *Trimethyl*-n-*amylammonium bromide*, m. p. 175—176°, and *trimethyl*iso*amylammonium bromide*, m. p. 202°, are described.

n-*Butyl* iso*butyl sulphide*, b. p. 177—178°, is converted by cyanogen bromide almost exclusively into *n*-butyl bromide and iso*butyl thiocyanate*, b. p. 175—176°. *Trimethyl*-n-*butylammonium bromide*, m. p. 177—178°, and *trimethyl*iso*butylammonium bromide*, m. p. 187—188°, are described. n-*Propyl* iso*propyl sulphide*, b. p. 132°, and *diiso*propyl *sulphide*, b. p. 120°, are largely resinified by cyanogen bromide.

Contrary to Hofmann and Cahours, allyl mercaptan cannot readily be prepared from allyl iodide and potassium hydrosulphide, the main products being allyl sulphide and the polymerised mercaptan. The latter *substance*, b. p. 67—68°, d_4^{25} 0·9250, is readily prepared from allyldithiourethane and sodium hydroxide. The tendency towards polymerisation is shared by *cinnamyl mercaptan*, b. p. 124—125°/13 mm., m. p. 7—8°, obtained from *cinnamyldithiourethane*, m. p. 124°.

H. WREN.

Compounds of iodoform with quaternary salts. W. STEINKOPF, J. ROCH, and K. SCHULTZ (J. pr. Chem., 1926, [ii], **113**, 159—165).—In general, quaternary ammonium, arsonium, phosphonium, stibinium, and sulphonium salts combine with iodoform in equimolecular proportions, but in certain cases more complex compounds are formed. An examination of the molecular compounds mentioned below does not reveal any relationship between the constitution of the ammonium, arsonium, etc. salt and the complexity of the compound with iodoform. The following *compounds* are described:

$NPh(CH_2Ph)Et_2I$, m. p. 111°;
$2NPh(CH_2Ph)Et_2I,3CHI_3$, m. p. 123°;
$N(CH_2Ph)_2Me_2I,CHI_3$, m. p. 128°; $N(CH_2Ph)_3PrI$, m. p. 194—195°; $2N(CH_2Ph)_3PrI,3CHI_3$, m. p. 101—102° (decomp.); $As(CH_2Ph)Me_3I$, m. p. 191° (decomp.); $As(CH_2Ph)Me_3I,CHI_3$, m. p. 99°;
$As(CH_2Ph)_2Me_2I,I_2$, m. p. 78—82°;
$2As(CH_2Ph)_3MeI,3CHI_3$, m. p. 91°;
$As(CH_2Ph)_4I,CHI_3$, m. p. 137°; $S(CH_2Ph)_3I,CHI_3$, m. p. 95°; $[IPh_2]I,CHI_3$, m. p. 156°; $[(o\text{-}CH_3\cdot C_6H_4)_2I]I,I_2$, m. p. 146°; $[(p\text{-}CH_3\cdot C_6H_4)_2I]I,I_2$, m. p. 140°. Tetrabenzylammonium and dibenzyldialkylarsonium iodides could not be prepared.

J. S. H. DAVIES.

Reduction of organic [nitro-]compounds with hyposulphites. H. BUCHERER.—See B., 1926, 528.

Reduction of nitro-derivatives by means of sodium amalgam. G. PELLEGRINI.—See B., 1926, 576.

Manufacture of diarylamines. SOC. OF CHEM. IND. IN BASLE.—See B., 1926, 528.

Alternating effect in carbon chains. IV. Abnormal reactions as evidence of the incipient ionisation of certain hydrogen atoms in hydrocarbon radicals. E. L. HOLMES and C. K. INGOLD (J.C.S., 1926, 1305—1310).—*p*-Toluenesulphonbenzylmethylamide is converted by potassium hydroxide into toluene and sulphurous acid, which are probably derived from *p*-toluenesulphinic acid, together with benzylidenemethylamine. Analogously, *p*-toluenesulphonbenzylamide gives toluene and sulphurous acid, together with ammonia, benzaldehyde, and benzoic acid. It is supposed that the attack by hydroxyl ions begins at the methylene group, in which the hydrogen atoms are in a state of incipient ionisation. With p-*toluenesulphonphenylmethylamide*, m. p. 93°, abnormal reaction can be detected, but

the principal change consists in formation of *p*-cresol, *p*-hydroxybenzoic acid, sulphur dioxide, aniline, and methylaniline. With *p*-toluenesulphonanilide, where the mechanism cannot operate at all, the decomposition gives rise to aniline, *p*-cresol, and *p*-hydroxybenzoic acid; here direct ionic fission of the sulphur–nitrogen linking is postulated. F. M. HAMER.

Laws of aromatic substitution. V. Directing effect of electrolytically dissociated groups. B. FLÜRSCHEIM and E. L. HOLMES (J.C.S., 1926, 1562—1570).—Nitration of benzyldiethylamine in sulphuric acid solution (cf. Noelting and Kregczy, A., 1916, i, 803) gives a 44% yield of *m*-nitro-derivative. (*Benzyldiethylamine picrate* has m. p. 120°, and the picrate of the *o*-nitro-derivative has m. p. 122°.) This result is ascribed to *m*-nitration of the electrolytic ion of the ammonium salt. By doubling the dilution, the yield is increased to 52%, whilst saturation of the nitrating solution with ammonium sulphate leads to a 34% yield: *m*-nitration runs parallel with the degree of electrolytic dissociation, in agreement, approximately, with Sugden's cubic law. It is claimed that Flürscheim's theory explains the experimental results as regards the benzylammonium salts, whereas Robinson's would require *m*-substitution in the undissociated as well as in the dissociated portion. F. M. HAMER.

α-Naphthylcarbimide as a reagent for phenols and aromatic amines. H. E. FRENCH and A. F. WIRTEL (J. Amer. Chem. Soc., 1926, 48, 1736—1739; cf. this vol., 517).—α-Naphthylcarbimide reacts readily in the hot with phenols, and with acetamide and acetanilide, and at the ordinary temperature with aromatic amines, as well as with the oximes of acetone, benzophenone, and benzaldehyde. The reaction is catalysed by tertiary aliphatic amines. Polyhydric phenols do not react. *α-Naphthylurethanes* and *-carbamides*, derived, respectively, from the following phenols and amines, are described: *phenol*, m. p. 132—133°; o-*cresol*, m. p. 141—142°; m-*cresol*, m. p. 127—128°; p-*cresol*, m. p. 146°; *thymol*, m. p. 160°; *carvacrol*, m. p. 116°; o-*nitrophenol*, m. p. 112—113°; m-*nitrophenol*, m. p. 167°; p-*nitrophenol*, m. p. 150—151°; o-*chlorophenol*, m. p. 120°; m-*chlorophenol*, m. p. 157—158°; p-*chlorophenol*, m. p. 165—166°; o-*bromophenol*, m. p. 128—129°; p-*bromophenol*, m. p. 168—169°; 2 : 4 : 6-*tribromophenol*, m. p. 153°; 6-*chloro*-m-*cresol*, m. p. 153—154°; o-4-*xylenol*, m. p. 141—142°; m-4-*xylenol*, m. p. 134—135°; p-*xylenol*, m. p. 172—173°; *resorcinol monomethyl ether*, m. p. 128—129°; *guaiacol*, m. p. 118°; *eugenol*, m. p. 122°; iso*eugenol*, m. p. 149—150°; *orcinol*, m. p. 160°; α-*naphthol*, m. p. 152°; β-*naphthol*, m. p. 156—157°; α-*nitro*-β-*naphthol*, m. p. 128—129°; o-*aminophenol*, m. p. 201°; *methylamine*, m. p. 196—197°; *ethylamine*, m. p. 199—200°; *dimethylamine*, m. p. 158—159°; *diethylamine*, m. p. 127—128°; *benzylamine*, m. p. 202—203°; iso*amylamine*, m. p. 131—132°; *di*iso*amylamine*, m. p. 94—95°; *di*iso*butylamine*, m. p. 118—119°; *di*-n-*propylamine*, m. p. 92—93°; *acetoxime*, m. p. 68—69°; *benzaldoxime*, m. p. 149°; *acetamide*, m. p. 211—212°, and *acetanilide*, m. p. 116—117°. F. G. WILLSON.

Diphenyl series. I. Migration reactions. F. BELL, J. KENYON, and P. H. ROBINSON (J.C.S., 1926, 1239—1247).—The migration reactions characteristic of β-phenylhydroxylamine, phenylacetylchloroamine, and nitrosomethylaniline, when repeated in the diphenyl series, result in migration to the adjacent 3-position, not to the 4′-position, of which there seemed a possibility, in the first two cases, whilst in the last case decomposition occurred. Details for the preparation of diphenyl by the thermal decomposition of benzene are given.

4-*Hydroxylaminodiphenyl* is obtained by reduction of 4-nitrodiphenyl with aluminium amalgam in ether. It has m. p. 152—154°, setting and melting again at 188—190°; it forms a *hydrochloride* and a *diacetyl* derivative, m. p. 119°. By 10% sulphuric acid, 4-hydroxylaminodiphenyl is partly converted into a *compound*, m. p. 156°, $C_{24}H_{20}N_2$, which may be 4-*diphenylyl*-(4-*amino*-3-*diphenylyl*)*amine*. The above diacetyl derivative is converted by concentrated hydrochloric acid into a *base*, $C_{12}H_{10}NCl$, m. p. 69° (*acetyl* derivative, m. p. 146°). The same acetyl compound and base are obtained by the action of glacial acetic acid on *diphenylyl*-4-*acetylchloroamine*, m. p. 127°; the base is therefore taken to be 3-*chloro*-4-*aminodiphenyl*.

4-*Methylaminodiphenyl*, m. p. 38° (*hydrochloride*, *acetyl* derivative, m. p. 118—119°, p-*toluenesulphonyl* derivative, m. p. 128°), is obtained by methylating 4-acetamidodiphenyl and hydrolysing the product. In the preparation of the *nitrosoamine*, m. p. 116°, there was obtained as a by-product 4-*diazomethylaminodiphenyl*, $C_{25}H_{21}N_3$, decomp. 187°. 4-Aminodiphenyl *p*-toluenesulphonate has m. p. 160°. H. BURTON.

Theory of colour on the basis of molecular strain. Effect of chromophoric superposition. S. DUTT (J.C.S., 1926, 1171—1184).—The absorption maxima of coloured organic compounds have been measured and an attempt is made to show that selective absorption is due to molecular strain, such strain being imparted to a molecule by any of the following causes: (*a*) formation of double or triple linking, (*b*) formation of cyclic from open-chain compound, (*c*) unequal distribution of masses attached to an atom. Two sources of strain in close proximity have a greater effect than when remote, the greatest effect being caused by origination in the same atom. A dye containing two different and distantly situated chromophores has an absorption maximum approximately the mean of the maxima of the two components. The following compounds are described: p′p″-*diamino*-p-*hydroxytriphenylmethane*, m. p. above 295°; p′p″-*diamino*-p-*dimethylaminotriphenylmethane*, m. p. 152°; p-*benzeneazo*-p′p″-*diaminotriphenylmethane*, m. p. 174°; p-4-*dimethylaminobenzeneazo*-p′p″-*diaminotriphenylmethane*, m. p. 165°; p-4-*hydroxybenzeneazo*-p′p″-*diaminotriphenylmethane*, m. p. 162—163°; *benzeneazobenzeneazobenzeneazophenol*, m. p. 248°; *benzeneazobenzeneazobenzeneazoaniline*, m. p. 194°; *benzeneazobenzeneazobenzeneazodimethylaniline*, m. p. 218°; *benzeneazobenzeneazobenzeneazobenzeneazophenol*, m. p. above 290°; *benzeneazobenzeneazobenzeneazobenzeneazodimethylaniline*, m. p. above 290°; s-*tetra*-(p-*dimethylaminophenyl*)*ethane*, m. p.

96—98°; *tetra*-(p-*dimethylaminophenyl*)*ethylene diacetate*; leuco*dimalachite-green*, $(NMe_2{\cdot}C_6H_4)_2CH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}CH{\cdot}(C_6H_4NMe_2)_2$, by heating *p*-bromo*leuco*malachite-green with copper bronze, m. p. 135—138°; *dimalachite-green* (*diacetate*); *dipyronine G* by condensing glyoxal (1 mol.) with dimethyl-*m*-aminophenol and oxidising the *leuco*-compound; *difluorescein*, m. p. above 300°, by condensing pyromellitic acid with 4 mols. of resorcinol, *di-Meldola's blue* from *p*-nitrosodimethylaniline and 2 : 7-dihydroxynaphthalene; *phenazineazine*, $C_{18}H_{10}N_4$, by condensing 2 : 3-diaminophenazine with *o*-benzoquinone, m. p. above 290°; *phenazineazine-azine*, $C_{24}H_{12}N_6$, from the condensation of 2 : 3-dihydroxy- with 2 : 3-diamino-phenazine, m. p. above 290°. When 3 : 3′-*tetramethyldiaminodiphenyl* (m. p. 126—128°, obtained by reduction of 3 : 3′-dinitrodiphenyl and methylation of the diamine) is heated with benzylidene chloride in carbon disulphide solution in presence of aluminium chloride, 3 : 6-*tetramethyldiamino*-9-*phenylfluorene*, m. p. 92—94°, is formed. On oxidation it forms a green *dye* (green crystalline *acetate*), which may be regarded as a bridged malachite-green. By condensing 3 : 3′-dihydroxydiphenyl with phthalic anhydride, a *dye* is obtained, $C_{20}H_{12}O_4$, which is regarded as a bridged phenolphthalein. H. BURTON.

Basic dyes of the malachite-green series [from tri- and tetra-chlorobenzaldehyde]. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1926, 577.

Triphenylmethane dye. W. DUISBERG, W. HENTRICH, W. SCHEPSS, and GRASSELLI DYESTUFF CORPN.—See B., 1926, 577.

Mechanism of the rearrangement of diazoaminobenzene into aminoazobenzene. I. Some salts of diazoaminobenzene. K. SUIZU and N. YOKOZIMA (J. Soc. Chem. Ind. Japan, 1926, **29**, 32—35).—The cause of the rearrangement of diazoaminobenzene into aminoazobenzene is concluded to be the negative diazo-residue attached to the amino-nitrogen; the hydrochloric acid, used in the form of aniline hydrochloride, also combines with the amino-nitrogen, increasing its negativity. Diazoaminobenzene hydrochloride is obtained as a yellow precipitate (1HCl) which changes at once to a white one (2HCl), although it is kept cold. Diazoaminobenzene also forms two sulphates, one yellow ($1H_2SO_4$), and the other white ($2H_2SO_4$); but only one picrate is formed, yellow, with 1 mol. of picric acid. The two hydrochlorides are formulated NPh:N·NHPh,HCl and N(HCl):NPh·NHPh,HCl. K. KASHIMA.

Mechanism of the formation of formazyl compounds. M. BUSCH and H. PFEIFFER (Ber., 1926, **59**, [*B*], 1162—1165).—Benzeneazophenylhydrazine and benzaldehyde, preferably in the presence of alcoholic ethoxide, afford formazylbenzene. Under similar conditions, *p*-anisaldehyde gives *formazyl*-p-*methoxybenzene*, m. p. 154°, obtained also from anisaldehydephenylhydrazone and benzenediazonium acetate. *Formazyl*-m-*nitrobenzene*, m. p. 185°, is described. Benzeneazobenzylhydrazine and benzaldehyde yield *benzeneazobenzaldehydebenzylhydrazone*, m. p. 108—109° (decomp.), $CH_2Ph{\cdot}N(N{:}CHPh){\cdot}N{:}NPh$. The formation of formazyl compounds is explained by the scheme: $R'{\cdot}N{:}N{\cdot}NR{\cdot}NH_2 + R''{\cdot}CHO \longrightarrow R'{\cdot}N{:}N{\cdot}NR{\cdot}N{:}CHR'' \longrightarrow R{\cdot}NH{\cdot}N{:}CR''{\cdot}N{:}NR'$. H. WREN.

Preparation of potassium phenoxide. H. ERLENMEYER (Helv. Chim. Acta, 1926, **9**, 648—650).—Pure potassium phenoxide ($+2H_2O$) is obtained by the addition, with constant shaking, of an equivalent quantity of fused phenol to fused potassium hydroxide, and crystallisation of the product from the minimum quantity of hot water. The substance becomes anhydrous when heated in a current of hydrogen. J. W. BAKER.

Halogenation of phenols. F. G. SOPER and G. F. SMITH (J.C.S., 1926, 1582—1591).—By examination of the speeds of interaction of hypochlorous acid with phenol, *o*-chlorophenol, *m*-cresol, *o*- and *p*-nitrophenol, and salicylic acid, in acid and in alkaline solution, it is concluded that the phenoxide ion and un-ionised hypochlorous acid are involved; this view is confirmed by the abnormally large initial interaction which occurs on mixing hypochlorous acid with the sodium salt of the phenol. The velocity constants of chlorination by hypochlorite have been measured in the case of phenol, *o*-, *m*-, and *p*-cresol, *o*- and *p*-chlorophenol, 3-chloro-*p*-cresol, *o*-, *m*-, and *p*-nitrophenol, and *m*-4-xylenol. The reactivity of the ions of the simple phenols is approximately proportional to their affinity for hydrogen ions. Phenolic ethers do not react with hypochlorous acid, but are chlorinated in presence of hydrochloric acid, owing to the formation of chlorine, which can react with the un-ionised phenol molecule; this method of chlorination has been studied in the cases of *p*-cresol, phenol, phenetole, anisole, and *p*-nitrophenol, and it appears that the rate of chlorination by chlorine is more rapid than the rate of production of chlorine from hydrochloric and hypochlorous acids. The mechanism of halogenation of phenols is discussed. F. M. HAMER.

Nature of the alternating effect in carbon chains. VI. Relative directive efficiencies of oxygen and fluorine in aromatic substitution. E. L. HOLMES and C. K. INGOLD (J.C.S., 1926, 1328—1333).—Dinitration of o-*fluoroanisole*, b. p. 154—155° (prepared by the action of aqueous hydrogen fluoride on o-*diazoanisolepiperidide*, m. p. 30°), gives (probably) 4 : 6-*dinitro*-2-*fluoroanisole*, m. p. 86—87°. Mononitration gives 6-*nitro*-o-*fluoroanisole* [also synthesised, b. p. 110°/1 mm., from the *diazopiperidide* from 6-nitro-*o*-anisidine (6-*nitro*-o-*anisidine hydrochloride*, m. p. 198°)] and 4-*nitro*-o-*fluoroanisole* (also synthesised, m. p. 52—53°, from the *diazopiperidide*, m. p. 95—96°, from 4-nitro-*o*-anisidine), in yields of 66% and 31%, respectively, whilst the net yield of the 3- and 5-nitro-derivatives is less than 3%. It is concluded that oxygen is a more effective directing agent than fluorine. F. M. HAMER.

Bromophenols. XVIII. Tri- and tetrahalogenated phenols. M. KOHN and S. SUSSMANN (Monatsh., 1926, **46**, 575—595; cf. A., 1925, i, 134, 1264; this vol., 282).—2 : 3 : 4 : 6-Tetrabromo-

phenol (of which the methyl ether previously described has b. p. 338—342°) is oxidised by fuming nitric acid to tribromobenzoquinone, m. p. 148°. Nitrous acid in glacial acetic acid solution yields 2 : 3 : 4-tribromo-6-nitrophenol, m. p. 121°, identical with the substance obtained by demethylating the tribromonitroanisole obtained by Kohn and Strassmann (A., 1925, i, 1264) from *m*-bromophenol. This methyl ether is now found to melt at 109° instead of 105° as previously stated (cf. also Jackson and Fiske, A., 1903, i, 689). By analogy, the compound obtained by Zincke (A., 1905, i, 879) by the action of nitrous acid on tribromo-*p*-cresol is probably 2 : 3-dibromo-5-nitro-*p*-cresol. 2 : 4-Dibromoanisole is converted by excess of bromine at 100° into 2 : 4 : 6-tribromoanisole. 2 : 4-*Dichloro*-6-*bromoanisole*, m. p. 65°, b. p. 253—258°, furnishes on nitration 2 : 4-*dichloro*-6-*bromo*-3 : 5-*dinitroanisole*, m. p. 120°, which yields the corresponding 2 : 4-*dichloro*-6-*bromo*-3 : 5-*dinitrophenol*, m. p. 171°, on demethylation. The action of an excess of bromine in cold aqueous solution on 2 : 4-dichlorophenol produces 2 : 4-*dichloro*-4 : 6-*dibromo*-1-*keto*-$\Delta^{2:5}$-cyclo*hexadiene*, which is converted by concentrated sulphuric acid into 2 : 4-*dichloro*-3 : 6-(or 5 : 6-)*dibromophenol*, m. p. 89°, oxidised by nitric acid to 2-*chloro*-3 : 6-(or 5 : 6-)*dibromobenzoquinone*, m. p. 159°. The *methyl ether*, m. p. 79·5°, b. p. 305—312°, of this dichlorodibromophenol yields a *mononitro*-derivative, m. p. 100°, demethylated to 2 : 4-*dichloro*-3 : 6-*dibromo*-5-*nitrophenol* (or 2 : 4-*dichloro*-5 : 6-*dibromo*-3-*nitrophenol*), m. p. 135°.

2 : 4-Dichlorophenol is converted by iodine in alkaline solution into 2 : 4-*dichloro*-6-*iodophenol*, m. p. 63° (*methyl ether*, m. p. 35°, b. p. 278—285°), and 2 : 4-dibromophenol yields in the same manner 2 : 4-*dibromo*-6-*iodophenol*, m. p. 106°, of which the *methyl ether*, m. p. 76°, is monoclinic. 2 : 6-Dichloro-4-bromophenol, m. p. 68°, b. p. 264—266°, is methylated to give 2 : 6-*dichloro*-4-*bromoanisole*, m. p. 69°, b. p. 250—255°, which on nitration yields 2 : 6-*dichloro*-4-*bromo*-3 : 5-*dinitroanisole*, m. p. 123°, demethylated to the corresponding 2 : 6-*dichloro*-4-*bromo*-3 : 5-*dinitrophenol*, m. p. 170—172°. An excess of bromine in cold solution converts 2 : 6-dichloro-4-bromophenol into 2 : 6-*dichloro*-4 : 4-*dibromo*-1-*keto*-$\Delta^{2:5}$-cyclo*hexadiene*, which loses bromine on warming, and is oxidised by fuming nitric acid to 2 : 6-dichlorobenzoquinone. Warm, concentrated sulphuric acid transforms it into 2 : 6-*dichloro*-3 : 4-*dibromophenol*, m. p. 91°, which is oxidised by nitric acid to 2 : 6-dichloro-3-bromobenzoquinone, m. p. 166°, and yields a *methyl ether*, m. p. 73°, b. p. 309—313°. The latter is nitrated by fuming nitric acid to 2 : 6-*dichloro*-3 : 4-*dibromo*-5-*nitroanisole*, m. p. 85·5°, demethylated to the corresponding 2 : 6-*dichloro*-3 : 4-*dibromo*-5-*nitrophenol*, m. p. 156—158°. The action of iodine in alkaline solution on *p*-bromophenol produces 4-*bromo*-2 : 6-*di-iodophenol*, m. p. 130°, of which the *methyl ether*, m. p. 81°, is monoclinic.

G. M. BENNETT.

Bromophenols. XIX. Brominated nitro- and dinitro-cresols. M. KOHN and A. SEGEL (Monatsh., 1926, **46**, 661—669).—On treatment with bromine in acetic acid solution, *o*-cresol is converted into 3 : 5-*dibromo*-o-*cresol*, b. p. 263—266°/745 mm., which on methylation yields the *methyl ether*, m. p. 38°, b. p. 266—269°/742 mm., and this on nitration with a mixture of fuming nitric and sulphuric acids yields the *methyl ether* of 3 : 5-*dibromo*-4 : 6-*dinitro*-o-*cresol*, m. p. 149—151°. This on demethylation with hydrogen bromide in acetic acid solution yields 3 : 5-*dibromo*-4 : 6-*dinitro*-o-*cresol*, m. p. 188°. Similarly, from *p*-cresol are obtained 3 : 5-*dibromo*-p-*cresol*, b. p. 268—271°/738 mm. (*methyl ether*, b. p. 257—261°/744 mm.), 3 : 5-*dibromo*-2 : 6-*dinitro*-p-*cresol*, m. p. 198° (*methyl ether*, m. p. 172°). 2 : 3 : 5-Tribromo-*p*-cresol yields a *methyl ether*, m. p. 70°, b. p. 311—314°/748 mm., which on nitration with fuming nitric acid yields 2 : 3-dibromo-5-nitro-*p*-cresol (Zincke, A., 1905, i, 879), but the *methyl ether* of 2 : 4 : 6-tribromo-*m*-cresol, m. p. 78°, b. p. 308—311°/748 mm., nitrates normally to yield the *methyl ether* of 2 : 4 : 6-*tribromo*-5-*nitro*-m-*cresol*, m. p. 127°. Tribromoanisole (Kohn and Fink, A., 1925, i, 133) on nitration yields 2 : 4 : 6-*tribromo*-3-*nitroanisole*, m. p. 80—82°.

J. W. BAKER.

Monochloro-derivatives of *m*-cresol. G. P. GIBSON (J.C.S., 1926, 1424—1428).—Monochlorination of *m*-cresol in carbon tetrachloride yields a mixture of 2-*chloro*-m-*cresol*, m. p. 55—56° (*methyl ether*, m. p. 24·2°, b. p. 218·5°), inferred by conversion into 2-chloro-*m*-methoxybenzoic acid, 4-*chloro*-m-*cresol*, m. p. 46°, b. p. 196° (*methyl ether*, b. p. 212·5°; *acetate*, b. p. 122—123°/11 mm.; *benzoate*, m. p. 40°; p-*toluenesulphonate*, m. p. 96°), and 6-chloro-*m*-cresol, m. p. 57°, b. p. 234° (*methyl ether*, b. p. 213·5°; *acetate*, b. p. 123—124°/11 mm.; *benzoate*, m. p. 86°; p-*toluenesulphonate*, m. p. 98°). The ehloro-*m*-cresols were converted into the corresponding chloro-*m*-methoxybenzoic acids, which were also synthesised from 2-, 4-, and 6-nitro-*m*-cresols, by successive methylation, reduction, substitution of chlorine for the amino-group, and oxidation of the chloro-*m*-tolyl methyl ethers. 5-*Chloro*-3-*methoxy*-o-*toluidine*, m. p. 47°, b. p. 140—142°/11·5 mm. (*acetyl* derivative, m. p. 170°); 2 : 5-*dichloro*-m-*tolyl methyl ether*, m. p. 52°, b. p. 119—120°/12·5 mm.; 6-*chloro*-2-*nitro*-m-*tolyl methyl ether*, m. p. 112°, and 6-*chloro*-3-*methoxy*-o-*toluidine*, m. p. 50°, b. p. 145—146°/12 mm. (*acetyl* derivative, m. p. 154°), are described.

H. BURTON.

Velocities of the reactions between ethyl iodide and the sodium salts of various substituted phenols in ethyl-alcoholic solution. L. J. GOLDSWORTHY.—See this vol., 805.

Separation of monohydric phenols and monoethers of dihydric phenols. R. HUERRE (J. Pharm. Chim., 1926, [viii], **3**, 507—509).—Experiments on the separation of mixtures of phenol, guaiacol, and cresol by treatment with strontium hydroxide proved ineffective. In such cases, it is necessary to demethylate the monoether of the dihydric phenol.

B. FULLMAN.

Action of chlorosulphonic acid on phenols. II. Derivatives of resorcinol. J. POLLAK, E. GEBAUER-FÜLNEGG, and E. BLUMENSTOCK (Monatsh., 1926, **46**, 499—514; cf. this vol., 514).—The action

of chlorosulphonic acid on resorcinol at the ordinary temperature in carbon disulphide solution yields resorcinol-4 : 6-disulphonic acid, the potassium salt of which is converted by phosphorus pentachloride at 140° into 1 : 3-dichlorobenzene-4 : 6-disulphonyl chloride, m. p. 123° (see A., 1915, i, 529), and by fusion with potassium hydroxide yields phloroglucinol. If a larger excess of chlorosulphonic acid is used and the mixture at once poured into concentrated hydrochloric acid, the product is *resorcinol*-4 : 6-*disulphonyl chloride*, m. p. 179°, rapidly hydrolysed by water, and yielding the *disulphonamide*, m. p. above 300°, and the *disulphonanilide*, m. p. 262°, which couples with diazotised *p*-nitroaniline to give 2-(4′-*nitrobenzeneazo*)*resorcinol*-4 : 6-*disulphonanilide*, m. p. 247°. When resorcinol is heated at 110° with 50 parts of chlorosulphonic acid, it is converted into *resorcinol*-2 : 4 : 6-*trisulphonyl chloride*, m. p. 168°, extremely readily hydrolysed by water (*trisulphonanilide*, m. p. 243°) and converted by phosphorus pentachloride at 140° into 1 : 2 : 3-*trichlorobenzene*-4 : 6-*disulphonyl chloride*, m. p. 175° (*disulphonanilide*, m. p. 100—110°). The action of a large excess of chlorosulphonic acid on resorcinol at still higher temperatures produces trichlorobenzoquinone, m. p. 165°, tetrachlorobenzoquinone, m. p. 270—280°, chloranil, and finally perchlorobenzene, m. p. 228°.

G. M. Bennett.

Alternating effect in carbon chains. V. Aromatic substitution with reference to the respective rôles of polar and non-polar dissociation; relative directive efficiencies of oxygen and nitrogen. C. K. Ingold and E. H. Ingold (J.C.S., 1926, 1310—1328).—Experiments were made on the nitration of derivatives of *o*-aminophenol, to determine the relative orienting efficiencies of the oxygen and nitrogen atoms. Nitration of aceto-*o*-anisidide gives the 5-, 4-, and 3-nitro-derivatives, in yields of 74%, 13%, and 1·5%, respectively. 4-*Nitro*-o-*acetamidophenyl acetate* has m. p. 183—184° and 4-*nitro*-o-*acetamidophenol*, m. p. 278° (decomp.). Treatment of 3-nitro-*o*-acetamidophenyl acetate with sodium hydroxide and methyl sulphate gives 3-*nitro-aceto*-o-*anisidide*, m. p. 158—159°, which is hydrolysed to 3-*nitro*-o-*anisidine*, m. p. 75—76°. 4- and 5-Nitroaceto-*o*-anisidide are described, m. p. 174—175° and 153—154°, respectively, whilst reduction of 2 : 6-dinitroanisole gives 6-*nitro*-o-*anisidine*, m. p. 67°; 6-*nitroaceto*-o-*anisidide*, m. p. 103—104°. Nitration of *o*-acetamidophenyl acetate gives 3-*nitro*-o-*acetamidophenyl acetate*, m. p. 183°, in 23% yield, and 5-nitro-*o*-acetamidophenyl acetate in 48% yield [3-*nitro*-o-*acetamidophenol*, m. p. 169°; 5-*nitro*-o-*acetamidophenol*, m. p. 269° (decomp.)], whilst the product, m. p. 202°, formed by more drastic treatment is probably 3 : 5-*dinitro*-o-*acetamidophenol*. Heating 4-nitroanisidine with methyl iodide and methyl alcohol, followed by treatment with acetic anhydride, gives 4-*nitro*-NN-*dimethyl*-o-*anisidine*, m.p. 38—39·5°, 4-*nitro*-N-*methylaceto*-o-*anisidide*, m. p. 127—128° (4-*nitro*-N-*methyl*-o-*anisidine*, m. p. 87°; *nitrosoamine*, m. p. 119—120°), and 4-*nitro*-3(or 5)-*methylaceto*-o-*anisidide*, m. p. 127—128°. Nitration of N-*methylaceto*-o-*anisidide*, b. p. 158—160°, m. p. 51—53°, gives 5-*nitro*-N-*methylaceto*-o-*anisidide*, m. p. 119—120·5° (hydrolysable to 5-*nitro*-N-*methyl*-o-*anisidine*, m. p. 101—102°, which is also prepared from 5-nitroanisidine), 4-*nitro*-N-*methylaceto*-o-*anisidide*, and 3(or 6)-*nitro*-N-*methylaceto*-o-*anisidide*, m. p. 105—106°, in 64%, 4%, and 5% yields, respectively. *o*-Methylaminophenol, m. p. 88°, gives o-*acetmethyl-amidophenyl acetate*, b. p. 160—170°/2 mm., m. p. 63—64°. It is concluded that the group containing nitrogen has greater *op*-directive influence than that containing oxygen. The question of aromatic substitution is discussed at length, and it is suggested that both polar and non-polar dissociation are concerned therein, the main determining condition being the electronic constitution of the reagent.

F. M. Hamer.

Acyl derivatives of *o*-aminophenol. I. R. E. Nelson and H. L. Davis (J. Amer. Chem. Soc., 1926, **48**, 1677—1679).—Treatment of *o*-acetamidophenol in alkaline solution with propionic anhydride affords a *product*, m. p. 57—75°, apparently homogeneous, which affords *o*-acetamidophenol on hydrolysis, and appears to be *o*-acetamidophenyl propionate in equilibrium with a small proportion of *o*-propionamidophenyl acetate. Similar treatment of *o*-propionamidophenol with acetic anhydride affords an apparently homogeneous *product*, m. p. 85—103°, affording *o*-acetamidophenol on hydrolysis, which appears to be *o*-propionamidophenyl acetate in equilibrium with a small proportion of *o*-acetamidophenyl propionate.

F. G. Willson.

Acyl derivatives of *o*-aminophenol. II. R. E. Nelson and W. C. Aitkenhead (J. Amer. Chem. Soc., 1926, **48**, 1680—1683).—n-*Butyl*, m. p. 87·5°, iso*butyl*, m. p. 86°, n-*propyl*, m. p. 78°, and iso*propyl* o-*hydroxycarbanilate*, m. p. 85°, were prepared by the action of the appropriate alkyl chloroformates on *o*-aminophenol in ethereal solution. Treatment of ethyl *o*-hydroxycarbanilate with *n*-butyl chloroformate affords the corresponding *carbethoxy*-derivative, liquid, which is identical with that obtained when the acyl groups are inserted in the reverse order, and yields *n*-butyl *o*-hydroxycarbanilate on hydrolysis. On distillation in a vacuum, the dicarbalkoxy-derivative decomposes with formation of a crystalline *product*, m. p. 64·5°, which also yields *n*-butyl *o*-hydroxycarbanilate on hydrolysis. Similarly, the introduction of carbo-*n*-propoxy- and carbo-*n*-butoxy-groups into *o*-aminophenol, in either order, yields the same *dicarbalkoxy*-derivative, liquid, which on hydrolysis yields *n*-butyl *o*-hydroxycarbanilate, and on distillation yields a *product*, m. p. 72—73°. Treatment of *iso*propyl *o*-hydroxycarbanilate with *n*-propyl chloroformate affords a *dicarbalkoxy*-derivative, liquid, whih is converted into a *product*, m. p. 54—56°, on distillation, and yields, on hydrolysis, a mixture of *n*- and *iso*-propyl *o*-hydroxycarbanilates. Introduction of the carbo-*n*- and -*iso*-propoxy-groups in the reverse order yields a *liquid*, which on hydrolysis yields a similar mixture, m. p. 77·5—78° (the m. p. of either mixture being depressed by the presence of the other), which, on distillation, yields a *product*, m. p. 53·5—55·5°, not identical with that, above, of m. p. 54—56°. Treatment of

*iso*butyl *o*-hydroxycarbanilate with *n*-butyl chloroformate affords a liquid, which, on hydrolysis, affords a mixture containing a preponderance of *iso*butyl *o*-hydroxycarbanilate, and, on distillation, affords a product of m. p. 54—56°. Treatment of *n*-butyl *o*-hydroxycarbanilate with *iso*butyl chloroformate affords a liquid, which, on hydrolysis, yields *n*-butyl *o*-hydroxycarbanilate, and, on distillation, yields a *product*, m. p. 63·5—64·5°. F. G. WILLSON.

Dehydration of glycols derived from α-naphthylglycollic acid. A. MCKENZIE and W. S. DENNLER (J.C.S., 1926, 1596—1603; cf. *ibid.*, 1923, **123**, 79; 1924, **125**, 844, 2105; A., 1924, i, 729).—α-Naphthylglycollic acid, m. p. 98·5—99·5° (*silver* salt described), is prepared from α-naphthoic acid or from α-naphthyl methyl ketone, but preferably from magnesium α-naphthyl bromide and chloral (*α-naphthylglycollamide*, m. p. 134—135°). Methyl α-naphthylglycollate is converted by means of magnesium phenyl bromide into 1-α-*naphthyl*-2 : 2-*diphenylethylene glycol*, m. p. 126—127°, whilst 1-α-*naphthyl*-2 : 2-*dimethylethylene glycol*, m. p. 81·5—82°, and 1-α-*naphthyl*-2 : 2-*dibenzylethylene glycol*, m. p. 174—175°, are similarly obtained. 1-α-Naphthyl-2 : 2-diphenylethylene glycol is converted by cold concentrated or by hot dilute sulphuric acid into diphenylacetonaphthone; this change is regarded as a vinyl dehydration, involving no transposition of phenyl. Dehydration of 1-α-naphthyl-2 - 2-dimethylethylene glycol gives α-naphthyl *iso*propyl ketone, b. p. 304—306°/758 mm., but dehydration of 1-α-naphthyl-2 : 2-dibenzylethylene glycol yields a *substance*, b. p. 275—276°/15 mm., m. p. 58—59°, which is probably benzyl benzyl-α-naphthylmethyl ketone, formed, apparently, by a semipinacolinic transposition. F. M. HAMER.

Oxidation of chaulmoogric acid by permanganate. G. A. PERKINS (J. Amer. Chem. Soc., 1926, **48**, 1714—1725).—Oxidation of chaulmoogric acid by alkaline permanganate at about 2° affords α- and β-dihydroxydihydrochaulmoogric acids (cf. Barrowcliff and Power, J.C.S., 1907, **91**, 557). If the reaction mixture is heated to above 30° after decolorisation of the permanganate, amorphous substances are formed, together with a crystalline substance, m. p. 94°, probably identical with the lactone previously obtained (*loc cit.*) from methyl hydroxyketodihydrochaulmoograte. Direct separation of the α- and β-dihydroxy-acids is impossible on account of the formation of mixed crystals, and is best effected by conversion into the *o*-acetone ethers (see below), or the methyl esters of these, with subsequent hydrolysis. α-Dihydroxydihydrochaulmoogric acid has m. p. 106°, $[\alpha]_D^{20}$ +4·9° in alcohol. In presence of mineral acids, it reacts with acetone with formation of an *o-acetone ether*, $Me_2C<\begin{matrix}O\cdot CH\text{——}CH\cdot[CH_2]_{12}\cdot CO_2H\\ O\cdot CH\cdot CH_2\cdot CH_2\end{matrix}$; m. p. 64° $[\alpha]_D^{15}$ +28·6° in chloroform (*methyl* ester, m. p. 70°, $[\alpha]_D^{22}$ +27·6° in chloroform). β-Dihydroxydihydrochaulmoogric acid has m. p. 78° (+1H_2O) or m. p. 85° (anhydrous), $[\alpha]_D^{20}$ −38·2° in alcohol [*methyl* ester, m. p. 55°, $[\alpha]_D^{22}$ −34·3° in chloroform; *o-acetone ether*, m. p. 60°, $[\alpha]_D^{19}$ −10·5° in alcohol (*methyl* ester, m. p. 34·5°, $[\alpha]_D^{20}$ −8·7° in chloroform)]. Oxidation of chaulmoogric acid, in 90% acetic acid solution at 25°, by potassium permanganate, affords *n*-pentadecane-αγω-tricarboxylic acid, together with γ-keto-*n*-pentadecane-αω-dicarboxylic acid (*loc. cit.*), whilst similar oxidation of the dihydroxydihydrochaulmoogric acids yields the former acid only. F. G. WILLSON.

Properties of conjugated compounds. I. Conjugative associations in extended "conjugated systems." E. H. FARMER and J. ROSS (J.C.S., 1926, 1570—1577).—1-Methyl-Δ^1-*cyclo*hexen-3-one and ethyl cyanoacetate react, giving ethyl methyl*cyclo*hexenylidenecyanoacctate, as described by Knoevenagel and Mottek (A., 1905, i, 61), but their views as to the hydrolysis and methylation of this product are incorrect. It is converted by potassium hydroxide into an acid, m. p. 149°, which is not homogeneous (*ammonium* salt prepared); the silver salt on treatment with methyl iodide yields two isomeric (maleinoid and fumaroid) forms, m. p. 74° and 60°, respectively, of *methyl* 1-*methyl*-Δ^1-cyclo*hexenylidene*-3-*cyanoacetate* (*dibromides*, m. p. 77° and 65°, respectively), together with *methyl* 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-*cyanoacetate*, m. p. 42°. The two isomerides are also prepared, together with a *substance*, m. p. 88°, by condensation of the ketone with methyl cyanoacetate in presence of piperidine at 120—125°. Treatment of any one of the three esters with sodium methoxide gives the same equilibrium mixture of the three. Methylation of an equilibrated mixture gives *methyl* 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-α-*cyanopropionate*, b. p. 160°/11 mm., which may be converted into 1-*methyl*-$\Delta^{1:3}$-cyclo*hexadienyl*-3-*propionitrile*, b. p. 126°/11 mm. Each of the three esters on treatment with ammonia gives 1-*methyl*-Δ^1-cyclo*hexene*-3 : 3-*dicyanoacetamide*, m. p. 275°, and the *ammonium* salt, m. p. 188°, of the corresponding *cyanimide*, m. p. 195°, which products are also prepared by the action of ammonia on methyl*cyclo*hexenone and ethyl cyanoacetate. In the *cyclo*hexenylidene esters described, the acrylic group seems to be preserved as a definite unit. F. M. HAMER.

Structure of the carboxyl group. A. STEOPOE (Bul. Chim., Soc. Româna Stiinte, 1925, **28**, 19—28).—The strength of a carboxylic acid, R·CO_2H, is increased by increasing the energy of the R–C linking; *e.g.*, benzoic acid is much stronger than triphenylacetic acid. This can be explained, in terms of the theory of variable affinity, only by assigning to the "active" carboxyl group the formula [·CO_2]H, in which the hydrogen is directly attached to the carbon atom. On the basis of the classical formula, or that of Hantzsch (A., 1918, i, 4), the opposite effect would be expected. The new formula, moreover, unlike Hantzsch's, is analogous to Werner's co-ordination formulæ for other acids. H. E. F. NOTTON.

Chemical constitution, physiological action, and physical properties in a series of alkyl *p*-aminobenzoates. R. ADAMS, E. K. RIDEAL, W. B. BURNETT, R. L. JENKINS, and E. E. DREGER (J. Amer. Chem. Soc., 1926, **48**, 1758—1770).—The following p-*nitrobenzoates* were prepared by con-

densation of the appropriate alcohols with *p*-nitrobenzoyl chloride in benzene in presence of pyridine: *iso*propyl, m. p. 108·5°; sec.-*butyl*, m. p. 25°, b. p. 136—139°/2—3 mm., n_D^{25} 1·5170, d_{25}^{20} 1·1502; tert.-*butyl*, m. p. 115·5°; n-*amyl*, b. p. 159—161°/4 mm., n_D^{22} 1·5188, d_{20}^{20} 1·1410; and allyl *p*-nitrobenzoate, m. p. 28·5°, b. p. 165—168°/13 mm., 127—128°/1—2 mm., n_D^{20} 1·5459, d_{20}^{20} 1·2283. Reduction to the corresponding aminobenzoates can be effected by iron and hydrochloric acid, or, except in the case of the allyl ester, by hydrogen in presence of platinum oxide. The following new esters were prepared: sec.-*butyl*, m. p. 55°; tert.-*butyl*, m. p. 109·5°; and n-*amyl* p-*aminobenzoate*, m. p. 53°. The anæsthetic effect, on goldfish, of the following *p*-aminobenzoates is in the decreasing order: methyl, ethyl, allyl, *iso*propyl, *tert.*-butyl, *sec.*-butyl, *n*-propyl, *iso*butyl, *n*-butyl, and *n*-amyl, and this sequence is almost exactly followed by the surface tensions and the amyl acetate–water partition coefficients of the esters.

F. G. Willson.

Walden inversion. X. Reaction between water and the phenylchloroacetate and phenylbromoacetate ions. A. M. Ward.—See this vol., 805.

Reduction of ethyl dibenzylacetoacetate. (Miss) E. S. Hill (J.C.S., 1926, 956).—By the interaction of benzyl chloride, sodium methoxide, and ethyl acetoacetate in methyl alcohol, there is obtained, instead of ethyl dibenzylacetoacetate (m. p. 57°), *methyl dibenzylacetate*, m. p. 41°. Fittig and Christ's dibenzylacetoacetic acid (A., 1892, 962) is therefore more probably dibenzylacetic acid, m. p. 89°, which is obtained by hydrolysis of ethyl dibenzylacetoacetate. The last-mentioned ester strongly resists reduction, but by the action of a large excess of sodium on an ethereal solution of the ester floating on aqueous sodium hydroxide, there are obtained, in addition to dibenzylacetic acid, an oil (probably dibenzylacetone), b. p. 290°, and an acid, m. p. 152—153°, which is probably β-hydroxy-αα-dibenzylbutyric acid.

C. Hollins.

Substituted cinnamic amides and acids. H. A. Harrison and H. Wood (J.C.S., 1926, 1195—1199).—Condensation of *p*-nitrophenylacetonitrile and *m*-nitrobenzaldehyde in presence of piperidine or sodium ethoxide, gives 3 : 4′-dinitro-α-phenylcinnamonitrile, I, and 3 : 4′-*dinitro*-β-*hydroxy*-α-*phenylpropionitrile*, II, m. p. 135—136°. Sulphuric acid, pyridine, or piperidine converts II into I. When I and II are hydrolysed with sulphuric acid, an *amide* of 3 : 4′-*dinitro*-α-*phenylcinnamic acid*, III, m. p. 220°, is obtained from I, whilst a stereoisomeric *amide*, IV, m. p. 272·5—273·5°, is obtained from II. Amide IV, on further hydrolysis with sulphuric acid, gives *trans*-3 : 4′-dinitro-α-phenylcinnamic acid only, whereas amide III furnishes both *cis*- and *trans*-3 : 4′-dinitro-α-phenylcinnamic acids (this vol., 604). Nitrous acid converts amide III into the *cis*-form almost entirely. *m*-Nitrophenyl *p*-nitrobenzyl ketone is prepared from amide III, thus confirming its constitution (*loc. cit.*).

H. Burton.

Hydrophthalides. I. Action of magnesium alkyl iodides on Δ^2-tetrahydrophthalic anhydride. S. Berlingozzi and F. P. Mazza (Gazzetta, 1926, **56**, 88—98; cf. A., 1898, i, 665; 1899, i, 513).—By the action of magnesium alkyl iodides on Δ^2-tetrahydrophthalic anhydride, monoalkyltetrahydrophthalides are obtained. These compounds give (*a*) by oxidation with alkaline permanganate, hydroxyalkylbenzoic acids, (*b*) by reduction with sodium and alcohol, hydroxyalkylhexahydrobenzoic acids, and (*c*) by decomposition with strong alkali, Δ^1-tetrahydrobenzoic acid, an alcohol, and hydrogen. The following compounds are described: *methyl*-Δ^6-*tetrahydrophthalide*, b. p. 145°/13 mm.; *ethyl*-Δ^6-*tetrahydrophthalide*, b. p. 220°/80 mm.; *propyl*-Δ^6-*tetrahydrophthalide*, b. p. 185°/20 mm. All have odours recalling that of oil of celery and distil without decomposition. The molecular refractions and dispersions show an exaltation, corresponding with the formulæ of the alkyltetrahydrophthalides.

S. B. Tallantyre.

Syntheses in organic chemistry by radiant energy. I. Photosynthesis of αββ-triphenyllactic acid. R. de Fazi (Gazzetta, 1926, **56**, 186—191).—Exposure to sunlight of a sealed glass tube containing benzophenone and phenylacetic acid in benzene solution results in the formation of αββ-triphenyl-lactic acid, benzyl phenylacetate (?), carbon dioxide, benzopinacone, and a pungent, yellow oil, b. p. 315—322°, which is probably formed by the interaction of benzophenone and benzyl phenylacetate under the influence of light. The reactions involved are expressed by the following equations:

$COPh_2+CH_2Ph\cdot CO_2H=OH\cdot CPh_2\cdot CHPh\cdot CO_2H$;

$2CH_2Ph\cdot CO_2H=CH_2Ph\cdot CO_2\cdot CH_2Ph+CO_2+H_2$;

$2COPh_2+H_2=OH\cdot CPh_2\cdot CPh_2\cdot OH$ (cf. Paternò and Chieffi, A., 1911, i, 65).

T. H. Pope.

Synthetical work on the *iso*quinoline alkaloids. II. A method of opening the rings of cyclic ketones. G. A. Edwards (J.C.S., 1926, 813—817; cf. D.R.-P. 411955).—*Benzenesulphonyl*-1-*nitroso*-β-*naphthol*, m. p. 124—125° (decomp.), is converted at its m. p. into an *isomeride*, m. p. 141°. On hydrolysis with 8% sodium hydroxide solution at 60°, the low-melting compound gives *o*-cyano*allo*cinnamic acid, m. p. 137°, whilst the high-melting isomeride yields *o*-cyanocinnamic acid, m. p. 256°. The former acid also results when sodium hydroxide solution is added to a solution of 1-nitroso-β-naphthol and toluenesulphonyl chloride in acetone at 50—60°. Either acid gives *o*-carboxycinnamic acid, m. p. 182°, on hydrolysis. Electrolytic reduction of the crude *allo*-acid yields β-*o*-*cyanophenylpropionic acid*, m. p. 127°.

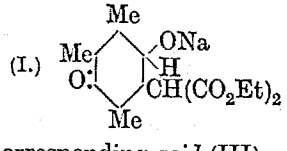
o-*Carboxycinnamonitrile*, m. p. 169—172°, was synthesised for comparison. Phthalideacetic acid, m. p. 151°, prepared by electrolytic reduction of phthalylacetic acid, is converted by way of the acid chloride into the *amide*, m. p. 182—183°, which by the action of phosphorus pentoxide gives *phthalideacetonitrile*, m. p. 111°; this gives *o*-carboxycinnamonitrile on hydrolysis.

2-*iso*Nitroso-1-hydrindone is converted by alkali and benzenesulphonyl chloride into *o*-carboxyphenyl-

acetonitrile, m. p. 126°. 2-Carboxy-4 : 5-dimethoxyphenylacetonitrile, m. p. 166—167°, and 2-carboxy-4 : 5-methylenedioxyphenylacetonitrile, m. p. 195°, are similarly prepared. C. HOLLINS.

Carboxylated β-diketones. G. T. MORGAN and C. R. PORTER (J.C.S., 1926, 1256—1262).—Condensation of *ethyl ω-chloro-*m*-toluate* (m-*carbethoxybenzyl chloride*), b. p. 140—150°/12 mm., with sodium acetylacetone gives 3-m-*carbethoxybenzylacetylacetone*, b. p. 209—215°/12 mm. (*copper* derivative, m. p. 173—176°), which on hydrolysis in concentrated sulphuric acid furnishes 3-m-*carboxybenzylacetylacetone*, m. p. 130° (alcohol) or 115° (benzene) (*monocupric* derivative, decomp. 235—240°). From sodium butyrylacetone by similar reactions, 3-m-*carbethoxybenzylbutyrylacetone*, b. p. 200—201°/6 mm. (*copper* derivative, m. p. 168—170°), and 3-m-*carboxybenzylbutyrylacetone*, m. p. 100—112° (aqueous alcohol) or 78—90° (benzene–petroleum), (*monocupric* derivative, m. p. 176—178°; *dicupric* salt, decomp. above 225°), are obtained. Hydrolysis of these diketones with dilute aqueous sodium hydroxide gives m-*carboxybenzylacetone* (*ω-acetonyl-*m*-toluic acid*), m. p. 77°. The carboxy-β-diketones, which exhibit keto–enol isomerism, form two types of metallic derivatives, through the presence of the chelate radical and the carboxyl group, of which the copper and *beryllium* compounds have been specially examined. The dimetallic salts are insoluble in organic media, but on treatment with dilute acid yield soluble monometallic derivatives, in which the metallic atom is probably attached to the chelate group, and, in the case of the copper derivatives, revert rapidly to the dimetallic salt. Alkaloidal salts of *beryllium* 3-m-*carboxybenzylbutyrylacetone* were ill-defined and unsuitable for resolution of the metallo-diketone. From ethyl ω-chloro-*o*-toluate and sodium acetylacetone, 3-o-*carbethoxybenzylacetylacetone*, b. p. 196°/14 mm. (*copper* derivative, m. p. 168—170°), was obtained.
H. BURTON.

Reaction between duroquinone and sodium malonic esters. L. I. SMITH and F. J. DOBROVOLNY (J. Amer. Chem. Soc., 1926, 48, 1693—1709).—When duroquinone is boiled in benzene solution for 8—10 days with ethyl sodiomalonate, the red, amorphous *sodium* salt (I) is precipitated, whilst if the reaction is carried out in an inert atmosphere, the solution contains duroquinol. Treatment of (I) with acids affords the *lactonic ester* (II), yellow, m. p. 184—185° (decomp.) (*acetyl* derivative, m. p. 177°), which is hydrolysed by concentrated acids or alkalis to the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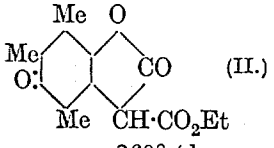
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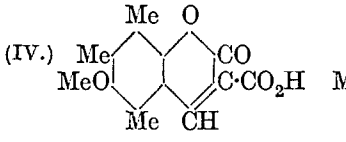
corresponding *acid* (III), yellow, m. p. 260° (decomp.) [*ammonium* salt; *silver* salt, greenish-yellow; *anilide*, yellow, m. p. above 200° (decomp.); *acetyl* derivative, m. p. 218°]. Esters of (III) can be prepared either by direct esterification, or by addition, as above, of the appropriate alkyl malonate to duroquinone; the following are described: *methyl*, m. p. 214° (*acetyl* derivative, m. p. 190°); n-*propyl*, m. p. 175° (*acetyl* derivative, m. p. 179°); iso*propyl*, m. p. 170°; n-*butyl*, m. p. 168° (*acetyl* derivative, m. p. 134°); iso*amyl*, m. p. 149°; glyceryl, m. p. 155° (decomp.); β-*chloroethyl*, m. p. 229°; and β-*bromoethyl* ester, m. p. 234—236° (decomp.). Treatment of (III), or of its methyl or ethyl ester, in alkaline solution, with excess of methyl sulphate, affords the *methyl ether* (IV), m. p. 195° (*silver* salt, yellow; *methyl* ester, m. p. 153—154°; *ethyl* ester, m. p. 108°). In neutral solution, a mixture of the methyl ether and the above methyl ester, m. p. 153—154°, is obtained, whilst if the ethyl ester of (III) be dissolved in methyl sulphate, and the solution treated with concentrated aqueous alkali, the product consists chiefly of the *tetramethyl* derivative, (V), m. p. 93°, and this, on hydrolysis with alcoholic sodium hydroxide, yields 2 : 5-*dimethoxy*-3 : 4 : 6-*trimethylbenzylidene-*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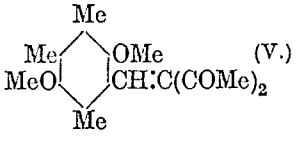
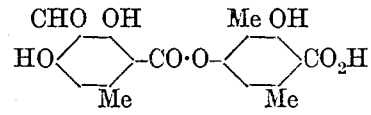

(V.)

malonic acid, m. p. 188° (decomp.) (*silver* salt). When fused with alkali, or heated at its m. p., the latter affords the above methyl derivative, m. p. 195°, whilst reduction with zinc dust and acetic acid yields 2 : 5-*dimethoxy*-3 : 4 : 6-*trimethylbenzylmalonic acid*, m. p. 154—155°, and oxidation with neutral permanganate affords 2 : 5-*dimethoxy*-3 : 4 : 6-*trimethylbenzaldehyde*, yellow, m. p. 84—85° (*oxime*, m. p. 132—134°). The aldehyde loses its yellow colour when kept in the dark, and regains it on exposure to sunlight. On reduction with sodium amalgam and methyl alcohol, it yields 2 : 5-*dimethoxy*-3 : 4 : 6-*trimethylbenzyl alcohol*, m. p. 115—116° (acetate, m. p. 65—66°), together with a *substance*, m. p., 242—244°, whilst treatment with nitric acid, *d* 1·4, affords nitrotrimethylbenzoquinone.
F. G. WILLSON.

Isomerisation of aldehydes to ketones. Isomerisation of di-*p*-tolylacetaldehyde to *p*-deoxytoluin. S. DANILOV and E. VENUS-DANILOVA (J. Russ. Phys. Chem. Soc., 1926, 57, 347—356, 428—438).—See this vol., 519, 726.

Constituents of lichens. I. Constitution of atranorin. A. S. PFAU (Helv. Chim. Acta, 1926, 9, 650—669).—The constitution of atranorin, isolated from the lichen *Evernia prunastri*, L. Ach., has been established and is represented by the annexed formula. Atranorin was isolated by the method of Hesse (A., 1916, i, 264; 1 to 3 g. per kg. of dried lichen), m. p. 194—195°, and is pale yellow, and not white as previously described. On heating with water or acetic acid, atranorin is converted into methyl β-orcinolcarboxylate (cf. Walbaum and Rosenthal, A., 1924, i, 758), which is hydrolysed by sodium hydroxide into β-orcinol and atranol (the physciol of Hesse, A., 1895, i, 298). Satisfactory separation of the two products cannot



be effected by crystallisation alone, but is readily effected by sodium hydrogen carbonate solution, in which the ester is insoluble. Atranol ($+0{\cdot}5H_2O$) (*semicarbazone*, m. p. 273—275°; *oxime*, m. p. 188—190°; *tetra-acetate*, m. p. 137°; *anilide*, m. p. 207—209°) on reduction by the Clemmensen method or catalytically, yields, among other products, β-orcinol (3 : 5-dihydroxy-*p*-xylene), and since the tetra-acetate regenerates the parent substance on hydrolysis, atranol must be either the aldehyde of *p*-orsellinic acid (3 : 5-dihydroxy-*p*-tolualdehyde, cf. Hoesch, A., 1913, i, 474) or 2 : 6-*dihydroxy*-p-*tolualdehyde*, m. p. 130—131°. The latter compound was synthesised from *p*-tolualdehyde by nitration of the dichloride, acetylation of the product to yield 3 : 5-*dinitro*-4-*methylbenzylidene diacetate*, m. p. 103·5—104°, catalytic reduction of this to the *diamine*, followed by diazotisation and hydrolysis, and was shown to be different from atranol. The structure of atranol was confirmed by oxidation by potassium permanganate to *p*-orsellinic acid, which was synthesised from orcinol, and by hydrogen peroxide in alkaline solution to 5-methylpyrogallol. The last on methylation yielded the trimethyl ether, which was finally oxidised by potassium permanganate to the trimethyl ether of gallic acid. Hæmatommic acid (Zopf, A., 1896, i, 103), obtained as its ethyl ester when atranorin is heated with alcohol, yields on hydrolysis atranol and carbon dioxide, and is therefore atranolcarboxylic acid (3 : 5-dihydroxy-*p*-tolualdehyde-2-carboxylic acid). J. W. Baker.

Method for determining *cis–trans*-isomerism in cyclic compounds. G. Vavon (Bull. Soc. chim., 1926, [iv], **39**, 666—673).—In isomeric compounds of the *cis–trans* type the steric effect of the two substituent atoms or groups is regarded as more important than the chemical effect in determining differences between the two isomerides. On the theory of steric hindrance, the reactions of the *cis*-derivative should be slower than those of the *trans*-isomeride, and the difference should be the more pronounced the greater the accumulation of groups at the position of *cis–trans*-isomerism. This deduction is in agreement with observed facts in the catalytic hydrogenation of cinnamic acids and their methyl esters (A., 1923, i, 464, 891) and of various nonanones (*ibid.*, 998). From steric considerations, it is shown that in the reduction of 1 : 2-alkyl*cyclo*hexanones the *cis*-isomeride should be formed in the greater proportion, since the alkyl group protects the *cis* and not the *trans* valencies of the ketone group. The *cis*-alcohol should esterify more slowly than the *trans*-form, and the *cis*-ester should be hydrolysed less readily than its *trans*-isomeride. All these requirements of the theory of steric hindrance are in harmony with the facts previously observed in the hydrogenation of 1 : 2-propyl*cyclo*hexanone and 1 : 2-*cyclo*hexyl*cyclo*hexanone, *l*-menthone (A., 1924, i, 1210), and *d*-camphor (A., 1925, i, 1079), and with the constitution of the *cis*- and *trans*-isomerides as determined by Auwers' method (A., 1920, i, 721). In the case of menthyl and *neo*menthyl *iso*valerates, however, the *cis*-form has the same density as the *trans*-form and a lower refractive index. R. Brightman.

Action of calcium hydride on organic compounds. III. Acetophenone. C. Porlezza and U. Gatti (Gazzetta, 1926, **56**, 265—277; cf. A., 1925, i, 788).—Under the influence of calcium hydride, acetophenone at its b. p. condenses slowly to give a product from which on distillation dypnone is isolated, with small quantities of *s*-triphenylbenzene, a substance, $C_{32}H_{26}O$, m. p. 135·5°, perhaps α-dypnopinacolin (cf. Delacre, A., 1892, 993), and also probably ethylbenzene, among other decomposition products. E. W. Wignall.

Influence of the solvent on the formation of naphthyl methyl ketone. A. S. Pfau and A. Ofner (Helv. Chim. Acta, 1926, **9**, 669—671).—Contrary to the work of Chopin (A., 1924, i, 861; F.P. 536257, 1921), α-naphthyl methyl ketone (*picrate*, m. p. 118°; *oxime*, m. p. 137—138°) possesses no characteristic odour, but the β-isomeride (*picrate*, m. p. 82°; *oxime*, m. p. 145—146°) has a strong odour resembling that of β-naphthyl methyl ether. The quantities of the two isomerides formed by Chopin's method depends on the solvent employed, the proportions of the α- and β-isomerides being 65 : 35 in carbon disulphide, 42 : 58 in chlorobenzene, and 11 : 89 in nitrobenzene. Separation by means of fractional distillation is unsatisfactory, but is readily effected by means of the picrates, the α-picrate crystallising first from alcohol. By means of the Beckmann change, the two oximes were converted into the corresponding acetonaphthalides, and hence to the free amines. J. W. Baker.

Action of organo-magnesium compounds on some aromatic *N*-dialkylamides. N. Maxim (Compt. rend., 1926, **182**, 1393—1395).—Condensation of a number of dialkylamides with magnesium alkyl halides in benzene, toluene, or ethereal solution gave solely ketonic derivatives in the normal manner, $R{\cdot}CO{\cdot}NR'_2+R''MgX \longrightarrow R{\cdot}CO{\cdot}R''+HNR'_2$. No trace of the secondary reactions recorded by Bouveault (A., 1905, i, 116), Busch and Fleischmann (A., 1910, i, 728), or Blaise and Montagne (A., 1925, i, 633) was observed. Benzdiethylamide, *phenylpropiondiethylamide*, b. p. 170°/11 mm., phenylacetamide, diphenylacetamide, and dibenzylacetamide all react normally with magnesium ethyl bromide to give ketones; *diphenylmethyl ethyl ketone* has b. p. 186°/14 mm. (*semicarbazone*, m. p. 189—190°), and β-*phenyl*-α-*benzylethyl ethyl ketone*, b. p. 205°/17 mm. (semicarbazone, m. p. 160—161°). Phenylacetdiethylamide, *diphenylacetdiethylamide*, m. p. 64—65°, and *dibenzylacetdiethylamide* (β-*phenyl*-α-*benzylpropiondiethylamide*), m. p. 56°, b. p. 225°/13 mm., do not react with magnesium ethyl bromide. H. J. Evans.

Addition of halogen to distyryl ketone. F. Arndt and P. Nachtwey (Ber., 1926, **59**, [*B*], 1073—1074; cf. Hellthaler, A., 1915, i, 267; Arndt, *ibid.*, 1925, i, 1307).—Addition of excess of chlorine to distyryl ketone at 0° gives the dichloride, m. p. 128—129°, whereas, at atmospheric temperature, the tetrachloride, m. p. 138—139°, is produced. The *monochloro*-derivative, m. p. 80—81°, and the *dichloride dibromide*, m. p. 178—179° after softening at 176°, are described. H. Wren.

Reactivity of *meso*-substituted anthracenes. I. J. W. Cook (J.C.S., 1926, 1282—1287).—Anthraphenone (9-benzoylanthracene), conveniently prepared by the action of benzoic anhydride on anthracene in presence of aluminium chloride, does not form additive compounds with bromine or nitric acid, but yields substitution products, viz., 10-*bromoanthraphenone*, m. p. 175—176°, and 10-nitroanthraphenone. With chlorine, one experiment gave the additive compound, 9 : 10-*dichloro*-9 : 10-*dihydroanthraphenone*, decomp. 110—111°, which on heating formed 10-*chloroanthraphenone*, m. p. 164—165°, and 9-chloroanthracene, but in all other cases substitution occurred. Nitrogen dioxide forms 9 : 10-*dinitro*-9 : 10-*dihydroanthraphenone*, decomp. 175°, which passes into 10-nitroanthraphenone by loss of nitrous acid. The effect of the *meso*-benzoyl group is shown to resemble that of other negative groups in rendering *meso*-additive compounds unstable, which is in harmony with Werner's theory of valency.

H. Burton.

Preparation of monocyclic ketones with more than nine ring members. M. Naef & Co.—See B., 1926, 608.

Preparation of substituted ketopolyhydronaphthalenes. J. D. Riedel A.-G.—See B., 1926, 610.

Isomerism of the styryl alkyl ketones. III. Methoxy-2- and 4-hydroxystyryl alkyl ketones. A. McGookin and D. J. Sinclair (J.C.S., 1926, 1578—1581).—Both forms of 5-methoxy-2-hydroxystyryl methyl ketone, m. p. 124°, on treatment with alkali give the *sodium* salt of 2 : 2′-*dihydroxy*-5 : 5′-*dimethoxydistyryl ketone*, m. p. 158°. The *colourless form* of 2-hydroxy-4-methoxystyryl methyl ketone, m. p. 131°, is prepared from 4-methoxysalicylaldehyde and acetone. With alkali, it yields the *sodium* salt of 2 : 2′-*dihydroxy*-4 : 4′-*dimethoxydistyryl ketone*, m. p. 170°. The product, m. p. 83°, obtained from 3-methoxysalicylaldehyde and acetone (cf. Heilbron and Whitworth, *ibid.*, 1923, **123**, 238; Nomura and Nozawa, A., 1918, i, 438) is regarded as a hydrate of 2-hydroxy-3-methoxystyryl methyl ketone; 3-*methoxy*-2-*acetoxystyryl methyl ketone*, m. p. 91°, is described, and it, like the corresponding benzoyl derivative, gives on hydrolysis the hydrated compound; this is converted by alkali into 2 : 2′-*dihydroxy*-3 : 3′-*dimethoxydistyryl ketone*, m. p. 182°. The substance, m. p. 77—77·5°, described by Nomura and Nozawa (*loc. cit.*) is not regarded as 2-hydroxy-3-methoxystyryl methyl ketone, because of its anomalous m. p. Addition of concentrated alkali to a solution of the yellow form of 4-hydroxy-3-methoxystyryl methyl ketone precipitates the *sodium* salt of the colourless form of the *ketone*, m. p. 129°; both forms are very stable. With alkali they yield the *sodium* salt of 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxydistyryl ketone*, m. p. 142° (*hydrate*, m. p. 121°).

F. M. Hamer.

Preparation of acyl and alkyl derivatives of resorcinol. A. R. L. Dohme, E. H. Cox, and E. Miller (J. Amer. Chem. Soc., 1926, **48**, 1688—1693).—n-*Hexoylresorcinol* (2 : 4-*dihydroxyphenyl* n-*amyl ketone*), m. p. 54·4—56°, b. p. 196—198°/6–7 mm., is obtained in 75% yield, calculated on the hexoic acid consumed, by adding resorcinol (95 g.) to a solution of anhydrous zinc chloride (125 g.) in hexoic acid (300 g.) at 125—135°, and stirring the mixture at this temperature for 2 hrs. (cf. Johnson and Lane, A., 1921, i, 340). On reduction with zinc amalgam and dilute hydrochloric acid, it yields n-*hexylresorcinol*, m. p. 67·5—69°, b. p. 178—180°/6—7 mm. The following acyl- and alkyl-resorcinols, obtained analogously, are described, all b. p. being at 6—7 mm.: *valeryl*-, m. p. 58·5—60°, b. p. 190—192°, and *amyl*-, m. p. 71·5—73°, b. p. 168—170°; *heptoyl*-, m. p. 48—50°, b. p. 204—206°, and *heptyl*-, m. p. 73—74·5°, b. p. 186—188°; *octoyl*-, m. p. 62·5—64°, b. p. 214—216°, and *octyl*-, m. p. 74—75°, b. p. 199—201°; *dodecoyl*-, m. p. 84—85·5°, b. p. 237—239°, and *dodecyl*-, m. p. 80—81·5°, b. p. 224—226°; iso*butyryl*-, m. p. 67—68·5°, b. p. 173—175°, and iso*butyl*-, m. p. 62—63·5°, b. p. 166—168°; iso*valeryl*-, m. p. 108—110°, b. p. 183—185°, and iso*amyl*-, m. p. 61—62·5°, b. p. 177—178°; and iso*hexoyl*-, m. p. 76—77·5°, b. p. 192—194°, and iso*hexyl-resorcinol*, m. p. 70—71·5°, b. p. 182—183°. Propylresorcinol has m. p. 81—82°, and butylresorcinol has m. p. 47—48° (cf. Johnson and Lane, *loc. cit.*).

F. G. Willson.

Union of indone and β-naphthaquinone nuclei by sulphur. K. Brass and G. Mosl (Ber., 1926, **59**, [*B*], 1266—1277).—2 : 3-Dichloroindone, m. p. 89—90° (2 mols.), is converted by sodium sulphide (1 mol.) in the presence of water at 50—60° into 3 : 3′-*dichloro*-2 : 2′-*di-indonyl sulphide*, $C_6H_4<\begin{matrix}CCl\\CO\end{matrix}>C\cdot S\cdot C<\begin{matrix}CCl\\CO\end{matrix}>C_6H_4$, m. p. 200° [*compound*, $(C_{18}H_8O_2Cl_2S)_2,SnCl_4$]. It is stable towards concentrated acids, except nitric acid, and does not yield a hydrazone or oxime. It is transformed by boiling aniline into the *dianil* of *dichlorodi-indonylaniline*, m. p. 250—260° (decomp.). Reduction with zinc dust and glacial acetic acid converts it into 1 : 1′-*dihydrodi-indenylene*, $C_{18}H_{12}O_2$ (*dibenzoyl* derivative). It could not be oxidised to a sulphoxide or sulphone. *Di-indonylenedithi-in*, $C_6H_4\cdot\begin{matrix}C\cdot S\cdot C\\CO—C\cdot S\cdot C\cdot CO\end{matrix}\cdot C_6H_4$, is readily prepared from the sulphide (1 mol.) and sodium sulphide (1 mol.) or from 2 : 3-dichloroindone (2 mols.) and sodium sulphide (2 mols.). It shows a marked tendency towards contraction of the ring, thus giving derivatives of thiophen or *cyclo*butadiene. Thus with concentrated sulphuric or nitric acid it affords quantitatively sulphur and di-indonylene (truxenequinone), also obtained from 2 : 3-dichloroindone and copper powder; this substance is reduced by zinc dust and acetic anhydride to di-indenylene (truxene). Reduction of di-indonylenedithi-in in alkaline solution affords 1 : 1′-dihydroxydi-indenylene (see above), whereas in acid solution only one sulphur atom is removed with production of *dihydroxydi-indenylthiophen*, m. p. 235—238° (decomp.). Whilst an oxime or hydrazone could not be prepared, the action of aniline at low temperature affords the normal *dianil* of *di-indonylenedithi-in*, whereas the

boiling reagent yields the *dianil* of *phenyldi-indonylene-thiazine*, $\begin{matrix} C_6H_4 & C & S & C & C_6H_4 \\ & \| & & \| & \\ & C(:NPh)\cdot C & \cdot NPh\cdot & C & \cdot C:NPh \end{matrix}$. The production of anil or thiazine is always accompanied by that of di-indonylene.

The behaviour of 3 : 4-dichloro-β-naphthaquinone towards sodium sulphide differs from that of 2 : 3-dichloroindone, since 2 mols. of the quinone require 2 mols. of sodium sulphide, one of which is required for reduction to the quinol with which reaction takes place; subsequent oxidation of the solution yields *dichlorodi-β-naphthaquinonyl sulphide*, m. p. about 240° (decomp.), in almost theoretical yield. Attempts to prepare a dithi-in were unsuccessful.

H. WREN.

Molecular weight of truxene and its derivatives. K. BRASS (Ber., 1926, **59**, [*B*], 1278—1279).—The identity of di-indenylene with truxene and di-indonylene with truxenequinone (cf. preceding abstract) combined with the mode of formation and determinations of mol. wt. establishes the bimolecular structure of truxene and related compounds. H. WREN.

Oxidation of the tribromo- and trichloro-derivatives of pyrogallol 1 : 3-dimethyl ether. W. H. HUNTER and A. A. LEVINE (J. Amer. Chem. Soc., 1926, **48**, 1608—1614).—Treatment of pyrogallol 1 : 3-dimethyl ether with bromine in carbon disulphide solution below 0° affords 4 : 5 : 6-*tribromopyrogallol* 1 : 3-*dimethyl ether*, m. p. 133·5° [*sodium* salt ($+4H_2O$); *benzoate*, m. p. 129—130°; *acetate*, m. p. 113—114°]. Chlorine affords similarly 4 : 5 : 6-*trichloropyrogallol* 1 : 3-*dimethyl ether*, m. p. 121·5° (*benzoate*, m. p. 103—104°; *acetate*, m. p. 102—103°). Oxidation of tribromopyrogallol 1 : 3-dimethyl ether with chromium trioxide in cold glacial acetic acid affords 3 : 5-dibromo-2 : 6-dimethoxybenzoquinone (I) (cf. Will, A., 1888, 457) in 40% yield. In cold 50% acetic acid, similar oxidation affords 3 : 5-*dibromo*-6-*methoxy*-2-(3′ : 4′ : 5′-*tribromo*-2′ : 6′-*dimethoxyphenoxy*)-*benzoquinone* (II), red, m. p. 214°, in 40% yield, whilst at 50—60°, traces of (I) and a colourless *substance*, m. p. 198—199°, are also obtained. Lead dioxide in cold glacial acetic acid affords similarly (II) in 60% yield, with a small proportion of (I), lead dioxide in benzene affords (II) in 70% yield, whilst sodium nitrite in glacial acetic acid affords (II) in 25% yield. Reduction of (II) with sulphur dioxide in aqueous acetone affords the corresponding *quinol* as an uncrystallisable oil (*acetate*, m. p. 150·5—151·5°).

Oxidation of 4 : 5 : 6-trichloropyrogallol 1 : 3-dimethyl ether with chromium trioxide in glacial acetic acid affords 3 : 5-dichloro-2 : 6-dimethoxybenzoquinone (cf. Graebe and Hess, A., 1905, i, 698), whilst chromium trioxide in 50% acetic acid at 50—60° affords 3 : 5-*dichloro*-2 : 6-*dimethoxy*-2-(3′ : 4′ : 5′-*trichloro*-2′ : 6′-*dimethoxyphenoxy*)*benzoquinone*, red, m. p. 211°, together with a trace of a colourless *substance*. 3 : 5-*Dibromo*-2 : 6-*dimethoxyquinol diacetate*, m. p. 100—101°, and 3 : 5-*dichloro*-2 : 6-*dimethoxyquinol diacetate*, m. p. 75°, were prepared.

F. G. WILLSON.

Oxidation of trichlorophenol. W. H. HUNTER and M. MORSE (J. Amer. Chem. Soc., 1926, **48**, 1615—1624; cf. preceding abstract).—Oxidation of 2 : 4 : 6-trichlorophenol with chromic acid in glacial acetic acid at 30—40° (cf. Kehrmann and Tiesler, A., 1890, 241) affords 2 : 6-dichlorobenzoquinone in 27% yield, together with 6-*chloro*-2-(2′ : 4′ : 6′-*trichlorophenoxy*)*benzoquinone* (I), yellow, m. p. 134—135° (cf. Ling, J.C.S., 1892, **61**, 559). The latter is also obtained by the oxidation of trichlorophenol with lead dioxide in glacial acetic acid or benzene, but is accompanied, in the last case, by 2 : 6-*di*-(2′ : 4′ : 6′-*trichlorophenoxy*)*benzoquinone* (II), deep yellow, m. p. 245°. Reduction of (I) with sulphur dioxide in aqueous acetone affords the corresponding *quinol*, m. p. 169°, which is also formed, together with 6-*chloro*-5-*anilino*-2-*trichlorophenoxybenzoquinone* (III), red, m. p. 194°, by the action of aniline (0·5 mol.) on (I) in presence of alcoholic hydrochloric acid. Reduction of (III) with stannous chloride affords the corresponding *quinol*, m. p. 156° (*triacetyl* derivative, amorphous). Treatment of (I) with excess of aniline affords 6-chloro-2 : 5-dianilinobenzoquinone (cf. Niemeyer, A., 1885, 1065) whilst treatment with methylaniline (0·5 mol.) yields 6-*chloro*-5-*methylanilino*-2-(*trichlorophenoxy*)*benzoquinone*, blue, m. p. 164°. Reduction of (II) with stannous chloride affords the corresponding *quinol*, m. p. 235° (*diacetate*, m. p. 238°), whilst treatment with excess of aniline affords 2 : 5-*dianilino*-6-(*trichlorophenoxy*)-*benzoquinone*, m. p. 189°. The formation of the above oxidation products is taken to indicate the intermediate production of unsaturated radicals.

F. G. WILLSON.

Derivatives of β-methylanthraquinone. VIII. Bromination of 1 : 8-dinitro-2-methylanthraquinone. R. EDER and O. MANOUKIAN (Helv. Chim. Acta, 1926, **9**, 676—678).—On treatment with bromine at 170—180° in nitrobenzene solution, 1 : 8-dinitro-2-methylanthraquinone yields *ω-bromo*-1 : 8-*dinitro*-2-*methylanthraquinone*, m. p. 249—250°, which on oxidation with nitric acid and chromium trioxide yields 1 : 8-dinitroanthraquinone-2-carboxylic acid, thus proving that the bromine has entered the side-chain. Attempts to replace the bromine by hydroxyl were unsuccessful, and treatment with 80—90% sulphuric acid yielded 3-*bromo*-8(?)-*nitro*-1(?)-*aminoanthraquinone*-2-*carboxylic acid*.

J. W. BAKER.

Derivatives of β-methylanthraquinone. IX. Action of sulphite on 1 : 5- and 1 : 8-dinitro-2-methylanthraquinone. R. EDER and O. MANOUKIAN (Helv. Chim. Acta, 1926, **9**, 679).—When heated with a 20% sulphite solution for 8—10 hrs., 1 : 8-dinitro-2-methylanthraquinone passes into solution, whilst the corresponding 1 : 5-dinitro-compound is not attacked; hence this method can be employed for the separation of the two isomerides from the mixture obtained by nitration of 2-methylanthraquinone. J. W. BAKER.

Action of thionyl chloride on hydroxyanthraquinones. II. Quinizarin. A. GREEN (J.C.S., 1926, 1428—1437).—Boiling thionyl chloride converts quinizarin into 10-*chloro*-1-*hydroxy*-4 : 9-*anthra*-

quinone (annexed formula), m. p. 225—226°, which is reconverted into quinizarin by hot concentrated sulphuric acid, hot sodium or potassium hydroxides, heating with methyl alcohol, ethyl alcohol, or acetic acid under pressure. The red colour of the compound supports the suggested structure. Ethyl alcohol with 3% hydrochloric acid converts the chloro-compound into 10-*ethoxy*-1-*hydroxy*-4 : 9-*anthraquinone*, m. p. 135°, which also gives quinizarin on treatment with hot concentrated sulphuric acid, whilst acetylation converts it into diacetylquinizarin. Condensation with aniline and *p*-toluidine gives an *anilino*-derivative, decomp. 290°, and a *p-toluidino*-derivative, softens 280—310°, whilst in the presence of boric acid a *dianilino*-derivative, m. p. above 310°, and a *di*-p-*toluidino*-derivative, decomp. 305°, are obtained. 1-*Chloro*-4-*acetoxyanthraquinone*, m. p. 176—177°, on hydrolysis gives pure 1-chloro-4-hydroxyanthraquinone, m. p. 192—193°, which is unaffected by hot concentrated sulphuric acid. Diacetylquinizarin exists in two polymorphic forms, m. p. 207—208° and 200—201°. H. BURTON.

Violanthrone dyes from benzofluorenones. E. GEORGEACOPOL (Bul. Chim., Soc. Româna Stiinte, 1925, **28**, 3—18).—The method of Schaarschmidt (A., 1918, i, 434) may be applied to the synthesis of the hitherto inaccessible benzo-substituted benzanthrones and the corresponding violanthrones and *iso*violanthrones. When 1 : 9-benzanthrone-2′-carboxylic acid is fused with alcoholic potassium hydroxide, *violanthrone*-1 : 12-*dicarboxylic acid* (for numbering see A., 1925, i, 1436) is formed at 185°, and violanthrone itself at 350°. 2′-Benzoyl-1 : 9-benzanthrone yields at 160—200° 1 : 12-*dibenzoylviolanthrone*, a bluish-violet dye. 1-Phenylnaphthalene-2′ : 3-dicarboxylic acid is converted on bromination into 4-*bromo*-1-*phenylnaphthalene*-2′ : 3-*dicarboxylic acid*, m. p. 282°. 3′-*Bromo*-2′-*benzoylbenzanthrone*, prepared from the latter by the Friedel–Crafts method, affords, on alkaline fusion at 165°, 6 : 12-*dibenzoyl*-iso*violanthrone*, a pure blue dye. Violanthrone dyes may also be prepared directly from benzofluorenones by alkaline fusion at 345°. Under these conditions, 3 : 4-benzofluorenone-1-carboxylic acid gives 45% of violanthrone and 1-benzoyl-3 : 4-benzofluorenone 60% of a violet *dye*. H. E. F. NOTTON.

Mono-oxamic acids of diaminoanthraquinones. BRITISH DYESTUFFS CORPN., LTD., H. M. BUNBURY, and R. ROBINSON.—See B., 1926, 528.

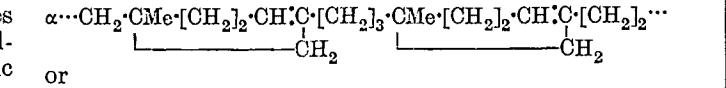
Benzanthrone dyes and intermediates. R. F. THOMPSON, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1926, 576.

Natural musk. H. WALBAUM (J. pr. Chem., 1926, [ii], **113**, 166—170; cf. A., 1906, i, 595).—Muskone, α_D −10° 6′, possibly a methylpentadecanone, on repeated oxidation with sodium dichromate and sulphuric acid yields an inactive, dibasic *acid*, $C_{16}H_{30}O_4$, m. p. 53—58°, b. p. 237°/3 mm., not obtained pure; the *barium* and *silver* salts are described. The ketone is readily reduced by sodium and amyl alcohol to the corresponding alcohol, *muskol*, m. p. 38°; *phenylcarbamate*, m. p. 97—98°; *formate*, b. p. 173—178°/8 mm. Muskonoxime, m. p. 46°, is converted into the iso*oxime*, m. p. 90—95°, when warmed with sulphuric acid. Valeric acid is shown to be present in musk oil.

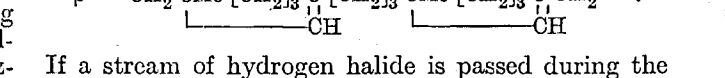
J. S. H. DAVIES.

Cochineal and kermes. E. JUSTIN-MUELLER (Bull. Soc. chim., 1926, [iv], **39**, 791—792).—The greater fastness towards alkali and to transpiration tests of the colouring matter from kermes (kermesic acid) as compared with that from cochineal is attributed to a polyhydric benzene radical in Dimroth's formula (A., 1910, i, 487) as compared with a polyhydric naphthalene nucleus in the carminic acid molecule (A., 1909, i, 485). R. BRIGHTMAN.

Isoprene and caoutchouc. IX. Formation of *cyclo*caoutchouc from caoutchouc hydrogen halides. H. STAUDINGER and W. WIDMER (Helv. Chim. Acta, 1926, **9**, 529—549).—Prolonged treatment of caoutchouc hydrochloride or bromide with zinc dust in boiling toluene, xylene, or tetralin solution without passing in a stream of hydrogen halide yields an isomeric *monocyclic caoutchouc* which contains only half the number of double linkings present in the original molecule, and for which the following constitution is suggested :



or



If a stream of hydrogen halide is passed during the reduction, a *polycyclic caoutchouc*, $(C_{20}H_{32})_x$, d_4^{17} 0·992, n_D^{17} 1·5387, heat of combustion 10,500 cal./mol., which has one double linking (unaffected by further reduction) for every four isoprene mols. present, is produced. The molecular complexity of the product (and hence also its m. p.) is greater the lower the b. p. of the solvent employed in the reduction. The same products, but less pure, are obtained if iron or tin is used for the reduction. Similar reduction of γ-chloro-γ-ethylnonane and 1-bromo-4-methyl-1-ethyl*cyclo*hexane, yields only the ethylenic hydrocarbons without ring formation occurring, but βζ-dichloro(dibromo)-βζ-dimethylheptane yields a mixture of α- and β-*cyclo*geraniolenes, hence for ring formation to occur it is necessary to have a second halogen atom in the δ-position to the first. Polycyclic caoutchouc has no elastic properties, and on reduction with hydrogen at 50 atm. and 270° in the presence of a nickel catalyst, it yields a *dihydro*-compound, $C_{20}H_{34}$ (saturated to bromine), which is also obtained, unexpectedly, by a similar reduction of monocyclic caoutchouc. Oxidation with ozone or potassium permanganate yielded caoutchouc oxide $(C_5H_8O)_x$ (cf. Pummerer and Bukhard, A., 1923, i, 49), whilst nitric acid yielded the same products as were obtained from caoutchouc, and hence in the latter case ring formation probably precedes oxidation. Polycyclic caoutchouc decomposes when heated either at atmospheric pressure or in a high

vacuum (350°), yielding products similar to those obtained from caoutchouc (cf. following abstract).

J. W. BAKER.

Isoprene and caoutchouc. X. Behaviour of caoutchouc on heating. H. STAUDINGER and E. GREIGER (Helv. Chim. Acta, 1926, **9**, 549—557).—The m. p. of caoutchouc is lower in air than in a vacuum, since liquefaction is favoured by auto-oxidation. Heated in a vacuum or an inert atmosphere, caoutchouc is stable up to 200°, above which temperature a polycyclic caoutchouc, $(C_5H_8)_{35}$, with similar properties to that obtained from caoutchouc hydrochloride or bromide (cf. preceding abstract), but containing one double linking for every five isoprene residues, is formed, a 50% yield being obtained at 300—320°. At this temperature, from the distillable products can be isolated a *cyclo*hexadiene, b. p. 72—73°, a tetrahydrotoluene, b. p. 103—105°, a little isoprene, and 40% of pure dipentene, together with sesquiterpenes and higher terpenes. At 350—400°, the polycyclic caoutchouc is decomposed, yielding a mixture of higher-boiling, cyclic hydrocarbons from which no simple substance was isolated, but no dipentene is formed in this decomposition. Complete pyrogenic decomposition of caoutchouc either at atmospheric pressure or in a vacuum yields 90—95% of distillable products. When caoutchouc is heated in ether solution at 250° for 2 days, conversion into the polycyclic caoutchouc is quantitative, and is probably represented thus: $\cdots CH_2\cdot CMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CH\cdot[CH_2]_2\cdot CMe{:}CH\cdot CH_2\cdots \longrightarrow CH_2\cdot C\cdot[CH_2]_3\cdot C\cdot[CH_2]_3\cdot C\cdot CH_2\cdots$ (with CH_2 bridges). Reduction of the polycyclic caoutchouc with hydrogen at 85 atm. and 290—295° with a nickel catalyst yields a *hydropolycyclic caoutchouc*, $(C_{25}H_{42})_x$, mol. wt. 2050, n_D^{16} 1·5263, d_4^{16} 0·986.

J. W. BAKER.

Resin of *Hevea* rubber. G. S. WHITBY, J. DOLID, and F. H. YORSTON (J.C.S., 1926, 1448—1457).—In the resin which forms about 3% of plantation rubber the following substances have been identified: a *steryl* ester, $C_{17}H_{33}O_2\cdot C_{27}H_{45}$, m. p. 83°, $[\alpha]_D^{24}$ −11·1°, −10·8° (all rotations measured in chloroform), which on hydrolysis yields a *sterol*, $C_{27}H_{46}O$, m. p. 133—134°, $[\alpha]_D^{21}$ −23·2°, the *acetate* of which has m. p. 113—114°, and an *acid*, $C_{17}H_{34}O_2$, m. p. 73—75° (*silver* salt, $C_{17}H_{33}O_2Ag$); a *sterol*, $C_{27}H_{46}O_2$, m. p. 125°, $[\alpha]_D^{23\cdot5}$ −24·6°, which yields an *acetate*, m. p. 114—115°, $[\alpha]_D^{22}$ −30·6°, a *propionate*, m. p. 98°, $[\alpha]_D^{23}$ −29·4°, and a *benzoate*, m. p. 144—145°, $[\alpha]_D^{22}$ −20·7°; a sterol glucoside, probably sitosterol *d*-glucoside, which forms an *acetate*, m. p. 165°, $[\alpha]_D^{22}$ −22·4°, and a *benzoate*, m. p. 198°, $[\alpha]_D^{22}$ +15·7°, +16·1°; *d*-valine; quebrachitol; stearic, oleic, and linoleic acids. These three acids make up the greater proportion of *Hevea* resin, which renders this resin unique amongst resins in general.

C. J. STILL.

Terpene and sesquiterpene of Mitsuba-zeri. N. HIRAO (Bull. Chem. Soc. Japan, 1926, **1**, 74—79).—See this vol., 408.

Constitution of oxidation products obtained by the action of chromyl chloride on terpenes, as deduced from a new interpretation of the reaction. J. SWORD (Chem. News, 1926, **133**, 1—4).—Chromyl chloride combines with certain hydrocarbons either by addition of $2CrO_2Cl_2$ at a double linking, or by displacing and combining with two hydrogen atoms from adjacent carbons or even from a single methyl group. Decomposition of the additive compound yields aldehydes, and ketones or diketones, according to circumstances.

B. W. ANDERSON.

Methylene derivatives of menthone. H. RUPE and A. W. GUBLER (Helv. Chim. Acta, 1926, **9**, 582—591).—Catalytic reduction of pulegone yields *d*-menthone, whilst from the mother-liquors of the semicarbazone formation is obtained another *semicarbazone*, m. p. 176°, from which the regenerated menthone has b. p. 89° (? 98°)/11 mm., but $[\alpha]_D$ +6·0° to +13·8°. Hydroxymethylenementhone, prepared in 55—65% yield by a modification of the method of Bishop, Claisen, and Sinclair (A., 1895, i, 62), using sodamide in place of sodium, on oxidation with ozone yields α-methyl-α-*iso*propyladipic acid (cf. Semmler and McKenzie, A., 1906, i, 373), and on catalytic reduction yields *menthylcarbinol*, b. p. 129—130°/11 mm., d^{20} 0·9875 (*acetate*, b. p. 147—148°/11 mm.; *formate*, b. p. 141—142°/11 mm.; *benzoate*, b. p. 118°/high vac.; p-*nitrobenzoate*, m. p. 102—103°). In some distillations of the crude carbinol, probably when traces of nickel remained, explosive heating occurred at 130°, and subsequent distillation then yielded methylmenthone, methylenementhone (see below), and s-*dimenthylethane*, b. p. 197°/11 mm., together with its *isomeride*, b. p. 224°/11 mm., both products being also obtained by the method previously employed for the preparation of *s*-dicamphylethane (Rupe and Akermann, A., 1919, i, 335). *Methylenementhone*, b. p. 98°/11 mm., d^{20} 0·9226, is also obtained by dehydration of the carbinol with calcium chloride or sulphuric acid (*d* 1·675). On oxidation with ozone or potassium permanganate, it yields γ-acetyl-α-*iso*propylbutyric acid, whilst with chromic acid is obtained an *aldehyde*, $C_{11}H_{14}O_2$, b. p. 114—115°/11 mm., d^{20} 1·032 (*oxime*, m. p. 146°; *semicarbazone*, m. p. 221—222°), which is provisionally regarded as 2-*methyl*-5-n-*propyl*-$\Delta^{1:4}$-cyclo*hexadien*-6-*one*-1-*aldehyde*.

J. W. BAKER.

Action of picric acid on *d*-α-pinene and on *l*-β-pinene (nopinene). M. DELÉPINE and A. ADIDA (Bull. Soc. chim., 1926, [iv], **39**, 782—788; cf. A., 1924, i, 1084, 1088).—Using a *d*-α-pinene (α +41°) from Aleppo turpentine and an *l*-β-pinene (nopinene) (α −18·8°), it is shown that picric acid behaves similarly to the carboxylic acids previously studied. *d*-α-Pinene and nopinene both yield a bornyl picrate, m. p. 134°, $[\alpha]_D$ +78·8°, contaminated with a little racemate and *iso*bornyl picrate, together with fenchyl picrate, and there is partial isomerisation into limonene and camphene, and of β-pinene into α-pinene (cf. Lextreit, A., 1886, 71).

R. BRIGHTMAN.

Constitution of the (so-called) potassium salt of bornyl picrate. M. DELÉPINE and M. GRANDPERRIN (Bull. Soc. chim., 1926, [iv], **39**, 788—790).—The red explosive compound obtained by the action of alcoholic potassium hydroxide on pinene or "turpentine" picrate (Lextreit, A., 1886, 71; Tilden and Forster, J.C.S., 1893, **63**, 1388) has the structure $C_{10}H_{17}O{\cdot}C_6H_2(OEt)(NO_2)_2{\cdot}NO{\cdot}OK$, and is a bornyl ether, similar to derivatives obtained by Jackson (A., 1900, i, 433) and Meisenheimer (A., 1902, i, 795). Bright red *cæsium* and *rubidium* compounds of the same type have been obtained by the action of the alcoholic alkali hydroxide on *d*-bornyl picrate, and a similar *potassium* compound from fenchyl picrate. R. BRIGHTMAN.

Production of bornyl esters from pinenes etc. V. ISAJEV.—See B., 1926, 608.

2-Azidocoumaran-3-one. K. FRIES and K. SAFTIEN.—See this vol., 849.

Derivatives of furfuraldehyde. I. Condensation of furfuraldehyde with aliphatic ketones. I. KASIWAGI (Bull. Chem. Soc. Japan, 1926, **1**, 90—95).—Furfuraldehyde condenses with aliphatic ketones in the presence of sodium hydroxide solution to form yellow oils with fruit-like odours. The following have been prepared: *α-furyl-Δ$^{\alpha}$-penten-γ-one*, b. p. 234—235°, d_4^{25} 1·068, n_D^{25} 1·627 (*semicarbazone*, m. p. 201·5—202·5°); *α-furyl-γ-pentanone*, b. p. 206—208°, d_4^{25} 1·003, n_D^{25} 1·468 (formed by reduction of the above); *α-furyl-β-methyl-Δ$^{\alpha}$-penten-γ-one*, b. p. 135°/12 mm., d_4^{25} 1·052, n_D^{25} 1·557 (*semicarbazone*, m. p. 175—176°); *α-furyl-β-methyl-γ-pentanone*, b. p. 93—100°/13 mm., d_4^{25} 0·995, n_D^{25} 1·466; *α-furyl-δ-methyl-Δ$^{\alpha}$-penten-γ-one*, b. p. 133—136°/18 mm., d_4^{25} 1·0199, n_D^{25} 1·557; and *α-furyl-δδ-dimethyl-Δ$^{\alpha}$-penten-γ-one*, b. p. 145—147°/35 mm., d_4^{25} 1·007, n_D^{25} 1·548. The differences between the observed and calculated molecular refractions of the above compounds are negligible with the saturated compounds, but large with the unsaturated (containing two conjugated double linkings). B. W. ANDERSON.

Preparation of xanthone, preparatory to that of xanthydrol. L.-J. SIMON (Bull. Soc. Chim. biol., 1926, **8**, 203—205).—Xanthone is readily obtained in 75% yield by the dry distillation of acetylsalicylic acid at atmospheric pressure (cf. Perkin, J.C.S., 1883, **43**, 35). C. P. STEWART.

Dissociation into free radicals of substituted dixanthyls. III. Effectiveness of secondary alkyl groups in promoting dissociation. J. B. CONANT, L. F. SMALL, and A. W. SLOAN (J. Amer. Chem. Soc., 1926, **48**, 1743—1757; cf. this vol., 158).—*Methylxanthyl perchlorate*, orange-yellow, m. p. 209—210° (decomp.) after darkening at 190°, is obtained, together with a green *product*, m. p. 198° after darkening at 185°, by the action of magnesium methyl iodide on xanthone, with subsequent treatment with perchloric acid. On reduction with vanadous chloride, it yields *dimethyldixanthyl*, m. p. 181—181·5°. This absorbs oxygen in bromobenzene solution. In ethyl benzoate solution, it assumes a yellow colour at 160°, deepening at 212°, and then fading owing to decomposition. *Ethylxanthyl perchlorate*, yellow, m. p. 191—192° (decomp.) (cf. Fosse and Baillon, Bull. Soc. chim., 1907, [iv], **1**, 861), similarly affords *diethyldixanthyl*, m. p. 194°, which also absorbs oxygen. *α-Naphthylmethylxanthydrol*, m. p. 137—138°, obtained from α-chloromethylnaphthalene (cf. Braun and Moldaenke, A., 1923, i, 1193), yields, on reduction, *di-α-naphthylmethyldixanthyl*, m. p. 182—183°, which absorbs oxygen rapidly in bromobenzene solution, but a peroxide could not be isolated.

β-Phenylethylxanthyl perchlorate, orange-red, m. p. 191—193·5°, *di-β-phenylethyldixanthyl*, m. p. 180—182°, *γ-phenylpropylxanthyl perchlorate*, yellow, m. p. 181—183·5°, and *di-γ-phenylpropyldixanthyl*, m. p. 190°, were prepared analogously.

Magnesium *iso*propyl bromide converts xanthone into iso*propylxanthydrol*, m. p. 75°, together with a *product*, $C_{26}H_{18}O_4$, m. p. 164° (*perchlorate*, red). The former yields a yellow *perchlorate*, decomp. 210—211° after turning black at 200°, on reduction of which *di*iso*propyldixanthyl*, yellow, blackening on exposure to air, is obtained. Solutions of this compound become colourless at −20°, and also when exposed to oxygen, owing to the formation of the *peroxide*, m. p. 124—127°. The following compounds, obtained analogously, are described: sec.-*butylxanthydrol*, m. p. 70° [*perchlorate*, orange-yellow, m. p. 161° (decomp.) after darkening at 158°]; *di*-sec.-*butyldixanthyl*, yellow [*peroxide*, m. p. 133—134° (decomp.)]; iso*butylxanthydrol*, m. p. 115—117° [*perchlorate*, yellow, m. p. 200—204° (decomp.) after becoming green at 167°]; and *di*iso*butyldixanthyl*, m. p. 139° [*peroxide*, m. p. 177° (decomp.)]. Di*cyclo*hexylphenylmethyl chloride yields *cyclo*hexylidene*cyclo*hexylphenylmethane, b. p. 134—135°/0·3 mm. (cf. Godchot, A., 1910, i, 104), when treated with molecular silver in toluene, and not *s*-tetra*cyclo*hexyldiphenylethane, as previously reported (cf. Gray and Marvel, this vol., 43).

F. G. WILLSON.

Rosenmund's aldehyde synthesis applied to [heterocyclic] nitrogen and sulphur compounds. C. A. ROJAHN and J. SCHULTEN (Arch. Pharm., 1926, **264**, 348—355; cf. this vol., 846).—Chiefly because the catalyst is so readily "poisoned," the application of Rosenmund's method cannot be extended in the way indicated. Thus thiophen-2-carboxyl chloride (b. p. 201—203°) gives, and only after repeated addition of catalyst, a poor yield of the aldehyde; most of the material is recovered as the *anhydride*, m. p. 61°. Similarly, dibromothiophen-2-carboxyl chloride gives only a small proportion of the *aldehyde* (*semicarbazone*, m. p. 248°; *oxime*, m. p. 139°), isolated as its hydrogen sulphite compound. Picolinyl chloride affords a trace of *aldehyde* (*semicarbazone*, m. p. 241°; *oxime*, m. p. 215°), together with the parent acid and pyridine. *iso*Nicotinyl chloride is similarly unfruitful, the *aldehyde* here being isolated only as the *semicarbazone*, m. p. about 258°. 2-Phenylcinchoninyl chloride (m. p. 73—74°; the compound described in D.R.-P. 252643 is an impure hydrochloride) affords the corresponding *anilide* (m. p. 198°) and *phenylhydrazide* (m. p. 215°). On reduction, it is converted chiefly into the *anhydride* (m. p. 185°; *methiodide*, m. p. 132°), but a trace of *aldehyde* (*oxime*, m. p. 126—127°,

decomp.; *aminoguanidone nitrate*, m. p. 141°, decomp.) is obtained. W. A. SILVESTER.

Compounds of thiophen. II. H. SCHEIBLER and F. RETTIG (Ber., 1926, 59, [*B*], 1194—1197; cf. A., 1921, i, 191).—Ethyl *n*-butylsodiomalonate and ethyl chloroacetate yield *ethyl* n-*hexane*-αββ-*tricarboxylate*, b. p. 183—185°/760 mm., which is transformed into *n*-butylsuccinic acid, m. p. 81°. Sodium *n*-butylsuccinate and phosphorus trisulphide afford 3-n-*butylthiophen*, b. p. 181—183°/760 mm., d_{20}^{20} 0·9587, n_D^{20} 1·51005, which, with acetyl chloride and aluminium chloride, yields 2-(5-)*acetyl*-3-n-*butylthiophen*, b. p. 145—146°/25 mm., n_D^{20} 1·50690 [p-*nitrophenylhydrazone*, m. p. 146—147° (corr.)]. Thiophen, butyryl chloride, and aluminium chloride give 2-n-*butyrylthiophen*, b. p. 123—124°/25 mm., d_{20}^{20} 1·0730, n_D^{20} 1·52418, which is reduced by zinc and hydrochloric acid to 2-n-*butylthiophen*, d_{20}^{20} 0·9554, n_D^{20} 1·50896. 5-*Acetyl*-2-n-*butylthiophen*, b. p. 160—161°/25 mm., d_{20}^{20} 0·9969, n_D^{20} 1·49135, and its p-*nitrophenylhydrazone*, m. p. 164° (corr.), are described. H. WREN.

Derivatives of thiosalicylic [*o*-thiolbenzoic] acid and 3-oxythionaphthen. F. ARNDT, A. KIRSCH, and P. NACHTWEY (Ber., 1926, 59, [*B*], 1074—1081).—*Ethyl* 3-*oxythionaphthen*-2-*carboxylate*, m. p. 73—74°, is prepared by condensation of dithiosalicyloyl dichloride, m. p. 153°, with ethyl sodioacetoacetate in ether or benzene and subsequent hydrolysis of the product, or by loss of alcohol from ethyl *o*-carbethoxyphenylthiolacetate. *o*-Aminobenzonitrile, m. p. 46—47° (cf. Kirsch, Diss., Breslau, 1924) is transformed into o-*thiocyanobenzonitrile*, m. p. 83°, which, with magnesium methyl iodide, gives mainly o-*methylthiolbenzonitrile*, m. p. 37° (prepared also from *o*-thiocyanobenzonitrile by successive treatment with alcoholic potassium hydroxide and zinc dust, and methyl sulphate). *Dithiosalicylodinitrile*, m. p. 101—102°, is obtained from *o*-thiocyanobenzonitrile by successive treatment with dilute alcoholic potassium hydroxide and potassium ferricyanide. o-*Thiocyanoacetophenone*, m. p. 60—61°, from *o*-aminoacetophenone, is converted by alcoholic potassium hydroxide or zinc dust and hydrochloric acid into 3-oxythionaphthen or thionaphthen, respectively.

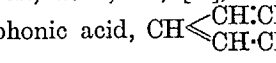
3-Oxythionaphthensulphone, m. p. 136° (cf. Lanfry, A., 1912, i, 293), prepared from 3-oxythionaphthen and hydrogen peroxide in cold acetic acid, is identical with the by-product obtained by the action of fuming sulphuric acid on ethyl benzoylacetate (cf. Feist, this vol., 74). The main product of the latter action (Feist's "anhydro-derivative") is readily hydrolysed to o-*carboxyphenylsulphonylacetic acid*, m. p. 166—168° (decomp.) [*monohydrate*, m. p. about 103° after softening at 70°; *methyl* ester, m. p. 103—104°], described by Feist as *o*-sulphobenzoylacetic acid, and hence has the constitution $C_6H_4<^{CO}_{SO_2}>CH\cdot CO_2Et$. *o*-Carboxyphenylsulphonylacetic acid is also prepared by oxidation of *o*-carboxyphenylthiolacetic acid by hydrogen peroxide. Similarly, 3-oxythionaphthensulphone is hydrolysed to o-*methylsulphonylbenzoic acid*, m. p. 138—140° after softening at 135° (*methyl* ester, m. p. 63—64°), prepared also by oxidising *o*-methylthiolbenzoic acid by hydrogen peroxide [o-*methylsulphoxidobenzoic acid*, m. p. 176—178° (decomp.) after softening at 175°, is also described]. Treatment of ethyl 3-oxythionaphthensulphone-2-carboxylate with methyl-alcoholic sulphuric acid gives, according to Feist, the methyl ethyl ester of *o*-sulphobenzoylacetic acid, whereas the authors find this to be only a by-product, the main product being *methyl* 3-*oxythionaphthensulphone*-2-*carboxylate*, m. p. 190—191° after softening at 185°. Feist's product is the dimethyl ester of *o*-carboxyphenylsulphonylacetic acid, which is readily hydrolysed by concentrated acid to 3-oxythionaphthensulphone, whereas ring closure does not occur similarly with the free acid. H. WREN.

Preparation of diphenylene sulphide. A. SCHÖNBERG.—See B., 1926, 528.

5- and 4-Nitroisatin. H. RUPE and L. KERSTEN (Helv. Chim. Acta, 1926, 9, 578—582).—Proof of the constitution of 5- and 4-nitroisatin (cf., respectively, Baeyer, A., 1879, 938; and Rupe and Stöcklin, A., 1924, i, 764, who erroneously described this isomeride as 6-nitroisatin) has been obtained by oxidation to the corresponding nitroisatic acids, and hydrolysis of these to the nitroanthranilic acids, which in turn were converted into the corresponding nitrosalicylic acid or nitrophenol. The 5-isomeride, on oxidation with chromic anhydride in acetic acid, yields 5-*nitroisatic acid*, m. p. 244°, which, when heated with mineral acids, yields 5-nitroanthranilic acid; this on treatment in acetic acid solution at 95° with a few drops of concentrated sulphuric acid and an aqueous solution of sodium nitrite yields *p*-nitrophenol. 4-*Nitroisatin*, m. p. 244°, similarly yields 4-*nitroisatic acid*, m. p. 245° (depressing the m. p. of the 5-isomeride), which yields 4-nitroanthranilic acid, and this in turn is converted into 4-nitrosalicylic acid (cf. Siedel, A., 1902, i, 159). *m*-Nitro*iso*nitrosoacetanilide, m. p. 172°, and *p*-nitro*iso*nitrosoacetanilide, m. p. 184° (cf. Borsche, Weussmann, and Fritzsche, A., 1924, i, 986), are described.
J. W. BAKER.

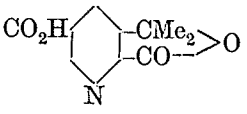
Reactions of 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid. Carbazole synthesis. S. H. OAKESHOTT and S. G. P. PLANT (J.C.S., 1926, 1210—1213).—*p*-Toluidine condensed with *cyclo*pentanone cyanohydrin yields 1-p-*toluidino*-1-*cyano*cyclo*pentane*, m. p. 55° (*nitroso*-derivative, m. p. 58°). Hydrolysis yields 1-p-*toluidino*cyclo*pentane*-1-*carboxylamide*, m. p. 120° (*nitroso*-derivative, m. p. 132°), and finally the *acid*, m. p. 144° (*nitroso*-derivative, decomp. 114°). This acid, on heating above its m. p., loses *p*-toluidine and water, forming the *lactone* of 1 : 1′-*hydroxy*cyclo*pentane*-1′-*carboxylyl*-p-*toluidino*cyclo*pentane*-1-*carboxylic acid*, m. p. 151°. When 1-*p*-toluidino*cyclo*pentane-1-carboxylic acid is heated with a mixture of sodium ethoxide and potassium hydroxide, it yields 3-methylcarbazole, thus indicating the enlargement of the *cyclo*pentane ring and the formation of a new benzene nucleus (cf. A., 1925, i, 1271). 3 : 6-*Dimethyltetrahydrocarbazole*, m. p. 112° (*picrate*, m. p. 147°), is described, and a convenient method of preparing

3-methyl- and 3 : 6-dimethyl-carbazoles from the corresponding tetrahydro-derivatives given. H. BURTON.

Degradation of pyridine to glutacondialdehyde. II. *N*-Pyridiniumsulphonic acid. P. BAUMGARTEN (Ber., 1926, **59**, [*B*], 1166—1171).—1-Pyridiniumsulphonic acid,  , m. p. about 175°, is prepared by the action of sulphur trioxide, chlorosulphonic acid, or ethyl chlorosulphonate on pyridine in cold carbon tetrachloride. It is converted quantitatively by hot water into pyridine and sulphuric acid. Cold concentrated sodium hydroxide solution transforms it into the *disodium* salt of *α-imino-ε-hydroxy-*$\Delta^{\beta\delta}$*-pentadiene-N-sulphonic acid*, which is hydrolysed by hot water mainly to pyridine, by acids mainly to glutacondialdehyde. Hot alkali hydroxide solution converts the disodium derivative into the sodium salt of δ-hydroxy-$\Delta^{\alpha\gamma}$-butadien-α-al, which, together with sulphamic acid, is similarly obtained from 1-pyridiniumsulphonic acid. H. WREN.

Products of the condensation of *iso*valeraldehyde with ammonia in presence of aluminium oxide as catalyst. (MLLE.) M. P. OPARINA (J. Russ. Phys. Chem. Soc., 1925, **57**, 319—341; cf. Ljubavin, A., 1873, 1023; Wischnegradsky, A., 1880, 269; Tschitschibabin, A., 1906, i, 451; 1923, i, 1121, 1122, 1123).—Condensation of *iso*valeraldehyde with ammonia in presence of alumina yields three bases: (1) $C_{15}H_{25}N$, b. p. 258—259°, which is formed in predominating amount and is identical with Ljubavin's valeritrine, regarded as 3 : 5-di*iso*propyl-2-*iso*butylpyridine by Tschitschibabin in the light of evidence which is now vitiated by the simultaneous formation in this condensation of (2) an isomeric base, termed *γ-valeritrine*, b. p. 255—256°, d_4^{15} 0·8888; the corresponding *picrate* has m. p. 134°, and the *chloroplatinate*, m. p. 210° (decomp.). (3) 3 : 5-*Di*iso*propylpyridine*, m. p. 46°, b. p. 223—224°, which gives a *picrate*, m. p. 131—132°, and a *chloroplatinate*, m. p. 185° (decomp.).

That Ljubavin's valeritrine, now termed α-valeritrine, is 3 : 5-di*iso*propyl-2-*iso*butylpyridine is shown as follows. When oxidised by means of nitric acid it gives 3 : 5-*di*iso*propylpyridyl*-2-*acetic acid*, $C_5H_2NPr^{\beta}_2{\cdot}CH_2{\cdot}CO_2H$, m. p. 146°, which forms an insoluble *silver* salt, and on further oxidation by permanganate yields: (1) 3-iso*propylpyridine*-2 : 5-*dicarboxylic acid*, m. p. 208° (decomp.). When distilled with lime, this acid gives 3-iso*propylpyridine*, b. p. 177—178°, d^0 0·9328, d^{16} 0·9227, which forms a *picrate*, m. p. 136°, a *chloroaurate*, m. p. 100°, and a *chloroplatinate*, m. p. 186°, and may be obtained synthetically by treating methyl nicotinate with magnesium methyl iodide (cf. Sobecki, A., 1909, **i**, 51) and reducing the resulting *dimethyl*-3-*pyridylalkine*, $OH{\cdot}CMe_2{\cdot}C_5H_4N$, m. p. 58°, b. p. 140—141°/12 mm. (*picrate*, m. p. 150°), by means of red phosphorus and hydriodic acid and then by zinc dust (cf. Koenigs and Happe, A., 1902, i, 394). The 2-position of the one carboxyl group of this acid is shown by the orange-red coloration given with ferrous sulphate, best in alcoholic solution, and the position of the second carboxyl group is shown by the inability of the acid to form an anhydride. (2) 3-*Hydroxy*iso*propylpyridine*-2 : 5-*dicarboxylic acid lactone* (annexed formula), m. p. 283°, which is formed by the further oxidation of 3-*iso*propylpyridine-2 : 5-dicarboxylic acid by the permanganate, and also gives the colour reaction with ferrous sulphate, owing to the partial formation of the hydroxy-acid on solution in water. When distilled with lime, this acid yields 3-*iso*propylpyridine, the *iso*propenyl group undergoing partial reduction to *iso*propyl. 3-iso*Propenylpyridine*, $C_5H_4N{\cdot}CMe{:}CH_2$, b. p. 187—188°, 110°/20 mm., d^{20} 0·9771, obtained by removal of the elements of water from dimethyl-3-pyridylalkine by the action of glacial acetic acid, gives a *chloroplatinate*, m. p. 152°, and a *picrate*, m. p. 156°.



Distillation of 3 : 5-di*iso*propylpyridyl-2-acetic acid with lime gives 2-*methyl*-3 : 5-*di*iso*propylpyridine*, $C_{12}H_{19}N$, b. p. 220—222°, which forms a *picrate*, m. p. 98—100°, and a *chloroplatinate*, m. p. 205° (decomp.), but gives no appreciable yield of a pyridine acid when oxidised by permanganate, and is not oxidised by nitric acid.

Oxidation of γ-valeritrine by nitric acid yields 3 : 5-*di*iso*propylpyridyl*-4-*acetic acid* (?), m. p. 104—105°, which gives no coloration with ferrous sulphate. The most probable constitution for γ-valeritrine is 3 : 5-di*iso*propyl-4-*iso*butylpyridine.

Oxidation of 3 : 5-di*iso*propylpyridine by permanganate gives *tetramethylpyridyl*-3 : 5-*dialkine*, m. p. 146°, which is converted quantitatively into dinicotinic acid by oxidation with nitric acid, and may also be obtained, together with the *keto-alcohol*, (? 3-aceto-5-α-hydroxy*iso*propylpyridine), m. p. 128°, by the interaction of dinicotinic acid dimethyl ether and magnesium methyl iodide. When heated with glacial acetic and concentrated sulphuric acids, this alkine loses $2H_2O$ to form 3 : 5-*di*iso*propenylpyridine*, $C_5H_3N(CMe{:}CH_2)_2$, b. p. 242—243°, d_4^{15} 0·9729, which instantly decolorises neutral or acid permanganate solution or bromine in acetic acid solution and yields dinicotinic acid when oxidised with nitric acid.

Oxidation of either of the isomeric valeritrines by nitric acid yields, besides acid products, also basic compounds. Thus, α-valeritrine gives 3 : 5-*dinitro*-iso*propyl*-2-iso*butylpyridine*, $CHMe_2{\cdot}CH_2{\cdot}C_5H_2N(CMe_2{\cdot}NO_2)_2$, which forms a *picrate*, m. p. 187°, and a *chloroplatinate*, m. p. 208°, and on distillation in a vacuum gives 3 : 5-*diacetyl*-2-iso*butylpyridine*, this forming a *picrate*, m. p. 139—140° Reduction of 3 : 5-dinitro*iso*propyl-2-*iso*butylpyridine by either tin and hydrochloric acid or zinc or iron and acetic acid yields ammonia and a small proportion of a base which forms a *picrate*, m. p. 142—143°, corresponding in composition with that of 3-*acetyl*-5-iso*propyl*-2-iso*butylpyridine*. T. H. POPE.

Quaternary pyridine bases. O. MAGIDSON and G. MENSCHIKOV (Ber., 1926, **59**, [*B*], 1209—1218).—1-Ethylpyridinium iodide, 1-*allylpyridinium iodide*, m. p. 102·5—104·5°, 1-*benzylpyridinium chloride* (corresponding *picrate*, m. p. 118°), 1-*propylpyridinium iodide*, and 1-iso*amylpyridinium iodide* have a more

or less distinct curare action, but there is no direct relationship between physiological effect and dissociation constant. Pyridine is converted by *iso*amyl iodide and sodamide in the presence of toluene into a mixture of 2-*iso*amylaminopyridine (*picrate*, m. p. 145·5—146·5°) and 2-*di*iso*amylaminopyridine*, b. p. 168—169°/20 mm., d_{20}^{20} 0·9141, n_D^{20} 1·5058 [*picrate*, m. p. 131—132°; *chloroplatinate*, m. p. 185° (decomp.)]. The tertiary base is converted into 2-*di*iso*amylamino-pyridinium methiodide* and 2-*di*iso*amylamino*-1-iso*amylpyridinium iodide*, which is very readily hydrolysed to *iso*amyl alcohol and 2-*di*iso*amylamino-pyridine hydriodide*. 2-Acetamidopyridine and methyl iodide afford 2-*acetamidopyridine methiodide*, m. p. 170—171°, which is converted by hydrochloric acid into 1-*methyl*-2-*pyridoneimine hydriodide*, m. p. 148°, transformed by potassium hydroxide into 1-methyl-2-pyridone. With hydriodic acid (30%) 2-acetamidopyridine methiodide gives the *periodide*, $C_6H_7N_2I_3$, m. p. 144—146°. 2-*Dimethylaminopyridine methiodide* is very hygroscopic; the corresponding *picrate* has m. p. 158°. 2 : 6-Diaminopyridine does not react with dry methyl iodide or methyl *p*-toluenesulphonate; the latter reagent in the presence of alcohol yields a mixture of 6-*acetamido*-1-*methyl*-2-*pyridoneimine* p-*toluenesulphonate*, m. p. 225—228°, and 2 : 6-*diaminopyridine* p-*toluenesulphonate*, m. p. 183°.

H. WREN.

Production of iodised pyridine derivatives. A. BINZ and C. RÄTH.—See B., 1926, 608.

Condensation of 2-aminopyridine with aliphatic aldehydes. L. SCHMID and B. BECKER (Monatsh., 1926, **46**, 675—678).—2-Aminopyridine (2 mols.) reacts quantitatively with 1 mol. of acetaldehyde or propaldehyde with the elimination of water to yield, respectively, *ethylidenedi*-2-*pyridyldiamine*, m. p. 112·5°, and *propylidenedi*-2-*pyridyldiamine*, m. p. 133·5—134°. With chloral, equimolecular proportions react to yield 2-βββ-*trichloro*-α-*hydroxyethylaminopyridine*, $CCl_3{\cdot}CH(OH){\cdot}NH{\cdot}C_5H_4N$, m. p. 106·5° (*acetyl* derivative, m. p. 99·5°).

J. W. BAKER.

Alkylation of pyridyl-2-nitroamine. A. E. TSCHITSCHIBABIN and G. P. MENSCHIKOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 315—318).—The experiments here described were made with the object of obtaining alkyl derivatives of the various possible tautomerides of pyridyl-2-nitroamine (cf. Tschitschibabin and Razorenov, A., 1915, i, 992), particularly of the *iso*nitroso-form, $C_5H_4N{\cdot}N{:}NO{\cdot}OH$. Treatment of the nitroamine with methyl alcohol gave negative results, but the action of methyl sulphate or methyl hydrogen sulphate in presence of sodium hydroxide converts the nitroamine into 1-*methylpyridonenitroimide*, $CH\langle^{CH{:}CH-}_{CH{\cdot}NMe}\rangle C{:}N{\cdot}NO_2$, m. p. 161°, which was obtained by Tschitschibabin and Konovalov (unpublished paper) by direct nitration of methylpyridoneimide in cold sulphuric acid solution. When heated gently with 5% sodium hydroxide solution, 1-methylpyridonenitroimide decomposes quantitatively into 1-methylpyridone and nitrous oxide, this reaction being analogous to the decomposition of nitroamide into water and nitrous oxide and to the Kishner–Wolff decomposition of hydrazones by the action of alkali hydroxide or alkoxide (cf. Thielepape and Spreckelsen, A., 1922, i, 1191). Further investigations demonstrate the general character of this reaction: $:C:N{\cdot}NO_2 = :C:O + N_2O$. These results support Thiele and Lachman's structure for nitroamide, $NH_2{\cdot}NO_2$ (A., 1896, i, 207; 1897, ii, 369) in preference to that proposed by Hantzsch, OH·N:N·OH (A., 1897, ii, 369).

1-*Ethylpyridonenitroimide*, $C_7H_9O_2N_3$, m. p. 139°, is prepared similarly to the methyl derivative and has similar properties.

T. H. POPE.

Condensation of 2-aminopyridine with thiocarbonyl chloride. L. SCHMID and B. BECKER (Monatsh., 1926, **46**, 671—674).—Condensation of 2-aminopyridine with thiocarbonyl chloride yields s-*di*-2-*pyridylthiocarbamide*, m. p. 163°, which when heated with mercuric oxide yields s-*di*-2-*pyridylcarbamide*, m. p. 175·3°, also obtained by the action of 2-aminopyridine on carbamide. With benzenesulphonyl chloride, 2-aminopyridine yields a *benzenesulphonyl* derivative, m. p. 172·5°.

J. W. BAKER.

Benzenediazo-2-aminopyridine. A. E. TSCHITSCHIBABIN and R. L. PERSIC (J. Russ. Phys. Chem. Soc., 1925, **57**, 301—304).—The action of phenyldiazonium chloride on 2-aminopyridine in presence of excess of sodium hydrogen carbonate or acetate (cf. Tschitschibabin and Zeide, A., 1915, i, 590) gives rise to benzenediazo-2-aminopyridine, $NPh{:}N{\cdot}NH{\cdot}C_5H_4N$, m. p. 176°, which yields aminoazobenzene and 2-aminopyridine when heated with aniline and aniline hydrochloride. When, however, benzenediazo-2-aminopyridine is heated with 2-aminopyridine and its hydrochloride, no aminoazopyridine is formed. At low temperatures no change occurs, whilst at higher temperatures nitrogen is liberated and a mixture of compounds, including 2-anilinopyridine, is formed. Hence, unlike 2-pyridone (cf. Mills and Widdows, J.C.S., 1908, **93**, 1372), 2-aminopyridine does not yield azo colouring matters by coupling with diazonium salts.

T. H. POPE.

2 : 5-Diaminopyridine. A. E. TSCHITSCHIBABIN and N. M. POZDNIAKOV (J. Russ. Phys. Chem. Soc., 1925, **57**, 297—299).—Although 2 : 5-diaminopyridine, which is readily obtainable from 5-nitro-2-aminopyridine (cf. Tschitschibabin, A., 1915, i, 591), is structurally analogous to *p*-phenylenediamine, a mixture of 2 : 5-diaminopyridine and phenol remains unchanged when lead peroxide paste is added even after the solution is heated. Further, 2 : 5-diaminopyridine and aniline fail to yield an indamine when oxidised together under conditions which convert *p*-phenylenediamine and phenol into indamine. The 5-amino-group of 2 : 5-diaminopyridine reacts readily with nitrous acid, with formation of 2-aminopyridine-5-diazonium salts, which yield colouring matters when coupled with aromatic amines or phenols. 5-*Nitro*-2-*acetamidopyridine* has m. p. 196°. 2-*Aminopyridine*-5-*diazo*-β-*naphthol*, cinnamon-brown crystals, m. p. 188—189°, dyes silk golden-yellow and wool cinnamon-yellow in acid solution.

T. H. POPE.

Rosenmund's aldehyde synthesis applied to [heterocyclic] nitrogen and sulphur compounds. C. A. ROJAHN and J. SCHULTEN.—See this vol., 842.

ω-Mono- and dibromo-derivatives of 2-methyl- and nitro-2-methyl-quinolines and their products of hydrolysis. D. L. HAMMICK (J.C.S., 1926, 1302—1304).—The hydrolysis of ω-tribromo-2-methylquinoline to quinoline-2-carboxylic acid (*ibid.*, 1923, **123**, 2882) has been extended to the preparation of the corresponding aldehyde and alcohol, which could not, however, be obtained by direct selective bromination. ω-Tribromo-2-methylquinoline is reduced to *ω-dibromo-2-methylquinoline*, m. p. 120°, or to *ω-monobromo-2-methylquinoline*, m. p. 83°, by the theoretical quantities of stannous chloride. These are both stable to acids and are destroyed by alkali, but silver nitrate gives a quantitative conversion to quinoline-2-aldehyde, m. p. 71° (*oxime*, m. p. 184°; phenylhydrazone, m. p. 204°; cf. A., 1913, i, 293), or to *ω-hydroxy-2-methylquinoline*, m. p. 64°. The following compounds have been prepared by similar methods: *ω-tribromo-8-nitro-2-methylquinoline*, m. p. 132°; 8-nitroquinoline-2-carboxylic acid, m. p. 182° (cf. A., 1906, i, 605), which gives 8-nitroquinoline on fusion; *ω-dibromo-8-nitro-2-methylquinoline*, m. p. 183° (by direct substitution with bromine); *8-nitroquinoline-2-aldehyde*, m. p. 152°.

The second nitro-2-methylquinoline, m. p. 82°, obtained by nitration of 2-methylquinoline (A., 1884, 1373), is shown to be the 5-nitro-derivative, in accordance with Decker and Remfrey (A., 1905, i, 828). *ω-Tribromo-5-nitro-2-methylquinoline*, m. p. 93°, yielded an *acid* (not purified) which gave 5-nitroquinoline on fusion. J. M. GULLAND.

[Quinoline derivatives. II. Synthesis of 2-phenyl-4-β-aminoethylquinoline and 6-methoxy-2-phenyl-4-β-aminoethylquinoline.] H. JOHN (Ber., 1926, **59**, [*B*], 1141; cf. A., 1925, i, 1317; Zöllner, this vol., 525).—A question of priority. H. WREN.

Constitution of the β-acid derived by hydrolysis of crude oryzanin. Y. SAHASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 207—233).—The β-acid of Suzuki, Shimamura, and Odake (A., 1912, ii, 980) is 2 : 6-*dihydroxyquinoline-4-carboxylic acid*, m. p. above 315° (*methyl* and *ethyl* esters, *sodium*, *potassium*, *barium*, *copper*, and basic *calcium*, $C_{10}H_5NO_4Ca$, salts described). Distillation with zinc dust affords quinoline, and decarboxylation at 400° yields 2 : 6-dihydroxyquinoline (cf. Gattermann, A., 1894, i, 503). *Diacetyl* and *monobenzoyl* derivatives, and a *tribenzoyl* compound, $C_9H_4N(OBz)_2{\cdot}CO_2Bz$, are described, and the orientation of the hydroxyl groups is established by the behaviour of the acid and its derivatives. Nitric acid oxidises the β-acid to oxalic acid and *3-nitro-2-hydroxypyridine-4 : 5 : 6-tricarboxylic acid*, decomp. 240—241°, which is reduced to pyridine by distillation with zinc dust. The dimethyl-β-acid, m. p. 302—303°, is identical with 6-methoxy-1-methylcarbostyril-4-carboxylic acid (Roser, A., 1895, i, 155) (*ethyl* ester, m. p. 166—167°), and is demethylated by Zeisel's method to *6-hydroxy-1-methylcarbostyril-4-carboxylic acid*, m. p. 303—304°, and converted by potassium permanganate into *5-methoxy-1-methylisatin*, m. p. 167—168° (cf. Friedländer and Ostermaier, A., 1882, 732), and a nitrogenous *substance*, m. p. 191—192°. J. M. GULLAND.

Labile nature of the halogen atom in organic compounds. XII. Halogen compounds of barbituric acids. A. K. MACBETH, T. H. NUNAN, and D. TRAILL (J.C.S., 1926, 1248—1253; cf. *ibid.*, 1922, **121**, 1117, 2173; 1923, **123**, 1129).—Partial reduction of dibromobarbituric acid (Baeyer, Annalen, 1864, **130**, 133; Whiteley, J.C.S., 1921, **119**, 377) is also produced by hydrazine hydrate; the evolved nitrogen was measured, and the hydrazides of the mono-halogen acids were isolated. The stability of these acids is probably connected with their enolic constitution in accordance with an explanation previously advanced. The reactivity of the halogen atom, which is in contrast with the results observed in the case of certain diketones, is explained by consideration of the polarity effects in the molecule. The absorption spectra of representative compounds are regarded as showing that the parent acids exist in the enolic form in water and in the ketonic form in acid solution, and that the dihalogen derivatives are of the *C*-dihalogen type, which excludes the attribution of reactivity to an oxygen–halogen linking (cf. J.C.S., 1922, **121**, 1109, 2601). The absorption spectra of dibromobarbituric acid and barbitone in alkali suggest enolisation probably involving an imino-group.

The *hydrazides* of monochloro- and monobromobarbituric acids do not melt below 300°. The *hydrazide* of 5-bromo-1 : 3-diphenylbarbituric acid has m. p. 220°. *1-Phenylbarbituric acid*, m. p. 262°, is converted by the theoretical amounts of bromine into 3 : *3-dibromo-1-phenylbarbituric acid*, m. p. 204°, and *5-bromo-1-phenylbarbituric acid*, m. p. 213° (*hydrazide*, m. p. 146°). J. M. GULLAND.

Barbituric acid derivative. W. URSUM, L. SCHÜTZ, and L. TAUB, etc.—See B., 1926, 609.

Preparation of a derivative of 1-phenyl-2 : 3-dimethyl-5-pyrazolone. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 611.

Rosenmund's aldehyde synthesis applied to heterocyclic compounds. 1-Methylpyrazole-3-, -4-, and -5-aldehydes. C. A. ROJAHN and H. E. KÜHLING (Arch. Pharm., 1926, **264**, 337—347; cf. this vol., 78).—When 3-methylpyrazole-5-carboxylic acid is treated with thionyl chloride in an attempt to obtain the chloride, the *anhydride*, m. p. 346°, is produced. *4-Bromo-3-methylpyrazole-5-carboxylic acid* has m. p. 253°. The *anhydride*, m. p. 320°, of 4-methylpyrazole-5-carboxylic acid is similarly produced. 3 : 5-Dimethylpyrazole-4-carboxylic acid and 3-phenyl-5-methylpyrazole-4-carboxylic acid also cannot be converted into their chlorides. The 1-methyl derivatives of these acids, however, yield chlorides normally; the corresponding aldehydes can therefore be prepared by Rosenmund's method, but the yields are meagre. Thus, *ethyl* 1 : 3 : 5-*trimethylpyrazole-4-carboxylate*, m. p. 37°, obtained either by methylating the corresponding 3 : 5-dimethyl compound, or from

ethyl diacetoacetate and methylhydrazine, is hydrolysed to the corresponding *acid*, m. p. 217°, which loses carbon dioxide at its m. p., giving 1 : 3 : 5-*trimethylpyrazole* (*picrate*, m. p. 144—145°). The unstable *chloride* (m. p. 67—68°; b. p. 140—150°/12 mm.) of this acid (*amide*, m. p. 200°; *anilide*, m. p. 159°) yields on reduction by Rosenmund's methods only traces of the *aldehyde* (*semicarbazone*, m. p. 213—214°); much of the acid is regenerated, accompanied by its *anhydride* (m. p. 143°) and by the *hydrochloride* of 1 : 3 : 4 : 5-*tetramethylpyrazole* (*picrate*, m. p. 176—178°).

1 : 5-Dimethylpyrazole-3-carboxylic acid (Rojahn, this vol., 624) yields a *chloride* (m. p. 60°; b. p. 120—125°/13 mm.) and an *amide* (m. p. 177—178°). The purified chloride is reduced, only by repeated addition of catalyst, to the *aldehyde* (m. p. 56°, b. p. 115—120°/13 mm), which yields no hydrogen sulphite compound, but a *semicarbazone* (m. p. 201°), *oxime* (m. p. 177—178°), and *aminoguanidone nitrate* (m. p. 200°). Similarly, 1 : 3-*dimethylpyrazole*-5-*carboxyl chloride* (b. p. 75—80°/12 mm.; acid, *loc. cit.*, *amide*, m. p. 165°) gives, in poor yield, the *aldehyde* (b. p. 80—83°/12 mm.; *semicarbazone*, m. p. 206°; *oxime*, m. p. 148°; *aminoguanidone nitrate*, m. p. 159°), together with regenerated acid and 1 : 3 : 5-trimethylpyrazole. 1 : 4-*Dimethylpyrazole*-3-*carboxyl chloride* (m. p. 40°; b. p. 90—95°/20 mm.; *amide*, m. p. 164°; *anilide*, m. p. 127°; acid, *loc. cit.*) yields the *aldehyde* (m. p. 126—127°; *semicarbazone*, m. p. 216°; *aminoguanidone nitrate*, m. p. 158°, decomp.), accompanied by 1 : 4-*dimethylpyrazole*, identified as its *picrate*, m. p. 165°, and *methiodide*, m. p. 187°. 1 : 4-*Dimethylpyrazole*-5-*carboxyl chloride* (m. p. 73—74°) gives the *amide*, m. p. 158—160°, and the *anilide*, m. p. 94°. W. A. SILVESTER.

Isomeric relationships in the pyrazole series. IX. 1 : 3- and 1 : 5-Dialkylpyrazoles and related compounds. K. VON AUWERS and H. HOLLMANN (Ber., 1926, 59, [*B*], 1282—1302; cf. this vol., 624).—Ethyl 3-methylpyrazole-5-carboxylate is converted by benzyl chloride and sodium ethoxide into a mixture of *ethyl* 1-*benzyl*-5-*methylpyrazole*-3-*carboxylate*, b. p. 216°/11 mm., d_4^{20} 1·125, n_{He}^{20} 1·5487, and *ethyl* 1-*benzyl*-3-*methylpyrazole*-5-*carboxylate*, b. p. 170—171°/9 mm., d_4^{20} 1·110, n_{He}^{20} 1·5409, of which the latter alone remains unaffected by Claisen's reagent. 1-*Benzyl*-5-*methylpyrazole*-3-*carboxylic acid*, m. p. 133—134°, is converted into 4-*bromo*-1-*benzyl*-5-*methylpyrazole*-3-*carboxylic acid*, m. p. 186°, which readily yields a *methyl* ester, m. p. 80—81·5°. 1-*Benzyl*-3-*methylpyrazole*-5-*carboxylic acid*, m. p. 156°, and 4-*bromo*-1-*benzyl*-3-*methylpyrazole*-5-*carboxylic acid*, m. p. 176—177°, are described. Elimination of carbon dioxide from the respective acids affords 1-*benzyl*-5-*methylpyrazole*, b. p. 132°/9 mm., d_4^{20} 1·062, n_{He}^{20} 1·5557 (*picrate*, m. p. 109°; *hydrochloride*, m. p. 148—149°), and 1-*benzyl*-3-*methylpyrazole*, b. p. 130°/9 mm., d_4^{20} 1·049, n_{He}^{20} 1·5518 (*picrate*, m. p. 114°; *hydrochloride*, m. p. about 105°).

The following quaternary salts and their fission products are described: 1 : 2 : 5-trimethylpyrazolium iodide, m. p. 256°, giving (?) approximately equal quantities of 1 : 5- and 1 : 3-dimethylpyrazole; 1 : 5-*dimethylpyrazole ethiodide*, m. p. 124—125°, giving exclusively 3-methyl-1-ethylpyrazole; 5-*methyl*-1-*ethylpyrazole methiodide*, m. p. 173°, giving quantitatively 5-methyl-1-ethylpyrazole; 1-*benzyl*-5-*methylpyrazole methiodide*, m. p. 167° (corresponding *picrate*, m. p. 128—129°), yielding approximately equal amounts of 1 : 3- and 1 : 5-dimethylpyrazole; 1 : 3-dimethylpyrazole benziodide, identical with the preceding compound; 1-*benzyl*-3-*methylpyrazole methiodide*, m. p. 154° (corresponding *picrate*, m. p. 132°), giving a mixture of 1 : 3- and 1 : 5-dimethylpyrazole (ratio 2 : 3); 1 : 5-dimethylpyrazole benziodide, identical with the preceding compound; 5-methyl-1-ethylpyrazole benziodide, m. p. 150—151°, giving exclusively 5-methyl-1-ethylpyrazole; 3-*methyl*-1-*ethylpyrazole benziodide*, m. p. 138° (corresponding *picrate*, m. p. 85—86°), yielding solely 3-methyl-1-ethylpyrazole; *methyl* 1 : 3- and 1 : 5-*dimethylpyrazole*-5(3)-*carboxylate methiodide*, m. p. 172°, giving methyl 1 : 5-dimethylpyrazole-3-carboxylate, m. p. 144°.

Treatment of 3(5)-methylpyrazole with methyl iodide at 100° affords approximately equal amounts of 1 : 3- and 1 : 5-dimethylpyrazole. With ethyl bromide and sodium ethoxide nearly equal quantities of 5-methyl-1-ethyl- and 3-methyl-1-ethyl-pyrazole are produced, whereas in the absence of alkali the ratio is 1 : 2. Benzylation in presence or absence of alkali affords mainly 1-benzyl-3-methylpyrazole with a little 1-benzyl-5-methylpyrazole.

The following condensations of aldehydes or ketones with hydrazines are described: α-bromocrotonaldehyde and methylhydrazine yield 1 : 5-dimethylpyrazole (described previously as the 1 : 3-derivative); β-ethoxycrotonaldehyde diethylacetal and phenylhydrazine give exclusively 1-phenyl-3-methylpyrazole, m. p. 35°; whereas with methylhydrazine a mixture of 1 : 3- and 1 : 5-dimethylpyrazoles is produced; hydroxymethyleneacetone and methylhydrazine give 1 : 5- and 1 : 3-dimethylpyrazole in the ratio 9 : 5 in alkaline solution, 5 : 4 in acid solution; the structure of hydroxymethyleneacetone benzoate is established by its oxidation to benzoic and pyruvic acids, whilst its conversion by phenylhydrazine into 1-phenyl-3-methylpyrazole (yield 86%), by methylhydrazine into a mixture of equal amounts of 1 : 3- and 1 : 5-dimethylpyrazole, and by benzylhydrazine mainly into 1-benzyl-3-methylpyrazole is described; hydroxymethyleneacetone benzoate semicarbazone, m. p. 181°, is described; ethyl acetoneoxalate and methylhydrazine afford *ethyl* 1 : 5-*dimethylpyrazole*-3-*carboxylate*, b. p. 154°/10 mm., m. p. 40—42° (acid, m. p. 175°), and *ethyl* 1 : 3-*dimethylpyrazole*-5-*carboxylate*, b. p. 98°/10 mm. (acid, m. p. 207°); ethyl β-acetyl-α-ethoxyacrylate, b. p. 125°/9 mm., $d_4^{15\cdot1}$ 1·0649, $n_{He}^{15\cdot1}$ 1·4756 (oxidised to pyruvic acid), and methylhydrazine afford ethyl 1 : 5-dimethylpyrazole-3-carboxylate (80—90%) and ethyl 1 : 3-dimethylpyrazole-5-carboxylate (20—10%), whereas with phenylhydrazine ethyl 1-phenyl-5-methylpyrazole-3-carboxylate and an unidentified substance, m. p. 195°, are produced; acetoneoxalic ester and phenylhydrazine yield 1-phenyl-5-methylpyrazole-3-carboxylic acid. H. WREN.

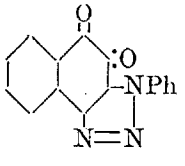
Condensation products of 2-aminopyridine with aliphatic-aromatic ketones. II. L. SCHMID and B. BANGLER (Ber., 1926, 59, [*B*], 1360—1362; cf. A., 1925, i, 1459).—ω-Bromoacetophenone and 2-aminopyridine afford 2-*phenylpyriminazole*, m. p. 135·5° (*methiodide*, m. p. 214°; *chloroaurate*; *chloroplatinate*, decomp. 202°), identical with the product obtained by the action of concentrated hydrochloric acid at 140° on 2-dypnoneaminopyridine (*loc. cit.*).

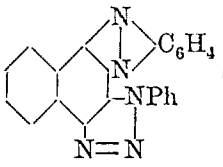
H. WREN.

6-Chloro-(bromo-)1-hydroxy-1 : 2 : 3-benztriazole. J. BOOY and J. W. DIENSKE (Rec. trav. chim., 1926, **45**, 449—451).—2 : 5-Dichloronitrobenzene reacts with hydrazine in absolute alcohol at 100° to give 6-*chloro*-1-*hydroxy*-1 : 2 : 3-*benztriazole*, m. p. 195° (decomp.) (metallic *salts* described). Similarly, 2 : 5-dibromonitrobenzene gives 6-*bromo*-1-*hydroxy*-1 : 2 : 3-*benztriazole*, m. p. 187° (decomp.).

F. M. HAMER.

Isomeric phenyl-αβ-naphthatriazolequinones. G. CHARRIER and A. BERETTA [with A. GISELLA] (Gazzetta, 1926, **56**, 191—195; cf. A., 1924, i, 1351, and following abstract).—3-*Phenyl*-αβ-*naphthatriazolequinone* (I), prepared by oxidising 3-phenyl-αβ-naphthatriazole in acetic solution by means of chromic acid, forms orange-yellow needles, m. p. 223°. The

(I.) 



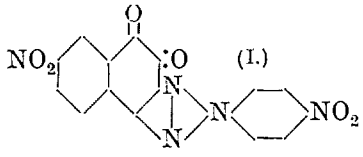
(II.)

corresponding *phenylhydroxyazo*-derivative, prepared by the action of phenylhydrazine on the quinone, is golden-red, m. p. 275°, and the *phenazine* (II), yellow, m. p. 268°. 1-*Phenyl*-4-o-*carboxyphenyl*-1 : 2 : 3-*triazole*-5-*carboxylic acid*, obtained by oxidising the quinone with alkaline permanganate, has m. p. 131°.

T. H. POPE.

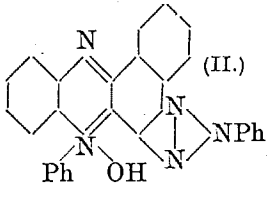
2-Phenyl-αβ-naphthatriazolequinone. G. CHARRIER and A. MANFREDI (Gazzetta, 1926, **56**, 196—207; cf. A., 1924, i, 1351).—Further study of the derivatives of this compound emphasises the analogy between the quinone and phenanthraquinone and hence that between 2-phenyl-αβ-naphthatriazole and phenanthrene; many of the corresponding derivatives of the two quinones have identical m. p. and almost identical physical and chemical properties. With phosphorus pentachloride or hydroxylamine, only one carbonyl group in 2-phenyl-αβ-naphthatriazolequinone reacts, and thus differs from the other. Comparison of these reactions with the oxidation of 2-phenyl-αβ-naphthatriazole oxide to 2-phenyl-αβ-naphthatriazolequinone, and not to the corresponding oxide, by means of chromic acid mixture indicates that the carbonyl group adjacent to the heterocyclic nucleus is influenced by the latter, so that its oxygen atom does not show the usual substitution reactions.

[With L. GORINI.]—2-Phenyl-αβ-naphthatriazolequinone (*loc. cit.*) may be prepared by the direct oxidation of phenylazo-β-naphthylamine without previous transformation into the naphthatriazole. 2-*Phenyl*-αβ-*naphthatriazolequinol* (4 : 5-*dihydroxy*-2-*phenyl*-αβ-*naphthatriazole*), obtained by reduction of the triazolequinone by means of tin and hydrochloric acid, readily undergoes oxidation to the quinone, and thus has no constant m. p.; its *diacetyl* derivative, m. p. 163°; *dimethyl ether*, m. p. 99—100°; *dibenzoyl* derivative, m. p. 212°; and its *dichloro*-derivative, m. p. 165°, were prepared.

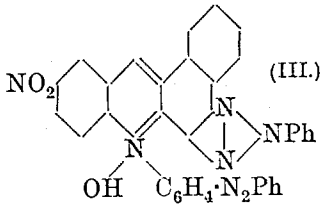

(I.)

Nitration of 2-phenyl-αβ-naphthatriazolequinone in presence of sulphuric acid yields the *dinitro*-compound (I), m. p. 287°, which, with phenylhydrazine, gives the corresponding *hydroxyazo*-compound, $NO_2{\cdot}C_6H_4{\cdot}N_3{:}C_{10}H_3(NO_2)(OH){\cdot}N{:}NPh$, m. p. 315°.

Like phenanthraquinone, 2-phenyl-αβ-naphthatriazolequinone condenses with *o*-aminodiphenylamine to form the *flavinduline* (II), which decomposes without melting at about 100° and gives a *hydrochloride*, m. p. 238° (decomp.), and a *nitrate*, m. p. 211°. Similarly,



(II.)



(III.)

condensation of the triazolequinone with 4-nitro-2-amino-4'-phenylazodiphenylamine gives the *flavinduline* (III), which decomposes without melting and forms a *hydrochloride*, m. p. 138°, and a *nitrate*, m. p. 115°.

2-*Phenyl*-αβ-*naphthatriazolequinoneoxime*, $NOH{:}C_{10}H_4O{:}N_3Ph$, has m. p. 229—230°.

T. H. POPE.

Oxidation of *o*-aminoarylazobenzenes in acetic acid solution by means of hydrogen peroxide. G. CHARRIER and G. B. CRIPPA (Gazzetta, 1926, **56**, 207—216).—Since the oxidation of *o*-aminoazo-compounds of the benzene series by peracetic acid yields, probably by way of *o*-aminoazoxy-derivatives, the 2-arylbenztriazole-2-oxides, $C_6H_4\langle{}^{N}_{N}{>}NAr{:}O$, the constitution of which has been established by other syntheses, it seems probable that similar oxidation of *o*-aminoazo-compounds of the naphthalene series should proceed in the same way and thus yield 2-aryl-αβ-naphthatriazole-1-oxides, $C_{10}N_6\langle{}^{NO}_{N}{>}NAr$. The behaviour of 2-phenyl-αβ-naphthatriazole oxide on oxidation and also certain properties of 2-phenyl-αβ-naphthatriazolequinone (cf. preceding abstract) seem, however, to indicate that the oxygen atom of the oxide occupies the 3-position, adjacent to the ethylene bridge, so that the matter remains undecided.

[With A. DANSI.]—The action of peracetic acid on *o*-aminoazobenzene yields: 2-phenylbenztriazole; 2-phenylbenztriazole oxide; 2-amino-4'-hydroxyazobenzene (?) (cf. Cusmano, A., 1921, i, 132); a yellow substance, m. p. 100—105°, probably a mixture of nitrophenols; a yellow substance, $C_{12}H_{11}ON_3$,

which decomposes, without melting, at 250—300°, and is probably a product of the polymerisation or condensation of *o*-aminoazoxybenzene; a *trisazoxy*-compound, $C_{24}H_{18}O_3N_6$, m. p. 278°, which yields aniline and *o*-phenylenediamine on reduction.

Oxidation of *o*-aminoazotoluene (*p*-tolylazo-*p*-toluidine) by peracetic acid gives 2-p-*tolyl*-6-*methylbenztriazole*-1-*oxide*, m. p. 131·5°; a yellow product, probably a mixture of nitrocresols; and 2 : 2′-*di*-p-*tolylazo*-4 : 4′-*dimethylazobenzene*, reddish-brown, decomp. (without melting) 393°; this yields *p*-toluidine and *o*-tolylenediamine on reduction.

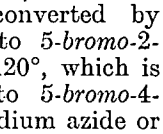
T. H. POPE.

Preparation of aminotetrazole. R. STOLLÉ and E. SCHICK.—See B., 1926, 566.

2-Azidocoumaran-3-one. K. FRIES and K. SAFTIEN (Ber., 1926, 59, [*B*], 1246—1254).—2 : 5-Dibromo-6-methoxycoumaran-3-one is converted by sodium azide in aqueous acetone into 5-*bromo*-2-*azido*-6-*methoxycoumaran*-3-*one*, m. p. 120°, which is transformed by alkali hydroxide into 5-*bromo*-4-*methoxysalicylic acid*, m. p. 250°, by sodium azide or acetate in alcohol into *ethyl* 5-*bromo*-4-*methoxysalicylate*, m. p. 123°, nitrogen, and hydrocyanic acid, and by alcoholic hydrogen chloride into *ethyl* 5-*bromo*-2-*hydroxy*-4-*methoxybenzoylformate*, m. p. 108°. *Ethyl* 5-*bromo*-4-*methoxyacetylsalicylate*, m. p. 63°, and *methyl* 5-*bromo*-4-*methoxysalicylate*, m. p. 145°, are described. The position of the bromine atom in 5-bromo-4-methoxysalicylic acid (and hence in the initial material) is established by its conversion into 4-bromoresorcinol, m. p. 91°. 5-Bromo-2-azido-6-methoxycoumaran-3-one is converted by sodium azide in glacial acetic acid into 4 : 5′-*bromo*-2′-*hydroxy*-4′-*methoxybenzoyl*-1 : 2 : 3 : 5-*tetrazole*, m. p. 236° (decomp.) after darkening at 230° (*sodium* salt; *acetyl* derivative, m. p. 214°). The unstable 2-*azidocoumaran*-3-*one* is transformed similarly into methyl salicylate and 4-*o*-*hydroxybenzoyl*-1 : 2 : 3 : 5-*tetrazole*, m. p. 172°, characterised by oxidation by potassium permanganate to 1 : 2 : 3 : 5-tetrazole-4-carboxylic acid (the silver salt and ethyl iodide yield the known *N*-ethyl-1 : 2 : 3 : 5-tetrazole-4-carboxylic acid), and thence to tetrazole. The *silver* salt of 4-*o*-hydroxybenzoyl-1 : 2 : 3 : 5-tetrazole and methyl iodide afford 4-*o*-*hydroxybenzoyl*-1-*methyl*-1 : 2 : 3 : 5-*tetrazole*, m. p. 115° (*acetyl* derivative, m. p. 94—95°). 5-Chlorocoumaran-3-one is converted by bromine in carbon tetrachloride into 5-*chloro*-2-*bromocoumaran*-3-*one*, m. p. 112°, which with sodium azide and acetic acid gives 4-(5′-*chloro*-2′-*hydroxybenzoyl*)-1 : 2 : 3 : 5-*tetrazole*, m. p. 180° (*dimethyl* derivative; *acetyl* compound, m. p. 124°). 4-Hydroxychloroacetylbenzene and sodium azide yield 4-*hydroxyazidoacetylbenzene*, m. p. 136°.

5-Nitro-2-aminophenol is transformed successively into 2-bromo-5-nitrophenol, m. p. 124°, 2-bromo-5-aminophenol, m. p. 159° (decomp.), and 4-bromoresorcinol, m. p. 91°. H. WREN.

***iso*Oxazoline oxides. V. Carboxyl derivatives.** E. P. KOHLER and G. R. BARRETT (J. Amer. Chem. Soc., 1926, **48**, 1770—1777; cf. this vol., 309).—*Ethyl* γ-*nitro*-βγ-*diphenylethylmalonate*, $NO_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH(CO_2Et)_2$, m. p. 132°, is obtained by condensing phenylnitromethane with ethyl benzylidenemalonate, whilst the corresponding *methyl* ester, m. p. 140°, is obtained similarly from ethyl malonate and nitrostilbene. When treated with bromine in chloroform or carbon tetrachloride, the esters yield *ethyl*, m. p. 74°, and *methyl* α-*bromo*-γ-*nitro*-βγ-*diphenylethylmalonate*, m. p. 125°, respectively, and these are converted, on treatment with potassium acetate in alcohol, into the corresponding *ethyl* ester, m. p. 107—108°, and *methyl* ester, m. p. 144°, of 3 : 4-*diphenyl*isooxazoline *oxide*-5 : 5-*dicarboxylic acid* (I) (+1H_2O), m. p. about 130° (decomp.). When heated at its m. p., or boiled in benzene solution, (I) decomposes with formation of a red oil, 3 : 4-*diphenyl*isooxazole-5-*carboxylic acid*, (II), m. p. 169—170°, and an *acid*, m. p. 158°. When boiled in aqueous solution, (I) is converted quantitatively into (II). When the above reaction with potassium acetate is carried out in aqueous alcohol, an *acid* (annexed formula), m. p. 172° (*copper* salt, yellow), is obtained, which is slowly hydrolysed in potassium hydroxide solution to the acid (II). Treatment of the above methyl ester of (I) with phosphorus pentachloride affords the *methyl* ester, m. p. 158°, of 3 : 4-*diphenyl*isooxazoline-5 : 5-*dicarboxylic acid*, m. p. 166° (decomp.) (anhydrous). The *iso*oxazoline is oxidised to the oxide by hydrogen peroxide. Reduction of the above ethyl ester of (I) affords *ethyl* 2-*hydroxy*-3 : 4-*diphenyl*isooxazolidine-5 : 5-*dicarboxylate*, which exists in two forms, m. p. 140° and 125°, respectively (*copper* salt; *acetate*, m. p. 86—87°). F. G. WILLSON.



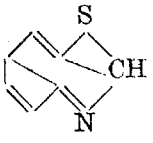
Aminobenzthiazoles. III. Tautomerism and unsaturation of the aminothiazole system. R. F. HUNTER (J.C.S., 1926, 1385—1401).—The author has established the tautomerism of the 1-aminobenzthiazole system with the 1-imino-1 : 2-dihydrobenzthiazole complex. Existing evidence of the symmetry type (A., 1879, 806; 1882, 1091; 1903, i, 866) is strengthened by synthesis of two series of isomeric derivatives, $C_6H_4\langle{}^{S}_{N}\rangle C{\cdot}NHR$ and $C_6H_4\langle{}^{S}_{NR}\rangle C{:}NH$ (R is Ac or Me), from stable and labile acetylphenylthiocarbamide, or from *s*- or *as*-phenylmethylthiocarbamide. Hydrolysis of the acetyl compounds affords the same 1-aminobenzthiazole. The base reacts in the imino-form on methylation or ethylation, and in the amino-form on acetylation, although small amounts of the other isomerides are probably present. The general chemistry of 1-aminobenzthiazole has been studied. The following new compounds are described: 1-*imino*-2-*methyl*-1 : 2-*dihydrobenzthiazole*, m. p. 123° (*dibromide*, softening at 125°; *tribromide*, whitening at 245°); 1-*methylaminobenzthiazole*, m. p. 138° (*tetrabromide*, decomp. 65—67°; *dibromide*, sintering at 136°, charring at 191°); 1-*imino*-2-*ethyl*-1 : 2-*dihydrobenzthiazole*, m. p. 86° (*tetrabromide*, decomp. 160—161°); 1-*imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole*, m. p. 118—120° (*dibromides*, orange, decomp. 130—132°, and purplish-red, decomp. 173°; *dibromide hydrobromide*, decomp. 180°); 1-*acetamidobenzthiazole tetrabromide*, m. p. 137—139°; 1-*benzamidobenzthiazole tetrabromide*, decomp. 185°; 5-*bromo*-1-*benzamidobenzthiazole*, m. p. 226°; *benz-*

thiazole-1-*azo*-β-*naphthol*, m. p. 146°; 1-*aminoazobenzthiazole*, m. p. 135° (*hydrochloride*, decomp. 232°); *ψ-aminobenzthiazole*, $C_6H_4<\begin{matrix}S\\N\end{matrix}>C\cdot NH_2$, decomp. 131° (*hydrochloride*, $C_6H_5<\begin{matrix}S=\\NCl\end{matrix}>C\cdot NH_2$, m. p. 239—240°, by action of ethyl nitrite on 1-aminobenzthiazole hydrochloride); *ψ-amino*-3-*toluthiazole hydrochloride*, decomp. 145°; *ψ-amino*-5-*toluthiazole hydrochloride*, decomp. 150°.

Tautomerism of the 5-bromo-derivatives is established by analogous syntheses. 5-*Bromo*-1-*aminobenzthiazole dibromide*, decomp. 80—82°; 1-*acetamidobenzthiazole hexabromide*, decomp. 160°; 5-*bromo*-1-*acetamidobenzthiazole*, m. p. 223°; and 5-*bromo*-1-*imino*-2-*acetyl*-1 : 2-*dihydrobenzthiazole*, m. p. 199—200°, are described.

Homologues of 1-aminobenzthiazole have been prepared: 1-*amino*-3-*methylbenzthiazole*, m. p. 136° (*dibromide*, m. p. 110°); *bromo*-1-*amino*-3-*ethylbenzthiazole*, m. p. 212° (*hydrobromide*, decomp. 290°); 1-*amino*-5-*methylbenzthiazole*, m. p. 142° (*dibromide hydrobromide*, decomp. 134°, on one occasion 106°); *bromo*-1-*amino*-5-*methylbenzthiazole*, m. p. 210°; 1-*amino*-4-*methylbenzthiazole*, m. p. 145° (*tetrabromide*, decomp. 250°); 1-*amino*-3 : 5-*dimethylbenzthiazole*, m. p. 116° (*tetrabromide*, very unstable red flakes, decomp. 80—90°, unmelted at 250°); 2-*amino*-β-*naphthathiazole*, m. p. 235—237° (*tetrabromide*, begins to decomp. 130°); 2-*amino*-α-*naphthathiazole*, m. p. 249—251° (*tetrabromide*, decomp. 165°).

Hot water instantly converts 1-aminobenzthiazole dibromide into 5-bromo-1-imino-1 : 2-dihydrobenzthiazole hydrobromide, an isomerisation analogous to the transformation of *N*-bromo- into *p*-bromoacetanilide. The change is explained by a bridged formula (annexed), which represents one of the tautomeric intra-annular phases of benzthiazole.



J. M. GULLAND.

Aminobenzthiazoles. IV. Stability of the bromides of the 1-xylidinodimethylbenzthiazoles. R. F. HUNTER (J.C.S., 1926, 1401—1404).—The instability of 1-amino-3 : 5-dimethylbenzthiazole tetrabromide (preceding abstract) is due to the combined effect of the *o*- and *p*-methyl groups, and is related to the mobility of the tautomeric hydrogen atom, because 1-arylaminobenzthiazole tetrabromides, in which the amino-phase is enhanced, show remarkable stability. 1-*m*-Xylidino-3 : 5-dimethylbenzthiazole (cf. Levi, A., 1925, i, 445) has m. p. 175° (*hexabromide hydrobromide*, red, decomp. 158°; *tetrabromide*, decomp. 130°). 1-p-*Xylidino*-3 : 6-*dimethylbenzthiazole* has m. p. 200° (*tetrabromide*, decomp. above 200°).

J. M. GULLAND.

Thiazole dyes. K. YAMADA (J. Soc. Chem. Ind. Japan, 1926, **29**, 36—42).—By heating a mixture of 100 g. of *o*-toluidine and 60 g. of sulphur at 185° for 24 hrs. dehydrothio-*o*-toluidine is obtained, m. p. 119·5—120°, b. p. 240°/16 mm. The yellow *bromine additive* compound sublimes at 174—175°; the *acetyl* derivative has m. p. 121—122°. *Dehydrothio*-*o*-*toluidinesulphonic acid* and its *salts* are described. Orthoprimuline is prepared by heating a mixture of 2 mols. of *o*-toluidine and 4·5 atoms of sulphur at 270°. The ammonium salt of orthoprimulinesulphonic acid may be separated from that of dehydrothio-*o*-toluidine, since it is more soluble in water. Many dyes (acid or acid-mordant as a rule) have been prepared by coupling dehydrothio-*o*-toluidine with Neville and Winther's acid, H acid, β-naphthol, etc., and their dye-properties examined. K. KASHIMA.

Dioximes. XXX. G. PONZIO (Gazzetta, 1926, **56**, 256—264; cf. A., 1925, i, 8, 1075).—The controversy with Gastaldi (A., 1924, i, 733; 1925, i, 987), whose results cannot be repeated, is continued. One form only of phenylhydroxyglyoxime is obtained, m. p. 191° (with decomp. to 5-hydroxy-3-phenyl-1 : 2 : 4-oxadiazole; cf. Falck, A., 1886, 797). This gives a *dibenzoyl* derivative, m. p. 183° (decomp.), of unknown structure, which with alcoholic alkali gives the above oxadiazole, and an isomeric *substance*, $C_8H_6O_2N_2$, m. p. 176° (decomp.), still under investigation, and when heated in alcohol isomerises quantitatively to a *substance*, $C_{22}H_{16}O_5N_2$, m. p. 153° (decomp.), possibly $BzON{:}CPh\cdot NBz\cdot CO_2H$, converted by alcoholic sodium hydroxide into the above oxadiazole. Phenylhydroxyglyoxime also forms a *triacetyl* derivative, m. p. 117—117·5°.

Complex *salts* of the composition $[C_{16}H_{12}O_6N_4Ni]M_2$, where $M=\frac{1}{2}Ni$, Na, K, or NH_4, are described. From the nickel salt phenylhydroxyglyoxime is regenerated on acidification.

E. W. WIGNALL.

Preparation of piperazyltheobromine. E. A. O. VIEL.—See B., 1926, 611.

Manufacture of hydrogenated cinchona alkaloids. HOWARDS AND SONS, and J. W BLAGDEN.—See B., 1926, 565.

Reactions produced by sunlight in the presence of uranium [and iron] compounds. Characteristic reactions for strychnine, morphine, codeine, and formaldehyde. J. ALOY, A. VALDIGUIÉ, and R. ALOY (Bull. Soc. chim., 1926, [iv], **39**, 791—795; cf. A., 1925, ii, 1081).—A sulphuric acid solution of strychnine containing uranium oxide or acetate becomes violet in sunlight, whilst one of codeine or morphine becomes dark blue. Codeine affords the blue colour in absence of sunlight if traces of formaldehyde are present, and therefore coloration may be due to formaldehyde produced photosynthetically from carbon dioxide. This reaction affords a very sensitive test for formaldehyde. Other aldehydes do not give the reaction, although it is given by ferrous as well as by uranous acetate. The phenanthrene ring of the alkaloids is probably involved, since, in the presence of formaldehyde, dionine (morphine ethyl ether) and phenanthrene give a similar blue colour.

R. BRIGHTMAN.

Unsaturated residues in chemical and pharmacological relationship. V. J. VON BRAUN, M. KÜHN, and S. SIDDIQUI (Ber., 1926, **59**, [*B*], 1081—1090; cf. A., 1923, i, 286).—The antagonistic action towards morphine or codeine exhibited by codeine derivatives in which the *N*-methyl group is replaced by other hydrocarbon residues appears to diminish

in approximate parallelism as the valency demand of the residue decreases.

*cyclo*Propylmethyl bromide is converted into cyclo*propylacetonitrile*, b. p. 142—144°, which is reduced to β-*cyclo*propylethylamine, giving a *benzoyl* derivative, b. p. 195°/13 mm., m. p. 46—47°, which, when distilled with phosphorus tribromide, affords β-cyclo*propylethyl bromide*, b. p. 129°, d_4^{17} 1·3117, together with much benzonitrile and dibromide, $C_5H_{10}Br_2$. *Propargyl bromide*, b. p. 83—88°, is prepared by the action of cyanogen bromide on methylpropargylaniline or *ethylpropargylaniline*, b. p. 119—120°/15 mm. (non-crystalline *picrate* and *methiodide*; hygroscopic *hydrochloride*, m. p. 133°); the latter base is obtained by the action of alkali hydroxide on *ethyl*-β-*bromoallylaniline*, b. p. 148°/13 mm. (non-crystalline *picrate* and *methiodide*; *hydrochloride*), whereby, however, the unsaturated residue is in part removed. *cyclo*Pentyl bromide, magnesium, and trioxymethylene afford *cyclo*pentylmethyl alcohol (mixed with di*cyclo*pentyl), from which non-homogeneous *cyclo*pentylmethyl bromide is derived. Similarly, *cyclo*heptyl bromide is converted successively into non-homogeneous cyclo*heptylmethyl alcohol*, b. p. 80—90°/15 mm., and cyclo*heptylmethyl bromide*, b. p. 80—82°/15 mm. The following derivatives of norcodeine are described: *propargylnorcodeine*, m. p. 137° (*hydrochloride*; *picrate*; *methiodide*, decomp. 172°; *bromo*-derivative, $C_{20}H_{20}O_3NBr$, m. p. 100—102°); *dibromoallylnorcodeine*, m. p. about 60°; cyclo*propylmethylnorcodeine*, m. p. 65° (*hydrochloride*, decomp. 250—252°; *chloroplatinate*, decomp. 199—200°; *picrate*, m. p. 110—115°); cyclo*butylmethylnorcodeine* (hydrochloride, m. p. 150°; *chloroplatinate*, decomp. 217°); β-cyclo*propylethylnorcodeine* [*hydrochloride*, m. p. 160° (decomp.)]; cyclo*pentylmethylnorcodeine*, m. p. 50° (*picrate*, m. p. 125—128°; *hydrochloride*, m. p. 171—174°); cyclo*hexylmethylnorcodeine*, m. p. 55—60° (*picrate*, m. p. 132—135°; *hydrochloride*, m. p. 171—176°); cyclo*heptylmethylnorcodeine*, m. p. 59—61° (*picrate*, m. p. 139°); α-*thienylnorcodeine*, $C_{16}H_{14}O(OMe)(OH)>N\cdot CH_2\cdot C_4H_3S$, m. p. 76° (*hydrochloride*, decomp. below 200°; *picrate*, m. p. 145° after softening). H. WREN.

Trypanocidal action and chemical constitution. V. Arylsulphonamides of some phenylarsinic acids. L. F. HEWITT, H. KING, and W. O. MURCH (J.C.S., 1926, 1355—1370).—Methyl sulphate and alkali at 100° convert 4′-toluenesulphonyl-4-aminophenylarsinic acid (cf. Little, Cahen, and Morgan, *ibid.*, 1909, **95**, 1482) into 4′-*toluenesulphonyl*-4-*methylaminophenylarsinic acid*, which yields 4-methylaminophenylarsinic acid on hydrolysis by cold sulphuric acid. An improved method is described for preparing sodium 3-nitrotoluene-4-sulphonate. Nitration of 3′-*nitro*-4′-*toluenesulphonyl*-4-*aminophenylarsinic acid* (*N-methyl* derivative described) and 3′-*nitrobenzenesulphonyl*-4-*aminophenylarsinic acid* yields exclusively the corresponding 3 : 3′-*dinitro-acids*. Reduction of these five nitro-acids with ferrous chloride and alkali affords 3′-*amino*-4′-*toluenesulphonyl*-4-*aminophenylarsinic acid* and its *N-methyl* derivative; 3′-*aminobenzenesulphonyl*-, 3 : 3′-*diamino*-4′-*toluenesulphonyl*-, and 3 : 3′-*diaminobenzenesulphonyl*-4-*aminophenylarsinic acids*. Further reduction of some of the above compounds by the usual methods yields 3′-*amino*- and 3 : 3′-*diamino*-4′-*toluenesulphonyl*-4-*aminophenylarsenious oxide*, and 3′-*amino*-4′-*toluenesulphonyl*- and 3′-*aminobenzenesulphonyl*-4-*aminoarsenobenzenes*. The last two substances are white in contrast to their benzamide analogues.

The colour reactions shown by weakly alkaline solutions of *o*-hydroxysulphonamides in presence of iron, cobalt, nickel, or copper salts are attributed to the formation of co-ordination complexes analogous to the pyrocatechol complexes of Weinland and Binder (A., 1912, i, 184). The acidic hydrogen of the group $SO_2\cdot NH$ is involved, since *N*-methyl derivatives or the benzamides do not form colours. 3′-*Nitro*- and 3′-*aminobenzenesulphonyl* derivatives of 3-*amino*-4-*hydroxy*- and 4-*amino*-2-*hydroxyphenylarsinic acids* are described. N-4-*Toluenesulphonyl*-3-*amino*-4-*hydroxybenzoic acid* has m. p. 250° (decomp.) and N-p-*toluenesulphonyl*-o-*methylaminophenol*, m. p. 127—128°. Reverdin's "*O*-toluenesulphonyl-*N*-*p*-monomethylaminophenol," m. p. 135° (A., 1909, i, 377), is *N*-*p*-toluenesulphonyl-*p*-methylaminophenol, m. p. 136—137°.

Dilute nitric acid oxidises p-*xanthylphenylarsinic acid* to *diphenyl disulphide*-pp′-*diarsinic acid* (*barium* salt described) and p-*sulphophenylarsinic acid*.

J. M. GULLAND.

Behaviour of arsenobenzenes towards molecular oxygen. I. E. MASCHMANN (Ber., 1926, **59**, [*B*], 1142—1148).—Solid arsenobenzene combines so vigorously with oxygen that explosions frequently result, whereas arsenophenylglycine, salvarsan, sodium salvarsan, salvarsanglycide, neosalvarsan, sulphoxylsalvarsan, 3 : 5 : 3′ : 5′-tetra-amino-4 : 4′-dimethylaminoarsenobenzene tetrahydrochloride, silver salvarsan, and silver neosalvarsan adsorb only a small proportion of oxygen, which is quantitatively evolved when the products are heated gently in a vacuum. The behaviour is independent of the age of the preparations. Variation in the toxicity of normally manipulated specimens cannot therefore be attributed to arsenoxides formed by atmospheric oxidation.

H. WREN.

Behaviour of arsenobenzenes towards molecular oxygen. II. E. MASCHMANN (Ber., 1926, **59**, [*B*], 1148—1159; cf. preceding abstract).—The absorption of molecular oxygen by substituted salvarsans in solution is due to chemical change in the substituent groups rather than to reactivity of the arseno-group, which, although very marked in arsenobenzene, is restricted by the presence of substituents in the derivatives. Neosalvarsan, $NH_2\cdot C_6H_3(OH)\cdot As{:}As\cdot C_6H_3(OH)\cdot NH\cdot CH_2\cdot O\cdot SONa$, in neutral aqueous solution absorbs oxygen vigorously with marked discoloration and separation of a brownish-black precipitate. "Sulphite salvarsan," containing the group $\cdot NH\cdot CH_2\cdot O\cdot SO_2Na$, is relatively very stable towards oxygen, as is sulphoxylsalvarsan. The probability that oxygen affects primarily the iminomethylenesulphoxylate group of neosalvarsan is supported by the exactly analogous behaviour of *o*-aminophenolsulphoxylate. 3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene hydrochloride in 6% or 10%

aqueous solution absorbs oxygen very slowly without change of colour, but with marked increase in viscosity; the latter property is not shown by 3 : 3′ : 5 : 5′-tetra-amino-4 : 4′-dimethylaminoarsenobenzene hydrochloride. Absorption of oxygen by solutions of 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene in aqueous sodium hydroxide increases greatly with increasing alkalinity and is accompanied by darkening of the solution and separation of a precipitate. Reaction is mainly due to the vicinal amino- and hydroxyl groups, and is shown also by *o*-aminophenol, 3-amino-4-hydroxyphenylarsinic acid, and 3-amino-4-hydroxybenzoic acid. Participation of the arseno-group to a minor extent is established by the isolation of 3-amino-4-hydroxyphenylarsinic acid in 7% yield. The formation of an arsinoxide could not be detected.

H. WREN.

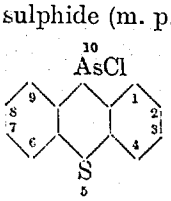
as-Chlorotetrahydroarsinoline and some quaternary arsonium compounds. E. ROBERTS, E. E. TURNER, and (in part) F. W. BURY (J.C.S., 1926, 1443—1447; cf. *ibid.*, 1921, **119**, 426).—*As*-Methyltetrahydroarsinoline (methiodide, m. p. 239—240°; *ethiodide*, m. p. 185—186°; *benzobromide*, m. p. 210—211°) forms a *dichloride* which, when heated, gives *As-chlorotetrahydroarsinoline*, m. p. 22°, b. p. 155°/16 mm. *γ-Phenylpropyldimethylethylarsonium iodide* has m. p. 118°. Interaction of the Grignard reagent and dimethyliodoarsine affords arsines of the type $Ph\cdot[CH_2]_x\cdot AsMe_2$; the m. p. of the corresponding methiodides show marked alternation. The following compounds are described: *benzyldimethylarsine*, b. p. 110°/8 mm. (*methiodide*, m. p. 195—196°; *ethiodide*, m. p. 163—165°); *δ-phenyl-n-butyldimethylarsine*, b. p. 150°/14 mm. (*methiodide*, m. p. 150—151°; *ethiodide*, m. p. 134—135°); *phenyl-β-phenylethylmethylarsine*, b. p. 187°/12 mm. or 190°/15 mm. (*methiodide*, m. p. 119°).

[With F. W. BURY.]—Attempted resolutions of arsenic compounds have been discontinued. Suitable Grignard reagents and arsenic derivatives yield *dicyclohexylphenylarsine*, b. p. 220°/14 mm. (*methiodide*, m. p. 187°; *ethiodide*, m. p. 188—189°); *tricyclohexylarsine*, b. p. 235°/12 mm. (*methiodide*, m. p. 153—154°; *benzobromide*, m. p. 197°); and *cyclohexylphenylmethylarsine*, b. p. 152—153°/12 mm. (*benzobromide*, m. p. 193°).

Phenylbenzylarsinic acid forms a *l-menthylamine* and a *strychnine* salt, $[\alpha]_D^{20}$ −31·2° in 50% aqueous acetone; these are partly hydrolysed on recrystallisation.

J. M. GULLAND.

10-Chlorophenthiarsine, and its rate of formation from o-phenylthiolphenyldichloroarsine. E. ROBERTS and E. E. TURNER (J.C.S., 1926, 1207—1210; cf. A., 1925, i, 1339).—o-*Phenylthiolphenyldichloroarsine* has been prepared from *o*-nitrodiphenyl sulphide (m. p. 79°, cf. Mauthner, A., 1906, i, 948) by way of o-*phenylthiolphenylarsinic acid*, m. p. 192—194°, and o-*phenylthiolphenylarsenious oxide*, m. p. 187—189°, and its rate of conversion into 10-*chlorophenthiarsine* (annexed formula), m. p. 129—130°, determined. Only 20% conversion takes place under conditions in which the oxygen analogue shows 60% conversion. o-*Phenoxyphenylmethylchloroarsine* is even more stable, losing only 10% of the theoretical amount of hydrogen chloride and some methyl chloride. Treatment of the residue with methyl iodide yielded 10-iodophenoxarsine, but none of the expected 10 : 10-*dimethylphenoxarsonium iodide*, m. p. 207°, which was prepared from magnesium methyl iodide and 10-chlorophenoxarsine.



J. M. GULLAND.

Mercury compounds of "medinal" and the official (Ph. G. V., Ergänzbd. IV) test for identifying "medinal." E. RUPP and K. MÜLLER (Arch. Pharm., 1926, **264**, 362—365).—"Medinal" (veronal-sodium) and mercuric acetate interact in aqueous solution to give a precipitate of *acetatomercuriveronal*, $CEt_2\langle{}^{CO\cdot NH}_{CO\cdot N\cdot Hg\cdot OAc}\rangle CO$. The corresponding *hydroxide* (the *nitrate* and *chloride* are also described) is soluble in sodium hydroxide; the solution obtained interacts with more "medinal" to give a precipitate of the *compound* $\left[CEt_2\langle{}^{CO\cdot NNa}_{CO\cdot NHg}\rangle CO\right]_2\overline{CO\langle{}^{N\cdot CO}_{N\cdot CO}\rangle CEt_2}$. The latter can also be produced by direct interaction of "medinal" and mercuric oxide in hot aqueous suspension.

The above compounds are evidently identical with those formed in the official test for identifying "medinal."

W. A. SILVESTER.

Action of mercuric acetate on m-chloroaniline. L. VECCHIOTTI (Gazzetta, 1926, **56**, 216—224; cf. A., 1925, i, 1058).—The action of mercuric acetate on *m*-chloroaniline in aqueous solution gives m-*chloroaniline*-2 : 4 : 6-*trimercuriacetate*, $NH_2\cdot C_6HCl(Hg\cdot OAc)_3$, m. p. 210°, but no mono- or di-mercuriacetate has yet been obtained. When treated with chlorine in presence of calcium chloride, the trimercuriacetate yields 2 : 3 : 4 : 6-tetrachloroaniline, identified by means of the corresponding tetrachloroacetanilide. m-*Chloroacetanilide*-2 : 4 : 6-*trimercuriacetate*, decomp. (without melting) 240°; m-*chloroaniline*-2 : 4 : 6-*trimercurihydroxide*, decomp. 225°, and the corresponding *chloride*, decomp. 205°, have been prepared.

T. H. POPE.

Racemisation. III. Action of alkali on glycyl-l-alanylglycine and glycylglycyl-l-alanylglycine. P. A. LEVENE and M. H. PFALTZ (J. Biol. Chem., 1926, **68**, 277—283; cf. A., 1925, i, 795, 1474).—The above peptides were exposed to the action of 0·1*N*-, 0·2*N*-, and *N*-sodium hydroxide for periods of 48 hrs. and of 39—50 days; the alanine obtained by hydrolysis of the resulting solutions possessed its full optical activity in the case of all the short experiments, and showed racemisation to the extent of 10% only in the long experiments, although in these cases the peptide was hydrolysed by the alkali to the extent of 80%. *Chloroacetylglycyl-l-alanylglycine* has m. p. 130° (decomp.), $[\alpha]_D^{20}$ +48·3°; *glycylglycyl-l-alanylglycine*, m. p. 205° (decomp.), $[\alpha]_D^{20}$ +53·7°.

C. R. HARINGTON.

Separation of l-leucyl-d-glutamic acid and its anhydride from a trypsin digest of gliadin. E. ABDERHALDEN (Z. physiol. Chem., 1926, **154**, 18—20).—The digest, after 8 weeks at 37°, is evaporated to

dryness, mixed with a little water and sand, and extracted with a series of organic solvents. From the methyl alcohol extract, the anhydride of *l*-leucyl-*d*-glutamic acid has been separated in 0·4% yield. The acid itself may be isolated from the extracted digest by dissolving in water and precipitating with silver nitrate and ammonia after having removed the greater part of the difficultly soluble amino-acids by fractional crystallisation. H. D. KAY.

Method for determining the constitution of the peptides. P. SCHLACK and W. KUMPF (Z. physiol. Chem., 1926, **154**, 125—170).—By heating the benzoylated peptide with a thiocyanate in presence of acetic anhydride and glacial acetic acid a substituted thiohydantoin is obtained. If the latter is treated with *N*-sodium hydroxide, it is hydrolysed to a simple thiohydantoin and a peptide having a chain shorter by one amino-acid. This treatment with thiocyanic acid followed by sodium hydroxide is then repeated as often as required. Unbenzoylated peptides do not give such good results as benzoylated peptides. Methods for purification and identification of the thiohydantoins produced are described. The various theories of protein structure which have been put forward are discussed at some length in relationship to the results obtained, or obtainable, by this new method. H. D. KAY.

Partial decomposition of thymus-nucleic acid. H. STEUDEL (Z. physiol. Chem., 1926, **154**, 116—124).—The breakdown of the thymus-nucleic acid molecule described by Thannhauser and Dorfmüller (*ibid.*, 1921, **114**, 39) as being brought about by boiling the acid with picric acid solution, has been reinvestigated. It had been stated that by this method of hydrolysis the purine nucleotides were decomposed, but not the pyrimidine nucleotides. The present author finds that not only is the yield of adenine and guanine picrate far from the theoretical, but also that the pyrimidine nucleotides are hydrolysed to a considerable extent. H. D. KAY.

Citrylhæmin. A. PARTOS (Biochem. Z., 1926, **172**, 126). H. GOLDMAN (*ibid.*, 127—132).—A crystalline compound, decomp. about 250°, was obtained by the action of methyl alcohol containing citric acid on coagulated blood in a yield of 0·4 g. to 0·7 g. per kg. of blood. The curve for the extinction coefficient at different wave-lengths differs slightly from that of tartarylhæmin, but is very similar to that of formylhæmin. The compound may have the formula :

$$(C_{34}H_{31}MeO_4N_4Fe)O\rangle C\langle \begin{matrix} CH_2\cdot CO\cdot O(C_{34}H_{31}MeO_4N_4Fe) \\ CH_2\cdot CO\cdot O(C_{34}H_{31}MeO_4N_4Fe) \end{matrix}$$
$$(C_{34}H_{31}MeO_4N_4Fe)O\cdot CO$$

H. I. COOMBS.

Proteins. II. Action of superheated water on proteins. II. I. S. KOMATSU and C. OKINAKA (Bull. Chem. Soc. Japan, 1926, **1**, 102—108).—Edestin, gliadin, and casein were digested severally for varying lengths of time with water at 110—120°. The proteins gave in each case an insoluble residue and soluble substances, the proportion of the latter increasing with longer treatment. The composition of the residue differed from that of the mother protein, and was not constant. With edestin, the amide groups were the first removed, the diamino-groups following gradually. The reverse occurs with casein, whilst gliadin stands between the two. A transformation of diamino-nitrogen into amide-nitrogen occours with edestin during the treatment, but not with gliadin. The p_H values of the pure proteins and of the solutions after digestion, and the analyses of the residues and the solutions are tabulated. B. W. ANDERSON.

Horn-dissolving action of alkali sulphides. P. PULEVKA (Z. physiol. Chem., 1926, **155**, 156).—A reply to Weiss (this vol., 749). E. C. SMITH.

Organic micro-analysis. B. FLASCHENTRÄGER (Z. angew. Chem., 1926, **39**, 717—722).—Extensive details are given of a uniform, valid system of organic micro-analysis, based mainly on the methods of Pregl. S. K. TWEEDY.

Elementary micro-analysis. Determination of sulphur and halogens. C. FUNK and S. KON (J. Amer. Chem. Soc., 1926, **48**, 1667—1671).—A modified technique for the micro-determination of sulphur, the halogens, and phosphorus is described. F. G. WILLSON.

Microchemical reactions for oxalic acid. M. WAGENAAR (Pharm. Weekblad, 1926, **63**, 722—727).—A *résumé* and amplification of previous work on microchemical detection of oxalic acid and its salts. S. I. LEVY.

Detection of minute quantities of formaldehyde. T. SABALITSCHKA and C. HARNISCH (Pharm. Zentr., 1926, **67**, 289—294, 309—312, 324—327, 339—342, 357—359, 371—374, 387—390).—Many tests for formaldehyde have been examined. In the presence of acetaldehyde, furfuraldehyde, carbohydrates, and other substances, the following tests may be used : for 1 : 50,000 formaldehyde solutions, the tests with phloroglucinol and potassium hydroxide, resorcinol and sulphuric acid, phenylhydrazine and sodium nitroprusside in alkaline solution, phenylhydrazine hydrochloride and sodium nitroprusside in alkaline solution, and magenta and sulphurous acid (according to Fincke); and only for higher concentrations of formaldehyde, the tests with naphthalene and concentrated sulphuric acid, *apo*morphine and sulphuric acid, and phloroglucinol and hydrochloric acid. The greatest sensitivity (1 part in a million) among the tests investigated is shown by those with phenylhydrazine hydrochloride and sodium nitroprusside in alkaline solution, phenylhydrazine hydrochloride with potassium ferricyanide and hydrochloric acid, peptone and hydrochloric acid with ferric chloride, and phloroglucinol and potassium hydroxide. A critical discussion of the methods is given, and in each case the sensitivity is indicated. B. FULLMAN.

Simple reaction to distinguish between cocaine and novocaine. D. GERHARDT (Pharm. Weekblad, 1926, **63**, 560—561).—Cocaine hydrochloride gives a precipitate with ammonia under conditions in which the novocaine salt gives none. This property may be used to effect partial separation of the bases in one operation. S. I. LEVY.

Separation of histidine and arginine. H. B. VICKERY and C. S. LEAVENWORTH (J. Biol. Chem., 1926, **68**, 225—228).—Treatment of a solution containing histidine and arginine with silver nitrate, and then with barium hydroxide until faintly alkaline to phenolphthalein, precipitates all the histidine and a considerable amount of arginine; this is in disagreement with the work of Kossel and Edlbacher (A., 1920, ii, 784), who state that histidine alone is precipitated under these conditions. C. R. HARINGTON.

Biochemistry.

Alveolar carbon dioxide tension following vigorous exercise. N. CORDERO (Amer. J. Physiol., 1926, **77**, 91—99).—The curve given by plotting the alveolar carbon dioxide against time following short vigorous exercise is not linear, as stated by Haldane and Quastel, but somewhat concave downwards, being roughly the inverse of published curves of the disappearance of lactic acid from the blood and the recovery from oxygen debt. The changes in alveolar carbon dioxide tension are governed by mass action considerations and not by limitation of available enzyme. R. K. CANNAN.

Relative sensitivity of the benzidine and phenolphthalein tests for blood. A. D. STAMMERS (Biochem. J., 1926, **20**, 620—621).—The phenolphthalein reagent is 10—30 times as sensitive as the benzidine reagent when used with blood diluted with water and 3—4 times as sensitive when used with urine containing blood. S. S. ZILVA.

Oxygen-, acid-, and base-combining properties of blood. II. Preparation of crystalline isoelectric hæmoglobin. W. C. STADIE and E. C. Ross (J. Biol. Chem., 1926, **68**, 229—237).—Electrodialysis of washed red blood-corpuscles, from the dog or horse, at 110 v. for 3—4 hrs. results in complete removal of inorganic electrolytes, hæmolysis of the cells, and separation of 60—70% of the hæmoglobin in crystalline form; it may be recrystallised by solution in alkali, removal of cell *débris* by centrifuging, and reprecipitation of the hæmoglobin by dialysis. The hæmoglobin so obtained possesses its full oxygen capacity and can be preserved for 5 days at 0°, in the moist condition, without appreciable inactivation; desiccation causes complete inactivation. The hæmoglobins of sheep- and ox-blood do not crystallise under the above conditions, and can therefore be obtained in concentrated solution in the presence of less base than is the case with the dog and horse hæmoglobin. C. R. HARINGTON.

Compounds of the prosthetic group of hæmoglobin with oxygen and carbon monoxide. Oxygen content of hæmatin. J. ROCHE (Bull. Soc. Chim. biol., 1926, **8**, 362—382).—Carbon monoxide–hæmochromogen loses its carbon monoxide quantitatively on treatment with strong acids and is converted into hæmochromogen in alcoholic solution and into hæmatin in aqueous medium. A method for the determination of hæmatin based on its power to combine with carbon monoxide after reduction is described. Hæmatin contains one molecule of oxygen per atom of iron, the oxygen having the same properties in both acid and alkaline hæmatin. H. J. CHANNON.

Naturally occurring porphyrins. XIX. Transformation of hæmin into protoporphyrin. Preparation of mesoporphyrin. H. FISCHER and B. PÜTZER (Z. physiol. Chem., 1926, **154**, 39—63).—Protoporphyrin, the porphyrin produced by direct removal of iron from blood pigments, may be prepared by the action of colloidal palladium or of iron powder, in presence of formic acid, on hæmin. Nickel, copper, or zinc may be used in place of palladium, but metal complexes of protoporphyrin are obtained. Protoporphyrin is isolated as the crystalline methyl ester, from which the free porphyrin is readily obtained. It forms a series of complex metallic salts; those of copper, zinc, cobalt, nickel, tin, and thallium are crystalline. The iron salt is hæmin, and may be obtained in good yield by adding the calculated amount of ferric chloride in glacial acetic acid solution to protoporphyrin, in presence of sodium acetate. Synthetic hæmin appears to contain 34 carbon atoms in the molecule. When the transformation of hæmin into protoporphyrin occurs slowly, mesoporphyrin is usually detectable in the reaction mixture. Ætioporphyrin, identical with Willstätter's compound, together with a porphyrin containing less hydrogen, which gives ætioporphyrin on reduction, results from the decarboxylation of protoporphyrin. H. D. KAY.

Method of representing the variations in the concentration of hydrogen ions in organic media, and especially blood. C. O. GUILLAUMIN (Bull. Soc. Chim. biol., 1926, **8**, 160—164).—In the system of notation proposed, the optimum hydrogen-ion concentration becomes 100 ($=p_H$ 7·35 for blood) and the lower limit (p_H 6·77 for blood) is the zero. C. P. STEWART.

Degradation of dextrose by the blood-corpuscles of the rabbit. J. T. IRVING (Biochem. J., 1926, **20**, 613—619).—The rate of disappearance of dextrose from an isotonic saline solution in which blood-corpuscles are suspended is independent of the initial concentration, being linear over a wide range of values. The temperature coefficient between 27° and 37° is 2·1. The glycolytic rate of laked corpuscles, which differs a great deal from sample to sample, is considerably less than that of intact cells. Evidence is produced which shows that dextrose does not diffuse into the blood-corpuscles. Propyl and ethyl alcohols inhibit the glycolytic action of the corpuscles. It is suggested that dextrose is degraded, although not necessarily oxidised, on the corpuscle surface. S. S. ZILVA.

Residual reduction of blood. R. EGE (J. Biol. Chem., 1926, **68**, 317—321).—The experiments of Hiller and others (A., 1925, i, 1200) are criticised on

the ground that these workers did not allow sufficient time for the removal of dextrose from the blood by yeast, in consequence of which their figures for the residual reducing substances were too high.

C. R. HARINGTON.

Residual reduction of blood. D. D. VAN SLYKE and A. HILLER (J. Biol. Chem., 1926, **68**, 323—324).—Further experiments are recorded in support of those of Hiller and others (A., 1925, i, 1200) and in opposition to the view of Ege (cf. preceding abstract).

C. R. HARINGTON.

Distribution of non-electrolytes between corpuscles and plasma of human blood. C. LUNDSGAARD and S. A. HOLBØLL (Biochem. Z., 1926, **173**, 269—274).—The distribution ratio of acetone, lævulose, galactose, and carbamide between corpuscles and plasma is, in each case, about 70 : 100.

P. W. CLUTTERBUCK.

Bimolecular layers of lipins on the chromocytes of the blood. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 314—317).—Lipins were extracted from blood by Bloor's method and measured by spreading out on a water surface in the Langmuir–Adam apparatus. The results confirm the conclusion previously reached (J. Exp. Med., 1925, **41**, 439) that the quantity of lipins contained in the chromocytes of different animals is exactly sufficient to cover the surface of these chromocytes in a layer 2 mols. thick.

M. S. BURR.

Spreading of different lipins from chromocytes of different animals. E. GORTER and F. GRENDEL (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 318—320).—The spreading values of the lipins of blood, kephalin (with 25% of lecithin), sphingomyelin, cholesterol, and cholesteryl palmitate have been measured. Determination of the cholesterol content of the blood of different animals shows that two-fifths of the surface occupied by all the lipins of the blood cells is taken up by cholesterol. Kephalin and lecithin are in the expanded condition (cf. Adam, A., 1922, ii, 687) at 37° and cholesterol and sphingomyelin in the condensed form. M. S. BURR.

Ammonia content of, and ammonia formation in, blood. VI. Ammonia content of circulating blood and the localisation of ammonia formation and disappearance in rabbits. J. K. PARNAS and A. KLISIECKI (Biochem. Z., 1926, **173**, 224—248).—Blood-ammonia is transiently increased during hunger, increased on injection of sodium dihydrogen phosphate, but is unaffected by breathing air rich in carbon dioxide. At death, a considerable increase in blood-ammonia occurs, independently of the method of killing (suffocation, poisoning by hydrogen cyanide, shock, etc.) due to anoxæmia, which deprives the liver of its power to utilise ammonia in the normal way. Ammonia is probably converted by the liver into carbamide, but not into the substance which yields ammonia when blood is kept. The chief source of ammonia in rabbits is the cæcum, the blood in the *V. mesenterica cæci* containing about fifty times as much as the peripheral blood. The blood of the jejunum, ileum, and transverse colon is rich, but of the ascending colon and rectum is poor in ammonia. Blood leaving the pregnant uterus is always rich in ammonia. In the dying animal, ammonia of blood sealed off in the heart and great veins increases, but capillary blood-ammonia does not increase (cf. this vol., 536).

P. W. CLUTTERBUCK.

Behaviour of the precursor of ammonia in blood and its importance in the regulation of neutrality. D. ADLERSBERG and M. TAUBENHAUS (Arch. exp. Path. Pharm., 1926, **113**, 1—39).—The blood-ammonia, which on withdrawal from the body is very small, increases rapidly *in vitro* and under certain conditions reaches a maximum after 24 hrs., when its value affords a measure of the amount of the precursor of ammonia originally present in the blood. The amount of this precursor in the blood of men or of animals is found to be remarkably constant under very varied conditions. It may be diminished in circumstances which result in a large excretion of ammonia by the urine, but during the extreme acidosis of diabetic coma it may be increased. Its constancy and relation to the amount of ammonia excreted by the kidney probably indicate that it is of importance in the mechanism for the maintenance of the neutrality of the blood. W. O. KERMACK.

Blood catalase content in mountain and valley dwellers in middle Asia. A. I. ALEXEEV (Biochem. Z., 1926, **173**, 433—439).—Mountain dwellers have an average of 38% more catalase per unit volume of blood than valley dwellers. Blood catalase is at its maximum in the morning, and reaches a minimum in the evening. H. D. KAY.

Solubility of calcium in blood serum. L. IRVING (J. Biol. Chem., 1926, **68**, 239—243).—Shaking for 24 hrs. in contact with calcium carbonate causes a loss of calcium from blood-serum unless the atmosphere to which the serum is exposed contains 20% or more of carbon dioxide. C. R. HARINGTON.

State of calcium in body fluids. J. MARRACK and G. THACKER (Biochem. J., 1926, **20**, 580—594).—When protein solutions are dialysed against protein-free calcium solutions the concentration of the calcium ion in the former eventually approximates to that of the latter. The protein solution also contains an undissociated calcium–protein compound, the amount of which is proportional to the concentration of the protein in the protein solution and to the concentration of calcium ion in the external solution. Such an undissociated compound accounts for the so-called indiffusible calcium of serum. The calcium-ion concentration of body-fluids is not regulated by the solubility of calcium carbonate and calcium phosphate. The calcium of body-fluids is partly in the form of an un-ionised compound and partly in the ionic form, and the calcium-ion concentration of plasma is slightly higher than the calcium concentration of cerebrospinal fluid. The value of the expression $[Ca^{\cdot\cdot}][HCO_3']/f_H{\cdot}[H^{\cdot}]$ in solutions saturated with calcite increases with increasing ionic strength of the solutions. Epilepsy is not caused by a reduction of calcium-ion concentration in body-fluids.

S. S. ZILVA.

Effect of pure protein solutions and of blood-serum on the diffusibility of calcium. R. F. LOEB (J. Gen. Physiol., 1926, **8**, 451—461).—When solutions, at p_H 7·4, of crystalline egg-albumin, serum-globulin, and human blood-serum were dialysed against 0·8% sodium chloride solution containing varying amounts of calcium chloride, the molar concentrations of calcium within the membrane were greater than in the outside solution, and the ratio Ca inside/Ca outside varied directly with the protein concentration. On the acid side of the isoelectric point of the protein, the concentration of calcium inside the membrane was less than outside. The results were thus in accordance with the Donnan theory. The magnitude of the ratio Ca inside/Ca outside was probably the resultant of the Donnan equilibrium and the formation of complex calcium–protein ions (such as exist in the case of zinc, potassium, and lithium ions). C. P. STEWART.

Chlorine in blood. Sodium chloride in blood and secretion of gastric juice. A. SINDLER (Z. ges. exp. Med., 1925, **47**, 156—166; from Chem. Zentr., 1926, I, 970).—During secretion of gastric juice, the sodium chloride content of the blood decreases. Administration of moderate amounts (up to 6 g.) of sodium chloride scarcely affects the chlorine content of the blood. There is a rapid decrease in sodium chloride content during hunger. G. W. ROBINSON.

Urea-nitrogen concentration of the blood. I. Physiological variations of the blood urea-nitrogen and the influence of fixation and anæsthesia on it. II. Effect of caffeine. K. TASHIRO (Tôhoku J. Exp. Med., 1925, **6**, 601—629, 630—643).—I. The urea-nitrogen concentration in the blood is equally distributed between corpuscles and plasma. The value is minimal on the third or fourth day of starvation. With the well-fed rabbit there is no daily variation, but the value is higher in the warmer season. Increase takes place under anæsthesia.

II. Small doses of caffeine increase, but large doses decrease, the blood urea-nitrogen concentration in the rabbit. The increase is arrested or converted into a decrease by the administration of paraldehyde. With atropinised or vagotomised rabbits, the blood urea-nitrogen content is not increased, but rather decreased, by caffeine. CHEMICAL ABSTRACTS.

Uric acid levels in the blood of man and animals. A. T. WEATHERS and H. C. SWEANEY (J. Lab. Clin. Med., 1925, **10**, 480—485).—Folin's and Benedict's methods are preferable to Folin and Wu's method for the determination of uric acid; polyphenols and amino-acids do not interfere. The normal level of uric acid in blood is 1—4 mg. per 100 c.c.; there is a slight decrease in far-advanced stages of tuberculosis. CHEMICAL ABSTRACTS.

Osmotic pressure of the proteins of human serum and plasma. E. B. VERNEY (J. Physiol., 1926, **61**, 319—328).—When the plasma is diluted, the osmotic pressure per 1 g. of protein nitrogen gradually falls. For dilutions up to 50% of the original concentration of protein, the relation $p(v-b)=k$ holds, where p is the osmotic pressure, v the reciprocal of the concentration of protein nitrogen, and b and k are constants. The value of b is that of a solution in which the colloidal particles are un-ionised and occupy an effective volume of 50% of the original plasma. R. K. CANNAN.

Fractionation of serum proteins. III. Precipitation by acids. G. ETTISCH and W. BECK (Biochem. Z., 1926, **172**, 1—9).—The electrolytes of serum play an important part in the precipitation of the proteins by acids. With normal electrolyte content, a precipitation by acid is impossible, and the quantity of protein precipitated is greater the freer the serum is from electrolytes. By protein precipitation a certain inner structure is destroyed which cannot be reproduced. H. I. COOMBS.

Increase in specific viscosity and colloidal state of serum proteins. II. L. PETSCHACHER (Z. ges. exp. Med., 1925, **47**, 325—347; from Chem. Zentr., 1926, I, 712).—Data are given for the changes in physical properties of the serum proteins (cf. Z. ges. exp. Med., 1924, **41**, 142). G. W. ROBINSON.

Changes in the colloidal state of serum proteins under physical influences. III. L. PETSCHACHER (Z. ges. exp. Med., 1925, **47**, 348—358; from Chem. Zentr., 1926, I, 712; cf. preceding abstract).—The specific viscosity and sensitivity to precipitation by ammonium sulphate of the proteins of native serum all increase more or less with time, heating to 56—58°, shaking, and irradiation with ultra-violet or *X*-rays. The total protein content remains unaltered. The changes observed are probably of similar character, and consist in an alteration in the structure of the protein molecule, leading finally to "denaturing." There is no necessity to postulate a change of albumin into globulin. G. W. ROBINSON.

Photoactivity. III. Effect of photoactive substances on the blood-sugar level. H. VOLLMER and S. LEE (Biochem. Z., 1926, **173**, 467—475).—With most substances investigated there was no correspondence between photoactivity and hyperglycæmic power. Certain strongly active vegetable oils, however, raise the blood-sugar of rabbits. H. D. KAY.

Physical and chemical influences in hæmolysis by hæmolytic immune-sera. M. PIETTRE (Compt. rend., 1926, **182**, 1569—1571; cf. this vol., 635).—The antibody will unite equally well with the corpuscular stromata when separated from the cells and with the stroma protein after it has been dissolved in alkali and reprecipitated by acid. This is cited as evidence for the chemical basis of hæmolysis. L. F. HEWITT.

Hæmolysis. II. Effect of salts and hæmolysis by saponin. R. MOND (Pflüger's Archiv, 1925, **209**, 499—511; from Chem. Zentr., 1926, I, 712; cf. this vol., 316).—Whilst potassium salts at varying p_H generally increase hæmolysis in the presence of other ions, there is a marked antagonism in the effect of sulphate and calcium ions. Sulphate ions oppose hæmolysis in the region of the isoelectric point, whilst calcium ions favour hæmolysis under the

same conditions. Further from the isoelectric point calcium ions antagonise the hæmolytic effect of hydroxyl ions. Salts show characteristic hæmolysis–time curves which may intersect. The ions of neutral salts, independently of the reaction, affect the permeability of saponin blood-corpuscles differently, and partly in the opposite sense, from that of normal cells. This is particularly shown in the course of hæmolysis by sodium sulphate and calcium chloride. With alkaline reaction, small concentrations of saponin, except in calcium chloride solution, markedly inhibit hæmolysis. G. W. ROBINSON.

Kinetics of hæmolytic systems. I. E. PONDER (Biochem. J., 1926, **20**, 507—514).—The difference of resistance of the cells of normal persons to saponin hæmolysis is small and is independent of the mere cell content of the blood. The relative resistances of the cells of a number of animals examined are: rabbit, 0·35; man, 1·0; pig, 1·2; cat, 4·5; ox, 8·0; and sheep, 9·0. In these experiments, too, the resistance is not dependent on the red-cell count. The unimolecular formula is inapplicable to hæmolysis by the simple hæmolysins. S. S. ZILVA.

Comparative study of turacin and hæmatin and its bearing on cytochrome. D. KEILIN (Proc. Roy. Soc., 1926, **B**, **100**, 129—151).—Turacin is a copper–porphyrin compound, differing from iron porphyrins in that it does not combine with nitrogen compounds, it does not show an oxidation or reduction effect, and it does not give a peroxydase reaction. Acid hæmatin prepared from hæmoglobin is the same as "oxidised hæm" prepared from hæmin; the solubility of the former is due to the protective action of the globin. The relation between the absorption bands of these substances and the degree of dispersion suggests that cytochrome may be a modified hæmochromogen compound present in two distinct degrees of dispersion. H. J. CHANNON.

Biochemical and serological examination of hens' eggs during hatching. S. IDZUMI (Mitt. med. Fak. Kais. Univ. Tokyo, 1924, **32**, 197—216).—The residual and amino-nitrogen increase, the total nitrogen remaining unchanged; the sugar is minimal at the 10th day, and falls rapidly after hatching. The glycogen increases after the 8th day, and decreases after hatching; the diminution of fat is continuous. Antitryptic substances, amylase, and Forssman antigen increase. The proteins of the unhatched egg differ antigenically from chicken serum, but approach it biologically during the incubation period. CHEMICAL ABSTRACTS.

Reducing substances found in alcoholic extracts of brain. E. G. HOLMES and B. E. HOLMES (Biochem. J., 1926, **20**, 595—597).—Creatinine has been identified as a constituent of alcoholic brain extract. Creatine and creatinine both reduce Hagedorn and Jensen reagents; their reduction curves, however, unlike those of several carbohydrates tested, are not straight lines. S. S. ZILVA.

Occurrence of fatty substances in the human ear. K. NAKAMICHI (Ni. Byor. Gak. K. Tokyo, 1922, **12**, 106—109).—The deposits, which increase with age, are largely glyceryl esters; cholesteryl esters are present if the deposits are extensive. CHEMICAL ABSTRACTS.

Chemical composition of the vitreous body of the eye, especially of the extractive matter. T. IKEDA (J. Orient. Med., 1924, **2**, 135—141).—The chemical constituents are: proteins, *d*-lactic acid, *l*-leucine (?), *d*-alanine, *l*- and *r*-proline, *l*-phenylalanine (?), *d*-valine (?), *d*-*iso*leucine (?), and hypoxanthine; 0·15 g. of fat and 0·5 g. of phosphatides per 29·49 g. of fluid. CHEMICAL ABSTRACTS.

Nuclein substances of the pancreas. K. HSÜ (Z. physiol. Chem., 1926, **155**, 42—51).—The nuclein substances are extracted by a method similar to that used by Hagihara in the case of the spleen (A., 1924, i, 903). The individual nucleic acids could not be completely freed from protein impurities, but guanylnucleic acid was isolated in a fairly pure condition. A protein intermediate in properties between the histones and the heat-coagulable proteins was precipitated from the aqueous extract by 50% alcohol. E. C. SMITH.

Adrenaline content of the suprarenal gland [of the rabbit]. K. TAKAHASHI (Hoku-Etsu Ig. Kw. Z. Niigata, 1922, **37**, 257—281).—The adrenaline content of the suprarenal gland of the rabbit is about 0·0825 mg. per kg. of body-weight. It decreases temporarily after bleeding, and is increased by nicotine or by electrical stimulation of the splanchnic nerves. CHEMICAL ABSTRACTS.

Physiology of the liver. XIII. Liver as a site of bilirubin formation. F. C. MANN, C. SHEARD, J. L. BELLMAN, and E. J. BALDES (Amer. J. Physiol., 1926, **77**, 219—224).—In dogs from which the spleen and gall bladder had been removed, and the common bile duct obstructed, there was demonstrated a notable increase of bilirubin in the hepatic vein compared with that in the arterial circulation. It is considered that this demonstrates some synthesis of the pigment in the liver. R. K. CANNAN.

Liver and spleen pigments of the toad. H. OKAMOTO (Frankf. Z. Pathol., 1925, **31**, 16—53).—Hæmosiderin and a decomposition pigment occur, with seasonal variations, in the endothelial cells of the liver and in the reticular cells and splenocytes of the spleen. CHEMICAL ABSTRACTS.

Corpus luteum. III. Presence of free amino-acids in the acetone extract. M. C. HART and F. W. HEYL (J. Amer. Pharm. Assoc., 1925, **14**, 770—773; cf. A., 1924, i, 904).—Sow's follicular fluid contains 7·31% of solids, 87% being protein. As the corpus luteum develops, the protein is reduced to 40% of the solids, suggesting enzyme action. The portion of the acetone extract of corpus luteum insoluble in ethyl alcohol consists of leucine, *iso*leucine, and probably valine. CHEMICAL ABSTRACTS.

Occurrence of trimethylamine oxide in *Clupea harengus*. K. POLLER and W. LINNEWEH (Ber., 1926, **59**, [*B*], 1362—1365).—Trimethylamine oxide is relatively abundant in the muscle of fresh herring. H. WREN.

Sugar and calcium in cerebrospinal fluid. K. BRUCKE (Deut. Arch. Klin. Med., 1925, **148**, 183—194; from Chem. Zentr., 1926, I, 714).—The calcium content of cerebrospinal fluid is 4·7—5·7 mg.% and is unchanged in diseases of the brain and meninges. The average sugar content is 0·056%; higher values may be obtained under pathological conditions.

G. W. ROBINSON.

Iodine content of human cerebrospinal fluid. D. CAMPBELL and W. R. SNODGRASS (J. Pharm. Exp. Ther., 1926, **27**, 355—360).—After administration of iodides by mouth or intravenously, iodine is found regularly in the cerebrospinal fluid, from which it is normally absent. W. O. KERMACK.

Quantitative analysis of woman's colostrum. M. NAKAMURA (Mitt. med. Fak. Kais. Univ. Tokyo, 1924, **32**, 235—250).—The fat content is higher, the lactose content lower (5%) than in permanent milk. The high protein (6—7%) and residual nitrogen (more than 7%) of the first 2 days reach the normal level on the 2nd to 4th day. CHEMICAL ABSTRACTS.

Stability of evaporated milk during sterilisation. A. G. BENTON and H. G. ALBERY (J. Biol. Chem., 1926, **68**, 251—263).—The tendency of milk to coagulate during sterilisation by heat is chiefly determined by the p_H, the coagulation time being maximum at about p_H 6·65; the heat coagulation can therefore be inhibited by addition of citrates or borates. The milk of an individual cow may vary considerably from day to day, and the presence or absence of clotting on mixing the milk with 70—75% alcohol does not give any certain indication as to the behaviour of the milk towards heat.

C. R. HARINGTON.

Secretion of pancreatic juice. J. MELLANBY (J. Physiol., 1926, **61**, 419—435).—Introduction of bile of suitable reaction into the duodenum of the cat causes a copious secretion of pancreatic juice. The active substance is cholic acid, but its activity is profoundly modified by association with taurine and glycine and by the mucin present, and the optimum p_H varies with the state of digestion. The immediate stimulus to secretion is secretin, which is carried into the portal blood with the bile salts absorbed from the intestine. R. K. CANNAN.

Rôle of electrolytes in the innervation mechanism of secretory processes. I. Effect of vegetable poisons on the activity and electrolyte content of the saliva of the submaxillary gland. II. Effect of section and stimulation of the nerve fibres on the activity and electrolyte content of the saliva of the submaxillary gland. D. ALPERN (Pflüger's Archiv, 1926, **209**, 723—737, 738—752; from Chem. Zentr., 1926, I, 709).—The saliva has a constant content of calcium and potassium salts. The ratio of calcium to potassium determines the character of the secretory processes of the salivary glands, and is variously affected by different substances. Increase in calcium content is accompanied by decrease in potassium content.

G. W. ROBINSON.

Chemical constituents of tears. IV. H. WADA (Taiwan Ig. Kw. Z., Taihoku, 1922, 551—562).—The potassium content of tears is nearly 3 times that of serum and about half that of urine; the quantity of sodium in tears is nearly equal to that in serum and slightly more than that in urine. Both the calcium and magnesium content in tears are lower than those in serum and in urine. CHEMICAL ABSTRACTS.

Crystalline pigment obtained from normal human urine by means of *p*-dimethylaminobenzaldehyde. I. G. SCHEFF. **II.** P. HÁRI (Biochem. Z., 1926, **168**, 451—452, 453—455).—I. A yield of 0·70 g. (from 100 litres of urine) of the pigment first isolated by Hári (A., 1922, i, 88) was obtained. The maximum of the light absorption in alcoholic solution is at 508 $\mu\mu$. The substance melted sharply at 228°, did not contain sulphur or chlorine, and was practically iron-free.

II. Elementary analyses of the substance corresponded with a formula representing the condensation of 2 mols. of skatoxyl and 1 mol. of *p*-dimethylaminobenzaldehyde. Whether the skatoxyl occurs in the urine as such or is formed by the hydrolysis of a conjugation product or from another compound during the isolation is not known. H. I. COOMBS.

[**Porphyrins in urine.**] H. FISCHER (Z. physiol. Chem., 1926, **155**, 96—98).—A reply to Schumm (this vol., 538, 751). E. C. SMITH.

Kidney function. I. Rate of filtration and reabsorption in the human kidney. II. Excretion of urea and chlorine analysed according to a modified filtration-reabsorption theory. P. B. REHBERG (Biochem. J., 1926, **20**, 447—460, 461—482).—I. The amount of creatinine present in urine after ingestion of this substance is so large that it requires a filtration of up to 200 c.c. per min. to explain it. It is considered that this result does not invalidate the filtration and reabsorption theory of kidney function, since such rapid filtration through the glomeruli and the subsequent reabsorption of correspondingly large quantities of water by the tubules are considered possible.

II. From experiments on the excretion of urea and chlorine it is concluded that urea is not reabsorbed in the sense of a threshold substance, although it may be reabsorbed by mere diffusion. Chlorine, which is considered to be the index of the threshold substance sodium, is actively absorbed as a threshold substance when the plasma content of it is below 375 mg.%. Chlorine and other threshold substances together with most of the water are absorbed in the proximal convoluted tubules, whilst the rest of the water is reabsorbed farther down the tubules.

S. S. ZILVA.

Urinary nitrogen not determined by the Kjeldahl method. W. MESTREZAT (Bull. Soc. Chim. biol., 1926, **8**, 341—351).—About 1% of the nitrogen of human urine cannot be determined by the usual method; in pathological conditions the amount may rise to 15%; this nitrogen can be dialysed.

H. J. CHANNON.

Relation between ammonia and acid in urine. R. RAFFLIN (Bull. Soc. Chim. biol., 1926, **8**, 352—361).—An experimental verification of the relation-

ships existing between p_H and the total, ammonia, and urea nitrogen in urine. H. J. CHANNON.

Relation between gastric acidity and hydrogen-ion concentration of the urine. Effect of histamine. F. D. ACKMAN (Canad. Med. Assoc. J., 1925, **15**, 1099—1106).—Urinary acidity varies inversely with the degree of (relatively normal) gastric acidity. Rich protein diets produce a marked tide; high carbohydrate and low protein diets have little effect. When the gastric acidity is normal or high, histamine given subcutaneously increases the secretion and produces a tide. The theory of the gastric origin of the alkaline tide is thus supported.
CHEMICAL ABSTRACTS.

Titration of organic acids in urine. W. W. PALMER (J. Biol. Chem., 1926, **68**, 245—249).—In using the method of Van Slyke and Palmer (A., 1920, ii, 131) for the determination of organic acids in urine, it is essential first to remove all traces of carbonate, phosphate, and protein; when these substances are present in small amount, the addition of excess of calcium hydroxide suffices for their removal; if the carbonate exceeds 0·5%, the urine should be acidified with hydrochloric acid to drive off the greater part of the carbon dioxide, and the last traces of protein should be removed by boiling in faintly acid solution. C. R. HARINGTON.

Lipin excretion. III. Quantitative relationships of fæcal lipins. W. M. SPERRY (J. Biol. Chem., 1926, **68**, 357—383).—The total daily excretion of non-volatile fatty substances by dogs of 5—13 kg. body-weight, when kept on a fat-free diet for several weeks, was 1·5—2·0 g. This amount consisted of 40% of fatty acids and soaps and 60% of neutral material, which, in turn, comprised 75% of unsaponifiable matter and 25% of fat. The non-volatile fatty acids consisted of 30% of a mixture of palmitic and stearic acids, and 60% of a mixture of a large amount of oleic acid together with traces of arachidonic (?) acid; the volatile fatty acids comprised 65% of acetic, 23% of butyric, and 12% of hexoic acid. The similarity in composition of the lipins excreted under the above basal conditions to that of the lipins of blood plasma, together with the presence of utilisable fatty acids, indicates that the lipins find their way into the fæces by leakage from the blood stream into the lower part of the intestine.
C. R. HARINGTON.

Chloride content of blood in pernicious anæmia. R. L. HADEN (J. Lab. Clin. Med., 1925, **10**, 557—561).—The chloride content of the blood is usually high in both primary and secondary anæmia; the plasma remains normal. No relation exists between the chloride content of the blood and the free hydrochloric acid of the gastric juice.
CHEMICAL ABSTRACTS.

Effect of protein on the excretion of ketonic substances in severe diabetes. Theory of diabetic disturbance. S. J. THANNHAUSER and W. MARKOWICZ (Klin. Woch., 1925, **4**, 2093—2099; from Chem. Zentr., 1926, I, 713).—Glycine and alanine, neither of which could from their constitution be expected to give ketonic substances, do not cause an increase in acetone formation in diabetes. In experiments with other amino-acids, no additional production of acetone, beyond what could be expected from their constitution, was observed. It is concluded that there is no specific effect of amino-acids on ketone formation. G. W. ROBINSON.

Amino-nitrogen of blood in experimentally produced fevers. J. DONATH and R. HEILIG (Arch. exp. Path. Pharm., 1926, **113**, 201—215).—Nucleic acid, as well as vaccineurin, introduced intravenously in corresponding doses, leads in animals to a rise in body temperature, to an increase in the amino-nitrogen of the blood, and to an increased elimination of nitrogen in the urine. Heat puncture, cooling of the heat centre, as well as tetrahydro-β-naphthylamine produce hyperthermia unaccompanied by blood amino-nitrogen increase or an increased urine-nitrogen elimination. From the failure of the action of nucleic acid after heat puncture in some of the cases, it seems to follow that the central apparatus regulating protein metabolism depends for its function on an intact heat centre. W. ROBSON.

Isolation of *d*-galactose from urine following the galactose test for liver function. J. HALBERKANN and H. KÄHLER (Z. physiol. Chem., 1926, **154**, 34—38).—By actual isolation of the sugar that is excreted after ingestion of *d*-galactose in certain cases of hepatic insufficiency, it has been confirmed that the dextrorotatory substance in the urine giving mucic acid on oxidation is indeed *d*-galactose.
H. D. KAY.

Glycerol treatment of nephrolithiasis. F. HANSEN and B. KAMM (Biochem. Z., 1926, **173**, 327—333).—The effect of nephrolithiasis cannot be due to the solution of the urinary calculi. The whirling calculi fall much more slowly in urine containing glycerol, and instead of falling on to the wall of the pelvis of the kidney, remain in suspension and are excreted. P. W. CLUTTERBUCK.

Excretion of ammonia and titratable acid in nephritis. D. D. VAN SLYKE, G. C. LINDER, A. HILLER, L. LEITER, and J. F. MCINTOSH (J. Clin. Invest., 1926, **2**, 255—288).—The variable ammonia : acid ratio averaged 1·0—2·0 for normal subjects, 1·0—2·9 in nephrosis, 0·8—1·6 in benign nephrosclerosis, 0·6—1·5 in acute glomerulonephritis, 0·4—0·9 in mild chronic glomerulonephritis, and below 0·5 in chronic glomerulonephritis and malignant nephrosclerosis. Blood ammonia-nitrogen varied between 0 and 0·9 mg./100 c.c. in nephritis.
CHEMICAL ABSTRACTS.

Renal function in pregnancy. K. YAMADA (J. Biochem. [Japan], 1925, **5**, 245—285).—A study of the excretion of sodium chloride, iodine, phenolsulphonephthalein, lactose, urea, amino-acids, and ammonia-nitrogen by rabbits indicate a delay in the excretion of sodium chloride, but not of nitrogenous substances, during pregnancy. Over-production of acids during pregnancy results in a high ammonia level and consequent intoxication. CHEMICAL ABSTRACTS.

Nature of urinary protein. A. HYND (Lancet, 1925, II, 910—915).—In "albuminuria of pregnancy" and other cases of proteinuria the protein excreted in

the urine had $[\alpha]_D$ closely corresponding with that of serum-albumin. In eclampsia there were two groups $[\alpha]_D$ −56·4° and −38·5°, respectively, corresponding with the values for serum-albumin (−54·47°) and cow lactalbumin (−41·17°), respectively. It would appear that in certain types of eclampsia the urinary albumin may be mainly lactalbumin.

CHEMICAL ABSTRACTS.

Amino-acids and polypeptides in blood in pregnancy and childbirth. H. SCHLOSSMANN (Z. ges. exp. Med., 1925, **47**, 487—502; from Chem. Zentr., 1926, I, 713).—In pregnancy and childbirth, the residual nitrogen, amino-acid nitrogen, and polypeptide nitrogen of the blood are unchanged. In the first days of nursing, there is an increase in all these values, particularly in polypeptide nitrogen. In toxæmia of pregnancy, the polypeptide nitrogen rises in relationship with the gravity of the clinical symptoms. It is not clear whether increase in polypeptide nitrogen is the cause or the effect of the toxæmia. Amino-nitrogen is unaffected.

G. W. ROBINSON.

Detection of pancreatic lipase in serum in pancreatic disease. V. JEDLIČKA and V. KREISINGER (Z. ges. exp. Med., 1925, **47**, 513—533; from Chem. Zentr., 1926, I, 693).—Pancreatic lipase occurs in the blood only when there is acute derangement together with destruction of parenchyma or when there is a comparatively large and sudden retention of the pancreatic secretion in the organ itself. It is improbable that pancreatic lipase passes into the blood in purely functional disturbance.

G. W. ROBINSON.

Blood lipase. V. JEDLIČKA (Z. ges. exp. Med., 1925, **47**, 534—541; from Chem. Zentr., 1926, I, 693; cf. preceding abstract).—Pancreatic lipase is inhibited by cholesterol and by ethyl palmitate (in this case only in protein-free solutions). It is not inhibited by serum, because in the latter cholesterol occurs only as an ester. Serum lipase is not affected either by cholesterol or by ethyl palmitate.

G. W. ROBINSON.

Attempts to control parathyroid tetany by oral administration of ammonium chloride. T. E. BOYD, W. C. AUSTIN, and E. F. DUCEY (Amer. J. Physiol., 1926, **77**, 225—232).—Ammonium chloride given by mouth to parathyroidectomised dogs in doses of 0·25 to 1 g. per kg. daily reduces the frequency and severity of tetany, prolongs survival, but does not usually lead to recovery. No consistent rise in blood calcium could be demonstrated.

R. K. CANNAN.

Distribution of phosphorus compounds in the blood in tuberculosis. K. L. MCCLUSKEY (J. Lab. Clin. Med., 1925, **10**, 466—474).—A decrease in the lecithin, and an increase in the acid-soluble phosphorus content of the cell and plasma are very unfavourable; the reverse is favourable. The acid-soluble phosphorus appears to be used in the synthesis of lecithin. In the terminal stages of exudative pulmonary tuberculosis phosphorus is present in the cell in excess of the sum of the lecithin and acid-soluble fractions.

CHEMICAL ABSTRACTS.

Abderhalden's reaction. E. KOMM (Z. physiol. Chem., 1926, **154**, 107—115).—Determinations of the total nitrogen in the serum before and after precipitation of proteins by the method of Folin and Wu indicate that in the serum of tuberculous animals, the non-protein nitrogen increases after the serum has been incubated with specific substrate previously prepared from the lungs of tuberculous animals, but not with substrate from the lungs of normal animals.

H. D. KAY.

Conditions of formation of malignant tumours. I. Lactic acid content of tissues. R. BIERICH. **II. Cytochrome in the tissues.** R. BIERICH and A. ROSENBOHM (Z. physiol. Chem., 1926, **155**, 245—248, 249—250).—I. The residual lactic acid content of a tissue does not represent the total lactic acid production. Besides the small amount which diffuses away into the adjacent tissues, a considerable proportion is carried away in the blood-stream. Determinations of the residual lactic acid content of healthy tissues show that, for the same organ in any given animal, moderately consistent values may be expected, although considerable variation occurs in different tissues. The lactic acid content of tumours of any specific organ shows very marked variation, the absolute limits lying about 100% higher than those for normal tissues. Preservation of the tissue at a low temperature between removal and investigation is essential. The high lactic acid content of cancerous tissues may be due either to increased breakdown of sugar or to checked resynthesis or to a combination of both these factors (cf. A., 1925, i, 328).

II. Cytochrome (cf. Keilin, *ibid.*, 1112) is found in all normal epithelial organs and carcinomata. It is absent from normal connective-tissue, but is present in muscle. Hæmoglobin occurs simultaneously in epithelial organs, and the degree of oxidation or reduction of the two pigments is interdependent. The nature of the oxidation-reduction equilibrium can be determined by spectroscopic observation. The number of absorption bands visible, which depends on the concentration and the degree of reduction, was used as an approximate measure of the pigment content of diseased and healthy tissues. The cytochrome and hæmoglobin content of normal tissues is moderately constant, whilst in cancer of the mammary gland it varies within very wide limits. M. CLARK.

Influence of temperature on metabolism and the problem of acclimatisation. N. R. DHAR (J. Physical Chem., 1926, **30**, 480—490).—Stefan's law of radiation is applied to certain biological facts of metabolism, and the connexion between enzyme activity in metabolism and longevity in cold- and warm-blooded animals, respectively, is discussed.

L. S. THEOBALD.

Cholesterol metabolism. I. Birds. M. YAMAGUCHI (Ni. Byor. Gak. K. Tokyo, 1922, **12**, 111—112).—Cholesteryl esters occur more abundantly in the bodies of birds than in the human body. On feeding egg-yolk, but not lanolin, to fowls or pigeons, large deposits of cholesterol are found in the liver.

CHEMICAL ABSTRACTS.

Relationship of rate of oxidation with changes in reaction. I. Effect of one-sided acid diet. R. DURR (Z. ges. exp. Med., 1925, **47**, 721—733; from Chem. Zentr., 1926, I, 714).—With abundant acid diet, the rate of oxidation may increase up to 14% in experimental periods of several days. The displacement of the acid–base equilibrium is shown by the decrease in the p_H of the urine and the alveolar carbon dioxide pressure and by the increase in the ventilation of the lungs. Addition of ammonium chloride to an acid diet depresses oxidation.

G. W. ROBINSON.

Changes in composition of blood of rabbits fed on raw soya beans. A. A. HORVATH (J. Biol. Chem., 1926, **68**, 343—355).—An exclusive diet of raw soaked soya beans resulted in an increase in the urea, uric acid, inorganic phosphates, and cholesterol of the blood; after 2 months on such a diet, no signs of arteriosclerosis could be detected.

C. R. HARINGTON.

Carbohydrate metabolism of infants. F. F. TISDALL, T. G. H. DRAKE, and A. BROWN (J. Lab. Clin. Med., 1925, **10**, 704—711).—A modification of the Shaffer–Hartmann method for the determination of blood-sugar, giving results accurate to 5%, is described. The average fasting concentration of blood-sugar in normal infants is 0·087%; in marasmus, 0·070% or less. The effect on the blood-sugar of interstitial and intravenous injection of dextrose is described. CHEMICAL ABSTRACTS.

Carbohydrate metabolism. VI. Determination of presence of new-glucose in biological fluids. VII. Transformation of liver glycogen into dextrose *in vitro*. VIII. Action of liver tissue and insulin on dextrose *in vitro*. C. LUNDSGAARD and S. A. HOLBØLL (J. Biol. Chem., 1926, **68**, 457—473, 475—483, 485—497; cf. A., 1925, i, 1494).—VI. A more extended description is given of the procedure for the detection of new-glucose in biological fluids and for the production of new-glucose *in vitro* from ordinary dextrose.

VII. The dextrose produced in the spontaneous *post-mortem* hydrolysis of the glycogen of the liver at p_H 7·30, whether in presence or absence of insulin, has the rotatory power of ordinary αβ-glucose.

VIII. Liver-tissue differs from muscle-tissue in that it cannot, in conjunction with insulin, bring about the conversion of ordinary dextrose into new-glucose, nor could any effect be observed on adding liver-tissue to a solution containing new-glucose. The above experiments therefore reinforce the conclusion that the part played by insulin in carbohydrate metabolism is the conversion, in conjunction with the muscle-tissue, of the dextrose derived from the food into new-glucose, which may subsequently be oxidised or stored as glycogen. C. R. HARINGTON.

Carbohydrate metabolism. I. Relation between optical activity and reducing power of normal blood filtrates. II. Interaction of muscle-tissue, insulin, and dextrose. A. B. ANDERSON and A. CARRUTHERS (Biochem. J., 1926, **20**, 556—563).—Concentrated ultrafiltrates and dialysates of ox- and pig-plasma and alcohol extracts of pig-plasma show a low rotatory power as compared with the reducing power. The optical rotation can be made to correspond with the reducing power by raising the hydrogen-ion concentration. This change, however, is not due to hydrolysis, since it is reversible. It is probable that an optically active substance or substances other than dextrose are responsible for this abnormal rotation. These substances are slightly soluble in 99% and soluble in 90% alcohol. On removing the carbohydrates with copper sulphate and calcium hydroxide, lævorotatory solutions becoming dextrorotatory at p_H less than 4·0 and having practically no reducing power are obtained. Laked corpuscles yield strongly lævorotatory ultrafiltrates with very little reducing power. No mutarotation takes place in any of the above solutions. Lundsgaard and Holbøll's observation (A., 1925, i, 208) of the formation of "new-glucose" from dextrose incubated with muscle-tissue and insulin is not confirmed. S. S. ZILVA.

Carbohydrate metabolism. I. Utilisation of dihydroxyacetone by the animal body and a method for its determination. W. O. KERMACK, C. G. LAMBIE, and R. H. SLATER (Biochem. J., 1926, **20**, 486—496).—Dihydroxyacetone is able to cause recovery of rabbits and mice from symptoms of insulin hypoglycæmia in approximately the same amounts and in the same time as in the case of dextrose. It is removed more rapidly from the blood-stream than dextrose or lævulose, and its disappearance, unless excessive amounts are given, is almost complete. After ingestion of 50 g. of dihydroxyacetone, the rise in blood-sugar in a diabetic was much smaller than if a similar amount of dextrose were consumed, and consequently a rapid conversion into dextrose did not take place. The dihydroxyacetone was determined colorimetrically by the addition of sulphuric acid and phenol to the deproteinised blood. The presence of 0·1 mg. can thus be detected.

S. S. ZILVA.

Response to continuous intravenous injection of large amounts of dextrose. J. D. BOYD, H. M. HINES, and C. E. LEESE (Amer. J. Physiol., 1925, **74**, 656—671).—When dextrose solution is injected intravenously into dogs at the rate of 4 g. per kg. per hr., the blood-sugar at first rises rapidly, and then tends to constancy, the value obtained not being an index of the associated glycosuria. About 20% of the injected dextrose is excreted in the urine. Observations were made on the plasma p_H and carbon dioxide content, hæmoglobin, respiratory quotient, and heat production. A. A. ELDRIDGE.

Utilisation of cellulose in the intestine after oral administration of a cellulose-splitting enzyme. F. MESSERLE (Biochem. Z., 1926, **172**, 31—33).—White mice are able to utilise cellulose when fed with lichenase from the liver of the snail (*Helix pomatia*). H. I. COOMBS.

Phosphates in non-irritable muscle. J. T. EDSALL (Biochem. J., 1926, **20**, 569—573).—There is great diminution in inorganic phosphate in normal and in non-irritable muscle under the influence of calcium chloride. The effect of the calcium is not

proportional to its concentration. *M*-Calcium chloride solution has little or no effect. The values for the lactacidogen phosphate of non-irritable muscle are slightly lower on the average than those for normal muscle. S. S. ZILVA.

Relation of calcium and phosphorus in the diet to the absorption of these elements from the intestine. W. J. ORR, L. E. HOLT, jun., L. WILKINS, and F. H. BOONE (Amer. J. Dis. Children, 1925, **28**, 574).—Excessive amounts of calcium in the diet tend to increase the total absorption and retention of calcium, but tend to impair phosphorus retention. Excessive amounts of phosphorus in the diet exercise an unfavourable influence on the calcium metabolism, and are accompanied by an increase in the calcium lost in the fæces. Formation of calcium phosphate explains this behaviour. CHEMICAL ABSTRACTS.

Calcium and phosphorus balances with dairy cattle. R. C. MILLER (J. Dairy Sci., 1926, **9**, 78—92).—Some evidence is obtained of the independence of calcium and phosphorus assimilation. Only a slight variation in the calcium and phosphorus content of the milk was observed on variation of the diet. CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism in dairy cows. E. B. MEIGS, W. A. TURNER, T. S. HARDING, A. M. HARTMAN, and F. M. GRANT (J. Agric. Res., 1926, **32**, 833—860).—Slight disturbances in the habits and routine of dairy cows used in feeding experiments may have a considerable effect on the assimilation of calcium. Under satisfactory conditions, 15—20% of the calcium in lucerne hay is assimilated. Changes in the calcium and phosphorus contents of the bodies of milking cows do not run exactly parallel, but a long-continued loss of calcium causes a roughly corresponding loss of phosphorus, even although the ration may contain plenty of assimilable phosphorus. Addition of cod-liver oil to the ration had no favourable effect on calcium assimilation. The milk yield tended to fall with a ration deficient in calcium. C. T. GIMINGHAM.

Maintenance requirement of cattle for protein as indicated by the fasting catabolism of dry cows. E. B. FORBES, J. A. FRIES, and M. KRISS (J. Dairy Sci., 1926, **9**, 15—27).—The nitrogen, crude fibre, and dry matter were determined in the urine and fæces. The average daily excretion of nitrogen per 1000 lb. in the last 4 days of a 9-day fast were 46·5 and 43·6 g., respectively, for two animals, representing 0·62 and 0·58 lb. of body-protein. CHEMICAL ABSTRACTS.

Effect of temperature on protein metabolism. G. E. YOUNGBURG and M. W. FINCH (J. Biol. Chem., 1926, **68**, 335—341).—Detailed examination of the urinary nitrogen of ten normal men for a period of a year indicated, on the average, no significant variations as between summer and winter; moreover, in these experiments in a temperate zone, the average daily excretion of total nitrogen was 11·12 g., which is closely similar to that recorded by Denis and Borgstrom (*ibid.*, 1924, **61**, 109) for a sub-tropical zone. The effect of temperature on nitrogenous metabolism is therefore small. C. R. HARINGTON.

Influence of prolonged maintenance of nitrogen equilibrium on the growing animal. S. WEISER (Biochem. Z., 1926, **173**, 14—25).—Young pigs were fed on just sufficient barley to maintain nitrogen equilibrium, and others on as much barley as they could take. In the young animal, receiving an insufficient diet, part of the food is used for the formation of new tissue, but the actual materials used for this process are derived from other parts of the body. P. W. CLUTTERBUCK.

Magnesium metabolism on purified diets. G. MEDES (J. Biol. Chem., 1926, **68**, 295—316).—Practically no change was observed in the percentage magnesium content of rats during normal growth, or under such abnormal conditions as inanition or variations in the intake of calcium, phosphorus, and magnesium, which cause marked variations in the content of calcium and phosphorus; the magnesium content remained throughout 0·045% of the body-weight. C. R. HARINGTON.

Mineral metabolism of the skin. K. BÖRNSTEIN (Biochem. Z., 1926, **172**, 133—140).—The calcium and potassium content of the skin of mice is not affected by changing the diet from an acid to a basic one. H. I. COOMBS.

Sulphur metabolism of the dog. III. Effect of benzene and of some derivatives of benzene on sulphur metabolism. E. H. CALLOW and T. S. HELE (Biochem. J., 1926, **20**, 598—605).—Benzene, *o*- and *m*-dichlorobenzene, like monochlorobenzene, raise the amounts of excreted neutral and ethereal sulphate. This suggests a formation of mercapturic acid. There is usually a close correspondence between "extra" sulphur and the halogen in organic combination excreted in the urine after the administration of the above compounds. Toluene and *o*-chlorotoluene have no effect on the sulphur metabolism, whilst potassium phenyl sulphate raises the ethereal sulphate only. S. S. ZILVA.

Sulphur metabolism of the dog. IV. Mechanism of mercapturic acid formation in the dog. H. I. COOMBS and T. S. HELE (Biochem. J., 1926, **20**, 606—612).—The influence of *p*-chloroacetanilide and *p*-chloroanisole (*p*-dichlorobenzene not being readily absorbed) on the excreted sulphur was studied, in order to test the theory whether the linking of cysteine to the benzene ring in the mercapturic acids was limited to the position *para* to the halogen. Neither of these nor the corresponding *ortho* or *meta* compounds, however, was found to lead to the excretion of mercapturic acid. The introduction of an acetamido- or methoxy-group, therefore, alters the metabolism from that of chlorobenzene. *p*-Chlorophenol does not give rise to mercapturic acid, and consequently cannot be an intermediary between chlorobenzene and mercapturic acid; nor does the administration of *o*- or of *m*-chlorophenol or of phenol itself result in its formation. S. S. ZILVA.

Effect of polarised radiations on animal metabolism. S. S. BHATNAGAR, R. B. LAL, and K. N. MATHUR (Nature, 1926, **118**, 11—12).—Exposure of rabbits or guinea-pigs to polarised light results in increased metabolic activity, measured by the amount of carbon dioxide exhaled, as compared with that of animals exposed to ordinary light of the same intensity. In the dark, after exposure to light, the order of the metabolic activities was reversed. A. A. ELDRIDGE.

Flavouring substances in foods. I. Effect of ethyl acetate and a few other substances on the nitrogen excretion in normal dogs and in partly thyroidectomised dogs. II. Effect of ethyl acetate and a few other substances on the rate of growth of rats. III. Thyroid of rats receiving aliphatic esters and essential oils by the mouth. U. G. BIJLSMA (Rep. Dutch Civil Med. Service, 1924, 696—771).—4 C.c./kg. of ethyl acetate are not injurious, 10 c.c. are lethal to the dog. Dogs with considerably reduced thyroid show an increase of nitrogen excretion with ethyl acetate. Normal male dogs show an increase, female a decrease of nitrogen excretion. Amyl acetate has the same effect. Cinnamon oil increased the nitrogen excretion in male animals. CHEMICAL ABSTRACTS.

Influence of cholesterol on the reproductive potency of white rats. U. SUZUKI and N. HASHIMOTO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **4**, 235—255).—The fertility of white rats is greatly increased by the presence of small amounts of cholesterol and of certain mineral salts in the diet. Larger amounts of cholesterol (1—2% of the diet) have a toxic effect. Observations of other authors that there is some specific relationship in man between cholesterol and pregnancy are supported. H. D. KAY.

Effect of calcium on man. II. Effect of calcium salts on nitrogen excretion in health and in renal disease. E. BARATH and T. VON GYURKOVITCH (Z. ges. exp. Med., 1925, **47**, 741—744; from Chem. Zentr., 1926, I, 715).—Calcium salts injected intravenously or administered in large doses orally decrease markedly the excretion of nitrogen both in health and in renal disease, and lead to a positive nitrogen balance. G. W. ROBINSON.

[Physiological properties after] partial bromination of phloridzin. III. K. MISAKI (J. Biochem. [Japan], 1925, **5**, 287—291; cf. *ibid.*, 1).—Dibromination greatly reduces the glycosuric effect of phloridzin. The blood-sugar level is not affected by administration of dibromophloridzin. CHEMICAL ABSTRACTS.

Pharmacology of cell respiration. VI. Cyanide-charcoal; cyanide-chopped muscle systems. P. ELLINGER and K. LENZBERG (Z. physiol. Chem., 1926, **154**, 85—106).—If the possible error introduced by the absorption of hydrocyanic acid by the sodium hydroxide in Barcroft's micro-respiration apparatus is avoided, it is found that both the above systems take up oxygen. Hydrocyanic acid is, in part, oxidised both by charcoal and by chopped muscle to cyanate. A further part of the added cyanide is transformed, without oxygen uptake, into some undetermined compound. H. D. KAY.

Biological significance of cystine and glutathione. I. Mechanism of the cyanide action. C. VOEGTLIN, J. M. JOHNSON, and H. A. DYER (J. Pharm. Exp. Ther., 1926, **27**, 467—483).—Although albino rats cannot be protected from a lethal dose of cyanide by iron salts, they are efficiently protected by cystine, cysteine, glutathione, or thioglycollic acid. It is considered, therefore, that cyanide does not act specifically on iron in the cell, but rather that it disturbs the equilibrium of the sulphur compounds. The best results are obtained when 5—10 atoms of sulphur are injected for each molecule of hydrogen cyanide. Many other compounds commonly present in the cell were tested, but afforded no protection against cyanide poisoning. Evidence is adduced that *in vitro* cyanide reduces the –S·S– grouping to the sulphydryl group and is itself oxidised to cyanate; it is suggested that this reaction is of importance in the detoxicating effect of these sulphur compounds on cyanide poisoning, an effect previously known to be given by thiosulphates. W. O. KERMACK.

Basis for the physiological activity of -onium compounds. VI. Rates of hydrolysis of certain esters of choline and its analogues. R. R. RENSHAW and N. BACON.—See this vol., 805.

Substances in ergot affecting the uterus. A. W. FORST (Arch. exp. Path. Pharm, 1926, **114**, 125—136).—A method is described for separating the alkaloidal constituents of ergot consisting principally of ergotamine and ergotoxine from the accompanying bases, and the pharmacological action of these combined alkaloids is investigated. W. O. KERMACK.

Narcotic action of pure ether. D. R. NIJK (Chem. Weekblad, 1926, **23**, 258—260).—The statements of Mackenzie Wallis (Lancet, 1921, I, 1173) and Cotton (J. Canad. Med. Assoc., 1917, Sept.) that pure ether is not a narcotic are found to be incorrect. The pure material, b. p. 34·6°/760 mm., obtained by warming the compound of benzidine and ether, was found to have the normal action on animals and on a child. Additions of the common impurities had very little effect, save in the cases of *iso*amyl alcohol and methyl ethyl ketone; both these substances increase the action and diminish the lethal concentration in the blood, but as these are both poisons, the explanation is obvious. "Ethanesal," said to contain 5% of methyl ethyl ketone, was found on analysis to contain 5% of *n*-butyl alcohol, a little ethyl acetate, and a trace of *iso*amyl alcohol. S. I. LEVY.

Dependence of poisonous action on the physico-chemical condition of the cell. K. BAADE (Arch. exp. Path. Pharm., 1926, **114**, 137—155).—The influence of various alkaloidal salts and other organic substances on the hæmolysis of red blood cells by hypotonic salt solutions is described. W. O. KERMACK.

Influence of adsorption on charcoal on toxicity. M. EISLER (Biochem. Z., 1926, **172**, 154—170).—Charcoal which has cholesterol adsorbed on it is able to adsorb more saponin than untreated charcoal. The antiseptic power of phenol and mercuric chloride is more or less depressed in the presence of charcoal, depending on the amount of adsorption. The depression is not so marked for phenol as for mercuric chloride, since the latter is almost wholly adsorbed. H. I. COOMBS.

Chemotherapy of antimonial compounds in kala-azar infection. XVII. Preparation of "urea stibamine." U. N. BRAHMACHARI (J. Indian Med. Res., 1925, **13**, 111—112; cf. this vol., 541).—The preparation of "urea stibamine," obtained when *p*-aminophenylstibinic acid is suspended in water and carbamide is added, is described.
CHEMICAL ABSTRACTS.

Pharmacology of germanium compounds. I. KEESER (Arch. exp. Path. Pharm., 1926, **113**, 232—236).—At higher concentrations than 1 : 1000, germanium dioxide solutions are not true solutions, but tend to form unstable colloidal states. Sodium germanium tartrate is very soluble, so that solutions can be prepared containing 10 mg. Ge per c.c. Subcutaneous injection of 10 mg. Ge per kg. body-weight has no action on rabbits, whilst a subcutaneous dose of 15 mg. Ge per kg. (as GeO_2) produces in rabbits a temporary increase of the erythrocytes. Parenteral application of 30 mg. Ge raises for several days the number of erythrocytes to 1·9 millions and the hæmoglobin content to 35%. Hence the oxide and the hydride are less active than the corresponding arsenic compounds. Neither subcutaneous injection of 90 mg. nor intravenous injection of 75 mg. of sodium germanium tartrate per kg. body-weight produces any effect. The number of the white blood-corpuscles and the differential count are not changed by germanium. W. ROBSON.

Antiseptic activity of mercury salts. E. KEESER (Arch. exp. Path. Pharm., 1926, **113**, 224—231).—The magnitude of the antiseptic efficacy of mercuric chloride, bromide, cyanide, and nitrate and their absorption by yeast run parallel. Measurements of surface tension, refractivity, and conductivity, as well as cataphoresis experiments, show that mercuric chloride in low concentrations of alcohol is present in solution as ethoxide. Just as the antiseptic activity of mercuric salts is increased by the addition of acids or acid salts—the mercury and hydrogen ions have an additive effect on cell protoplasm—so the increase in antiseptic activity of mercuric salts in aqueous solutions containing 20—30% of alcohol depends on the additive influence of mercury ions and alcohol on the cell colloids.
W. ROBSON.

[Antiseptic] effect of bile acids and of unsaturated fatty acids in the form of soaps. A. KOZLOWSKI (J. Exp. Med., 1925, **42**, 453—463; from Chem. Zentr., 1926, I, 977).—Unsaturated fatty acids, with one, two, or more double linkings, are present in a dilution of 1 : 600 in normal ox bile. Their sodium salts, isolated as such from bile, have an antiseptic effect approximately 100 times as great as that of the corresponding salts of the bile acids.
G. W. ROBINSON.

Affinity constants of enzymes. H. VON EULER (Arkiv Kemi, Min., Geol., 1926, **9**, No. 13, 1—7).—The affinity of a hydrolytic enzyme for its substrate comprises two factors—the affinity constants for the enzyme and each of the final products alone—it being assumed that in such reactions attachment to the substrate molecule must occur at two points. Such a hypothesis explains the large difference in the affinity constants of invertase for sucrose and for raffinose, respectively, and also the behaviour of a substrate in presence of two hydrolytic enzymes.
C. RIMINGTON.

Conditions for the autolytic formation of ammonia in the tissues. II. Influence of amino-acids and other nitrogenous substances on ammonia formation. P. GYÖRGY and H. RÖTHLER (Biochem. Z., 1926, **173**, 334—347; cf. this vol., 640).—Addition to liver pulp of amino-acids or of proteins or their derivatives exerts on autolytic ammonia formation, in acid reaction an inhibitory, and in alkaline reaction (up to p_H 8·4) a stimulatory or only faintly inhibitory influence. Addition of histidine or of Witte's peptone in alkaline, and of histidine in acid solution causes considerable liberation of ammonia, but addition of glutathione either in the reduced or the oxidised condition has no effect.
P. W. CLUTTERBUCK.

Enzymes of the skin. IV. J. WOHLGEMUTH. **Decomposition of sugar in the skin.** Y. NAKAMURA (Biochem. Z., 1926, **173**, 258—268).—Fresh human skin, skin of the cadaver and of the guinea-pig can utilise carbohydrate, acetaldehyde being formed. Considerable amounts of aldehyde are formed from dextrose, glycogen, starch, sucrose, lactose, lævulose, and galactose, only traces from calcium hexosephosphate and lactate, whilst *d*-alanine and glycine do not influence aldehyde formation. Insulin increases the amount formed from dextrose slightly, and that from glycogen considerably. The skin of diabetics is able to form aldehyde to the same extent as normal skin, but this power falls off when the diabetic condition is of long standing. In the latter case, insulin has a greater action (cf. this vol., 93; A., 1924, i, 203, 472). P. W. CLUTTERBUCK.

Complement of amylase. IV. H. PRINGSHEIM and G. OTTO (Biochem. Z., 1926, **173**, 399—410).—Endeavours have been made to concentrate "amylase complement," the agent in presence of which maltase is able to convert dextrin into maltose with up to 100% yield. It is found to be adsorbed by yeast protein or by egg-white. There is an apparent increase in amount of amylase complement present when the protein on which it is adsorbed is digested by pepsin, which is due, not to setting free of preformed complement from the protein surface, but to new formation of complement. Amylase complement is thermostable and dialysable. It is considered that amylase+complement forms a new enzyme system which is capable of attacking substrates (*e.g.*, tri-

hexosans) which amylase itself cannot hydrolyse (cf. Willstätter and Grassmann, A., 1924, i, 1146).
H. D. KAY.

Hydrogenase. V. J. GRÜSS (Woch. Brau., 1926, **43**, 265—266).—For the detection of hydrogen in gases from bacterial fermentation the author carries out the fermentation in an Einhorn vessel containing a strip of palladium, which is afterwards rinsed with water and introduced into a small stoppered cylinder containing a solution of tetramethyl-*p*-phenylenediamine hydrochloride previously converted into a colouring matter (violamine) by atmospheric oxidation. If the palladium has adsorbed hydrogen, the solution slowly becomes more or less decolorised. Results of a roughly quantitative character can be obtained in parallel experiments.
J. H. LANE.

Invertase. VI. H. VON EULER and K. JOSEPHSON (Ber., 1926, **59**, [*B*], 1129—1135; cf. A., 1925, i, 1008).—Analyses of invertase (*If* 303 and 320) derived from Munich Löwenbrau yeast and Stockholm *H* yeast give total nitrogen 10·3% and 10·8%, amino-nitrogen before hydrolysis 0·92% and 0·96%, amino-nitrogen after hydrolysis 6·3% and 7·8%, tryptophan 6·5% and 4·2%, respectively. The Munich preparation contained 1·4% of sulphur.
H. WREN.

Affinity of invertase. X. Effect of acidity on the enzymic breakdown of sucrose. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **155**, 1—30; cf. this vol., 542, 642).—On the acid side of the optimum p_H for invertase action the affinity constant of invertase for sucrose diminishes, on the alkaline side it remains practically constant. The affinity constant for dextrose and lævulose also diminishes with increasing acidity, but with increasing alkalinity the affinity constant for lævulose continues to increase, whilst that for dextrose diminishes rapidly, until at the neutral point the inhibitory action of added dextrose on the inversion of sucrose is negligible.
E. C. SMITH.

Affinity groupings of invertase. H. VON EULER and K. JOSEPHSON (Arkiv Kemi, Min., Geol., 1926, **9**, No. 25, 1—7).—Inhibition of the enzyme may occur by the fixation of a molecule to one or other of the groups by which attachment to the substrate is effected. The presence of galactose in the reaction mixture diminishes the inhibiting effect of added dextrose and does not alter that of lævulose. Galactose is attached therefore to the same grouping as is dextrose. Hexosephosphate behaves in a similar manner. Invertase is also inhibited by *m*-chloroaniline, but addition of dextrose causes an acceleration, probably due to its combining with the chloroaniline to form a compound of lesser inhibiting power.
C. RIMINGTON.

Affinity of invertase for different sugars. IV. K. JOSEPHSON (Arkiv Kemi, Min., Geol., 1926, **9**, No. 20, 1—5).—Dextrose inhibits most strongly at the optimum p_H for invertase, showing on both the alkaline and acid sides a smaller affinity for the enzyme. Lævulose, however, inhibits more strongly as the p_H increases. Assuming that the affinity of invertase for sucrose is a function of the product of its affinities for dextrose and lævulose, respectively, an increase in acidity should lead to a decreased affinity for sucrose. This was found to be the case.
C. RIMINGTON.

Hydrolysis of sucrose by invertase in the presence of α-methylglucoside. II. J. M. NELSON and C. I. POST (J. Biol. Chem., 1926, **68**, 265—275; cf. A., 1925, i, 739).—The course of hydrolysis of sucrose in 2—10% concentration by yeast invertase is practically unaffected by invert-sugar and α-methylglucoside when these substances are present together in concentrations of 6% and 0·125%, respectively, although the presence of either substance alone retards the hydrolysis. A similar mutual antagonism between these substances is observed in their effect on the relation of concentration of sucrose to rate of hydrolysis. The retardation of the rate of hydrolysis, by the presence of invert-sugar, is independent of the p_H.
C. R. HARINGTON.

Specificity of the disaccharases. II. Taka-maltase and taka-invertase. J. LEIBOWITZ and P. MECHLINSKI (Z. physiol. Chem., 1926, **154**, 64—84).—Taka-maltase is far more stable to alcohol than is yeast maltase. It hydrolyses α-maltose much more readily than β-maltose, but the reaction is inhibited by α- and β-glucose to the same extent. It therefore does not follow (cf. Kuhn, A., 1923, i, 1033) if an enzyme displays greater activity towards a combined α- or β-monosaccharide that therefore the corresponding α- or β-monosaccharide in the free state will have a greater affinity for the catalyst and hence inhibit its activity to a greater extent. Gluco- and fructo-invertases are defined as the sucroclastic enzymes which have a main affinity for the dextrose or lævulose fractions, respectively, of the substrate molecule. Gluco-invertases are only slightly affected by a change in the substrate molecule which does not involve the dextrose fraction, fructo-invertases by a change which does not involve the lævulose fraction. Yeast-invertase is a fructo-invertase, taka-invertase is a gluco-invertase.
H. D. KAY.

Enzymes contained in taka-diastase preparation. T. SANO (Chug. Ij. Shp. Tokyo, 1922, **42**, 730—734).—Besides enzymes previously reported, catalase, lactase, and emulsin are present.
CHEMICAL ABSTRACTS.

Hydrolysis of asymmetric esters by lipase. E. R. DAWSON, B. S. PLATT, and J. B. COHEN (Biochem. J., 1926, **20**, 533—536).—Preferential hydrolysis has been shown to take place in racemic mixtures of some aliphatic esters. Thus in the case of the ethyl esters of α-methyl-*n*-butyric acid, α-methyl-*n*-hexoic acid, and β-phenyl-α-methylpropionic acid the *d*-ester was more readily hydrolysed; in the ethyl ester of racemic acid there was preferential hydrolysis of the *l*-ester, whilst no preferential hydrolysis was observed in the racemic mixtures of the ethyl esters of α-ethyl-*n*-hexoic acid, β-phenyl-α-ethylpropionic acid, α-*p*-nitrobenzoyl-*n*-butyric acid, or β-phenyl-α-allylpropionic acid. The rate of hydrolysis is more rapid in the case of the diethyl and of the *iso*butyl esters of *l*-tartaric acid than in the corre-

sponding *d*-esters. Liver lipase, unlike pancreatic lipase, hydrolysed the esters of *d*-tartaric acid more readily than those of the *l*-acid. S. S. ZILVA.

Lipase of tissues. P. RONA and A. LASNITZKI (Biochem. Z., 1926, **173**, 207—223).—The lipolytic power of slices of tissue was investigated manometrically, tri- and mono-butyrin serving as substrate. The lipolytic powers, per mg. dry weight per hr., of two slices of tissue drawn from the same region of an organ often showed considerable difference, the lipolytic power being related to the surface as well as to the weight of the slice. Enzymes washed out from the slice caused a considerable part of the hydrolysis, which was greatly increased by disintegration of the tissue. Extracts of rat's tumour, per unit of weight of extracted substance per hr., hydrolysed about one-seventh as much as tributyrin liver extract and about one-sixth as much as kidney extract, whereas the lipolytic power of an extract of spleen was of the same order as that of the tumour extract. P. W. CLUTTERBUCK.

Enzyme action. XXXVI. Ester-hydrolysing actions of the castor bean. I. LORBERBLATT and K. G. FALK (J. Amer. Chem. Soc., 1926, **48**, 1655—1667).—The optimum p_H for the hydrolysis of phenyl acetate and triacetin by hull- and fat-free castor beans (cf. Noyes, Lorberblatt, and Falk, this vol., 757) is about 5·0, whilst hydrolysis of methyl and ethyl butyrates proceeds most rapidly at p_H 6·0—7·0. Benzoates are not hydrolysed. The values of the unimolecular reaction constants decrease progressively during the hydrolyses. The Schütz constant $(x/\sqrt{T})$ increases to a constant value and then decreases, whilst Northrop's constant (J. Gen. Physiol., 1919—1920, **2**, 471) also passes through a maximum. Contrary to the observations of Willstätter and Waldschmidt-Leitz (A., 1924, i, 919), the solubility of the castor-bean ester-hydrolysing material in water has been confirmed (cf. Sugiura, Noyes, and Falk, A., 1923, i, 1246). In esters derived from the same alcohol, the rate of hydrolysis by the water extract increases with the mol. wt. of the acid. The sodium chloride solution extract is practically without action on valeric, butyric, or propionic esters, whilst the rate of hydrolysis of esters of acetic acid decreases as the mol. wt. of the alcohol increases. Methyl valerate and methyl and ethyl butyrates are most affected by the aqueous extract, whilst phenyl and glyceryl acetates are most affected by the aqueous sodium chloride extract, the residues, and the original preparation. In most cases, the sum of the activities of the two extracts and of the residue was not equal to the activity of the original enzyme preparation. F. G. WILLSON.

Protein-splitting enzymes in macerated peas. A. FODOR and R. SCHÖNFELD (Kolloid-Z., **39**, 1926, 56—63).—The proteolytic action of extracts of macerated peas on peptone has been investigated, the degree of hydrolysis of the peptone being measured by the use of Sörensen's method. Attempts have been made to remove the protein by precipitation with acid and by adsorption by kaolin or aluminium hydroxide, and by the use of kaolin it has been found possible to obtain a filtrate giving no protein reaction, but still showing proteolytic activity. The stabilities of the various fractions obtained by adsorption have also been investigated. W. O. KERMACK.

Peptic hydrolysis. I. H. STEUDEL, J. ELLINGHAUS, and A. GOTTSCHALK (Z. physiol. Chem., 1926, **154**, 21—33).—A study of the rate of the liberation of carboxyl groups (determined by Willstätter's method) and of amino-groups (Sörensen, Van Slyke) from several different proteins under the action of pepsin shows that carboxyl groups are set free at a much greater rate than amino-groups. The authors conclude that in all the proteins examined a large proportion of the carboxyl is bound, not to nitrogen (at least not by a peptide linking), but to the hydroxyl group of hydroxyamino-acids. H. D. KAY.

Peptic hydrolysis. II. H. STEUDEL, J. ELLINGHAUS, and A. GOTTSCHALK (Z. physiol. Chem., 1926, **154**, 198—202; cf. preceding abstract).—Extension of previous experiments to fibrin, edestin, and vitellin shows that, in the peptic hydrolysis of these proteins also, the increase of titratable acid is greater than the increase of free amino-nitrogen; the difference is more marked in the early stages of hydrolysis, since the liberation of carboxyl groups appears to be the more rapid reaction, being, in the case of fibrin, practically complete after 4 hrs. It is suggested that the primary action of pepsin may be to split off those amino-acids, such as proline and lysine, in which part or the whole of the nitrogen is present in a form other than that of a free α-amino-group. C. R. HARINGTON.

Relation of trypsin and pepsin to their substrates. G. E. BRIGGS (Biochem. J., 1926, **20**, 574—579).—Northrop's results (A., 1924, i, 473; 1925, i, 864) are discussed critically, and it is concluded that much of the evidence points to a theory involving the combination of gelatin and similar proteins with enzymes such as trypsin and pepsin. S. S. ZILVA.

Enzyme affinity. II. H. VON EULER (Arkiv Kemi, Min., Geol., 1926, **9**, No. 24, 1—7).—Glycine does not inhibit the action of intestinal peptidase on glycylglycine or glycyl-*l*-tyrosine. The latter is, however, inhibited by *dl*-alanine. The velocity constant of the reaction remains unaltered in the case of glycylglycine, but decreases markedly during the hydrolysis of glycyl-*l*-tyrosine, this effect being more pronounced in solutions of high substrate concentration. C. RIMINGTON.

Rennin-like action of pepsin. R. AKIBA (Keio Ig., Tokyo, 1922, **2**, 1387—1391).—The rennin-like action of pepsin on milk may be caused by the autocatalysis of pepsin itself. On coagulation of milk by pepsin, a rennin-like enzyme is present in the serum at almost constant concentration. CHEMICAL ABSTRACTS.

Rennin. I. Effect of previous heating on the coagulability of caseinogen. II. Replaceability of calcium by other cations. III. Replaceability of phosphate by other substances. S. MARUI (Biochem. Z., 1926, **173**, 363—370, 371—380, 381—388).—I. The lessened ability

of boiled caseinogen solutions to clot in presence of rennin is not due to an increase, brought about by the heating process, in the affinity of caseinogen for calcium, although addition of a calcium salt to a boiled solution may restore its coagulability. The action of heat is reversible in the sense that a dry caseinogen preparation precipitated from a solution of the protein previously rendered uncoagulable by boiling, will, if again dissolved, exhibit the same ability to form a clot, in presence of rennin, as a fresh unheated caseinogen solution.

II. No univalent cation is able to replace calcium, but barium, strontium, and magnesium may, within certain limits, replace calcium in the rennin–caseinogen–casein system in milk. In the case of copper and zinc, and still more with the tervalent cations, the observations are complicated by the precipitation which follows their addition even in absence of rennin.

III. Phosphate is present even in pure caseinogen solutions. The cations which can replace calcium to a greater or lesser extent (see above) all form insoluble phosphates. Possibly a colloidal suspension of an insoluble phosphate is an essential part of the clotting mechanism. Calcium phosphate can be replaced by calcium oxalate in this system, provided the oxalate is kept in colloidal suspension. A gum mastic sol in dilute caseinogen solution is precipitated by calcium chloride if the latter is above a minimal concentration. Even below this concentration the mixture is readily precipitated by the addition of rennin. Caseinogen itself is precipitated by calcium chloride over certain limited zones of concentration of the salt. These zones are broadened in presence of rennin. H. D. Kay.

Mechanism of the action of Schardinger's enzyme. A. von Szent-Györgyi (Biochem. Z., 1926, **173**, 275—278).—The oxidation of acetaldehyde by Schardinger's enzyme is sensitive to cyanide and involves the activation of both oxygen and hydrogen. P. W. Clutterbuck.

Hydrolysis of salts of monophenylphosphoric and monoethylphosphoric acids by plant and animal phosphatases. R. Iwatsuru (Biochem. Z., 1926, **173**, 348—357).—The extent of hydrolysis of the potassium salt of monophenylorthophosphoric acid by vegetable phosphatase is 91%, and by animal phosphatase 55%, whilst that of monoethylorthophosphoric acid is by animal phosphatase 98%, and by fungus phosphatase 85%. P. W. Clutterbuck.

Chemical processes in fermentations. F. F. Nord (Chem. Reviews, 1926, **3**, 41—79).

Buffers. I. Buffer capacity and biochemical action. H. Moser (Helv. Chim. Acta, 1926, **9**, 414—419).—The fermentation of dextrose by yeast is retarded and eventually arrested by the addition of increasing amounts of disodium hydrogen phosphate. This is ascribed to a deleterious effect of excess of buffer solution. This effect is considered from the point of view of reactions in the animal organism. M. Clark.

Intermediate reactions in fermentation. H. von Euler and O. Swartz (Arkiv Kemi, Min., Geol., 1926, **9**, No. 21, 1—8).—Alkali succinates favour fermentation; alkali nitrates are without effect. The effect of ultra-violet light on the synthesis of organic phosphorus esters during fermentation is doubtful, whilst sodium fluoride is without effect. C. Rimington.

Method of arresting fermentation, particularly in the case of liquids containing alcohol and sugar, and of rendering such liquids non-fermentable. Boulard (Compt. rend., 1926, **182**, 1422—1424).—When the fermentation is quite active, the liquid is heated for 1 hr. at a temperature a few degrees higher than is necessary to kill the yeasts present; 45° is usually sufficient. It is then cooled and again brought to the optimum fermentation temperature, inoculated with the same yeasts, and, when fermentation is active, again heated. Three such operations suffice to render the liquid non-fermentable even after addition of a large quantity of yeast with an amount of unchanged sugar greater than 150 g. per litre. H. J. Evans.

Effect of temperature on the growth of yeast in various media. E. F. Sherwood and E. I. Fulmer (J. Physical Chem., 1926, **30**, 738—756; cf. Fulmer, Sherwood, and Nelson, B., 1924, 922).—The growth of yeast at various temperatures, 0—43°, in media adjusted to optimum conditions has been compared with that in unadjusted media. Two optimal concentrations of ammonium chloride appear when the growth of yeast in beer wort and in a synthetic medium containing ammonium and calcium chlorides, dipotassium hydrogen phosphate, calcium carbonate, and sugar is examined at several temperatures. The largest crops were obtained at 42° (cf. Slator, J.C.S., 1906, **89**, 128), but a sharp break occurs at 43°. The optimal normality of the salt is a linear function of temperature. The effects of varying the concentration of the other constituents of the medium are also given, but the optimal concentrations do not vary with temperature. Temperature coefficients for the growth of yeast in optimum media are compared with those obtained in unadjusted media. The phases of negative growth acceleration and the maximum stationary growth (Buchanan, J. Infect. Dis., 1918, **23**, 109) at different temperatures were also studied. L. S. Theobald.

Action of drugs and irradiation on yeast. II. Proof of action of Röntgen rays on substances by means of yeast. H. Zeller (Biochem. Z., 1926, **172**, 105—125).—If the following substances are irradiated by means of a Coolidge tube they affect the formation of carbon dioxide by fermenting yeast differently from non-irradiated samples: cholesterol, nucleic acid salts, thyreodin, hæmoglobin, yolk of egg, choline, hexamethylenetetramine, potassium cyanide, potassium ferrocyanide, thiosinamine, sodium salicylate, ammonium salts, iodides in large quantities, potassium dichromate, potassium permanganate, and potassium bromide. There is no difference between irradiated and non-irradiated sodium chloride, iodides in small doses, magnesium sulphate, potassium thiocyanate (?), silver nitrate (?),

sodium lactate, sodium glycerophosphate, sodium urate, lecithin, urine, and Witte's peptone. H. I. COOMBS.

Reductase (dehydrogenase) of yeast. IV. Purification of co-reductase. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **155**, 31—41).—The activity of co-reductase is increased sixty times by dialysis, probably owing to separation from an inhibitory substance. The activity can be further increased 50% by diffusion. The mol. wt. calculated from the diffusion rate is between 400 and 500. E. C. SMITH.

Co-zymase. VIII. E. JORPES, H. VON EULER, and R. NILSSON (Z. physiol. Chem., 1926, **155**, 137—155).—The authors have investigated the question of the identity of insulin with the co-zymase of lactic acid bacteria (Virtanen, A., 1925, i, 753). Extracts of *Thermobacterium helveticum* (=*B. casei* ε) can replace yeast co-zymase in its action on *apo*zymase, but insulin has no action. Neither yeast co-zymase nor active extracts of *T. helveticum* cause a fall in the blood-sugar of rabbits. Insulin cannot therefore be regarded as the co-zymase of blood. E. C. SMITH.

Equilibrium between *l*-aspartic acid, fumaric acid, and ammonia in presence of resting bacteria. J. H. QUASTEL and B. WOOLF (Biochem. J., 1926, **20**, 545—555).—Resting *B. coli* under anaërobic conditions at p_H 7·4 and at 37° is able, in the presence of growth inhibitors such as toluene, propyl alcohol, and sodium nitrite, to synthesise *l*-aspartic acid from fumaric acid and ammonia. This reaction is reversible and the equilibrium constant K=[fumaric acid][NH_3]/[aspartic acid] is 0·04. The mechanism which controls this equilibrium is thermolabile, since the reaction does not take place in the presence of organisms which have been previously boiled. In the absence of growth inhibitor, reduction to succinic acid takes place. The above equilibrium is attained both aërobically and anaërobically if 1% of sodium nitrite or 4% of propyl alcohol be present; 10% of this alcohol almost inhibits the reaction. Glutamic acid and glycine, unlike aspartic acid, do not liberate ammonia nor does glutaconic acid, maleic acid, or succinic acid absorb ammonia under the above conditions. With malic acid there is a slight but definite ammonia uptake in the presence of *B. coli*. S. S. ŽILVA.

Reversible change of hexose into lactic acid in lactic acid bacteria and in muscle. I. H. VON EULER and R. NILSSON (Z. physiol. Chem., 1926, **155**, 186—194).—*Thermobacterium helveticum* and *Streptococcus lactis* show no marked superiority over yeast in co-zymase content. The reductase-efficiency of fresh *T. helveticum* is not increased, as in the case of fresh yeast, by heating to 40°. Addition of co-reductase shows a checking effect. Dried yeast shows a marked superiority in reductase-efficiency over fresh yeast, probably owing to alteration in permeability. The results of co-reductase tests on the fresh bacteria are described. The bacteria retain their reducing power towards methylene-blue on drying (cf. Virtanen, A., 1924, i, 915). The co-reductase can be removed from the dried preparations by washing. M. CLARK.

Lactic acid fermentation. A. I. VIRTANEN and H. KARSTRÖM (Z. physiol. Chem., 1926, **155**, 251—258).—In confirmation of previously published results (this vol., 435), *B. casei* and *S. lactis*, typical lactic acid bacteria, do not ferment methylglyoxal or dihydroxyacetone with production of lactic (or other) acid. *B. coli* produces acid from both these substances. H. D. KAY.

Production of lactic acid from sugar by various methylglyoxal-dismuting bacteria, and a simple means of isolating [zinc] lactate. C. NEUBERG and G. GORR (Biochem. Z., 1926, **173**, 476—481).—The three types of bacterium (*Lactobacillus, B. propionicus*, and *B. coli*) which have recently been shown by the authors (this vol., 97, 325) to be capable of "dismuting" methylglyoxal to lactic acid to the extent of 100%, are now shown to be true lactic acid producers from dextrose. With the strain of *B. coli* used as much as 82% of the sugar fermented was found as lactate. In the isolation of lactic acid advantage is taken of the fact that lead lactate is very soluble in water. H. D. KAY.

Bacterial metabolism. LXXIII. Non-dextrose-fermenting bacteria and insulin. A. I. KENDALL. **LXXIV. Effect of insulin on cultures of *Bacillus bulgaricus* and *B. acidophilus*. LXXV. Effect of insulin on bacterial metabolism.** A. I. KENDALL and M. ISHIKAWA (J. Infect. Dis., 1925, **37**, 329—332, 333—336, 336—339).—Bacteria which do not ferment dextrose do not do so on addition of insulin. Insulin appears not to affect the amount of dextrose fermented by *B. bulgaricus* and *B. acidophilus*. Similar results were obtained with other bacteria. CHEMICAL ABSTRACTS.

Enzymic metabolism of bacteria. I. Respiration and glycolysis in the case of *B. coli*. II. Aërobic glycolysis and the splitting of some other sugars by *B. coli*. Micro-determination of invertase. P. RONA and H. W. NICOLAI (Biochem. Z., 1926, **172**, 82—104, 212—222).—I. Dextrose is anaërobically split into 2 mols. of fixed acid. The speed of this reaction is proportional to the quantity of bacteria present and between limits is independent of the concentration of sugar. The temperature coefficient is 2·2—2·5 and the optimum reaction between p_H 5·5 and 8·0. Under aërobic conditions, oxygen is used and carbon dioxide is formed along with the fixed acid. Whilst the oxygen consumption is proportional to the quantity of bacteria and independent, within limits, of the concentration of sugar, it is not possible to correlate it with the acid formed. The temperature coefficient is 2·2—2·5 and respiration is inhibited at p_H 4·03.

II. The oxygen uptake and carbon dioxide output of *B. coli* when growing on media containing maltose, sucrose, lævulose, dextrose, arabinose, and xylose were investigated. The carbon dioxide output of the bacteria after invertase has acted on sucrose was measured and this can be used to determine the amount of invertase present. H. I. COOMBS.

Inhibition of bacterial growth by cyanide. E. LÖFFLER and R. RIGLER (Biochem. Z., 1926, **173**, 449—454).—*B. typhosus* is more sensitive to cyanide than *B. dysenteriæ*, Shiga-Kruse. The ability to reduce nitrates and chlorates displayed by many bacteria is inhibited by cyanide, but in the case of the Shiga-Kruse bacillus cyanide has no such effect.
H. D. KAY.

Detection and determination of formaldyde in fermentations. K. MAURER (Biochem. Z., 1926, **173**, 201—206).—Formaldehyde, determined by a colorimetric method, is formed in the acid fermentation of cabbage, but in such small amount that its bactericidal action is negligible. P. W. CLUTTERBUCK.

Action of radium on *Aspergillus fumicatus*, Fresenius, grown in media with and without ionisable salts. A. SARTORY, R. SARTORY, and J. MEYER (Compt. rend., 1926, **183**, 77—79).—The morphological changes are described which result when cultures of *A. fumicatus*, Fresenius, on media with and without sodium chloride, are exposed to the action of radium for various lengths of time. These changes are paralleled by variations in the reducing power of the organism and in the hydrogen-ion concentration of the medium. G. M. BENNETT.

***Azotobacter agile*.** S. KOSTYTSCHEV, A. RYSKALTSCHUK, and O. SCHWEZOWA (Z. physiol. Chem., 1926, **154**, 1—17).—Molecular nitrogen is taken up by cultures of this organism growing in synthetic media. The first recognisable nitrogen compound formed is ammonia, from which the nitrogen of the bacterial protein is obtained. The process occurring in a mould previously studied which, when grown on a medium containing nitrate as sole source of nitrogen, first transforms the nitrate, by extracellular reduction, to ammonia, which is then taken up by the cell, is also found to take place when *Azotobacter agile* is grown on nitrate. No free nitrogen is liberated during the process. If the organism is already provided with nitrogen in the form of ammonium salts or nitrates, it will not take up molecular nitrogen. In a peptone medium, on the other hand, the uptake of molecular nitrogen still continues. Addition of sterilised garden soil to a synthetic medium containing dextrose greatly increases the amount of molecular nitrogen taken up per g. of dextrose utilised. The organism retains its power to utilise molecular nitrogen, even after a long period of growth on synthetic media. H. D. KAY.

Soluble enzymes secreted by the *Hymenomycetes* fungi. Oxidations. L. LUTZ (Compt. rend., 1926, **183**, 95—97).—Of eleven species of fungi examined, seven have considerable oxidising powers, the enzymes diffusing for a considerable distance in the medium around the point of inoculation before the organism has appreciably developed. In two species the effect was slight, and in two absent.
G. M. BENNETT.

Pigments of *Aspergillus niger*. A. FREY (Compt. rend., 1926, **182**, 1552—1554).—*A. niger* forms two pigments, brown aspergillin and a golden-yellow pigment, and a chromogen giving a dark yellow solution with alkalis. L. F. HEWITT.

Action of various substances, especially of insulin, on cell respiration. J. BORN and G. IVÁNOVICS (Biochem. Z., 1926, **173**, 190—200).—The Thunberg-Meyerhof co-enzyme of the lactic acid dehydrase cannot be identified with insulin, since the latter is unable to reactivate extracted, inactive muscle. P. W. CLUTTERBUCK.

Utilisation of insulin and dextrose. Effect of anæsthetics and pituitrin. C. G. LAMBIE (Brit. J. Exp. Path., 1926, **7**, 22—32).—The rate at which insulin accelerates the removal of dextrose from the circulation (of the cat) is unchanged under anæsthesia. If the blood-sugar level is maintained, and the liver excluded, doses of pituitrin which normally prevent the fall in blood-sugar under insulin fail to do so. CHEMICAL ABSTRACTS.

Nickel and cobalt in the pancreas. G. BERTRAND and M. MÂCHEBŒUF (Compt. rend., 1926, **182**, 1305—1307).—The pancreas of all the species of animals investigated contains relatively large amounts of nickel and cobalt compared with other organs. Insulin contains a relatively much larger proportion of nickel and cobalt than the pancreas, viz., some 0·045 mg. per 100 clinical units of insulin.
L. F. HEWITT.

Influence of nickel and cobalt upon the action of insulin on the rabbit. G. BERTRAND and M. MÂCHEBŒUF (Compt. rend., 1926, **182**, 1504—1507; cf. preceding abstract).—Injection of either nickel or cobalt salts (0·01—0·05 mg. per kg.) into rabbits increases the effect of a dose of insulin (0·2—0·26 clinical unit per kg.) unless the insulin preparation is rich in nickel and cobalt salts. The salts prolong the hypoglycæmia, cobalt being somewhat more active than nickel, without markedly accelerating the rate of removal of dextrose from the blood. Larger doses of the salts inhibit the effect of insulin. When both metals are injected together, the rate of removal of dextrose from the blood is diminished and the hypoglycæmia prolonged. L. F. HEWITT.

Influence of nickel and cobalt upon the action of insulin on the dog. G. BERTRAND and M. MÂCHEBŒUF (Compt. rend., 1926, **183**, 5—8; cf. preceding abstract).—The influence of nickel and cobalt on the hypoglycæmic effect of insulin in the dog is similar to that in the rabbit.
G. M. BENNETT.

Influence of muscle-tissue and insulin on rotatory power of dextrose. J. R. PAUL (J. Biol. Chem., 1926, **68**, 425—438).—The technique of Lundsgaard and Holbøll (A., 1925, i, 1494) and also the method of ultrafiltration were employed to investigate the effect on dextrose of the addition of muscle-tissue and of insulin, separately and together. Apart from a preliminary drop in the concentration of the dextrose, due probably to the diluting effect of the muscle-tissue added, no significant or constant effect on the ratio of reducing power to optical rotation was observed in any case. The results of Lundsgaard and Holbøll were therefore not confirmed. The minor variations which were observed in the rotatory power of the solutions are ascribed to

the presence of optically active compounds (*e.g.*, lactic acid) other than dextrose. C. R. HARINGTON.

Glycogen content of the liver of rabbits during the action of insulin. II. A. GREVENSTUK and E. LAQUEUR (Biochem. Z., 1926, **173**, 283—288).—The liver-glycogen content in fasting rabbits provided with abdominal windows was followed from time to time after subcutaneous injection of small doses of insulin (0·1 unit per kg.). A very small increase was obtained, but in control animals, injection of the same amount of 0·01*N*-hydrochloric acid had the same result (cf. *ibid.*, 1925, **163**, 390). P. W. CLUTTERBUCK.

Fate of sugar disappearing under action of insulin. C. H. BEST, J. P. HOET, and H. P. MARKS (Proc. Roy. Soc., 1926, **B**, **100**, 32—54).—An extension of the work of Burn and Dale (J. Physiol., 1924, **59**, 164) which showed that the increase in oxygen consumption after administration of insulin accounts for a small part only of the sugar disappearing from the blood of an animal. By studying the variations in muscle glycogen and lactacidogen, blood phosphate and sugar, occurring normally and under the action of insulin, the authors have investigated the fate of the sugar which disappears but is not burnt. Whilst the muscles of different animals and even different muscles of the same animal vary widely in their glycogen content, that of corresponding muscles from the two sides of the same animal is always practically identical; this solved the difficult question of control. The immediate effects of insulin, in the diabetic, are an accelerated combustion of dextrose and the synthesis of a further quantity of glycogen. The authors conclude that (1) no significant portion of the sugar which disappears from the blood under the influence of insulin is stored in the muscles as a phosphoric ester; (2) where excess of sugar is available, a large proportion of the sugar which disappears from the blood is deposited as glycogen in the skeletal muscles; (3) insulin hypoglycæmia, lasting 1—3 hrs., does not apparently lower the glycogen content of the resting skeletal muscles of the spinal cat; (4) in normal rabbits, the disappearance of muscle glycogen, produced by large doses of insulin, is chiefly due to the convulsions. W. ROBSON.

Oxidation and storage of dextrose under action of insulin. C. H. BEST, H. H. DALE, J. P. HOET, and H. P. MARKS (Proc. Roy. Soc., 1926, **B**, **100**, 55—72; cf. preceding abstract).—In an attempt to make a complete experimental balance sheet representing the fate of the whole of the dextrose disappearing from the blood, simultaneous measurements of the oxygen consumption and the accumulation of glycogen in the same animal preparation were made. In a normal preparation whilst the blood-sugar falls (*e.g.*, from 0·3 to 0·068%), the muscle glycogen content remains remarkably constant. The dextrose which disappears from an eviscerated spinal preparation under the action of insulin is equal to the sum of the glycogen deposited in the muscles and the dextrose equivalent of the oxygen absorbed; this balance is preserved, whether the blood-sugar is maintained at a high level by rapid infusion of dextrose, or allowed to sink to a very low level by restricting the supply. The view is advocated that the effects of insulin in excess represent an intensification of its physiological effects. W. ROBSON.

Effect of insulin on the lactacidogen content of the skeletal muscles. C. H. BEST and H. P. MARKS (Proc. Roy. Soc., 1926, **B**, **100**, 171; cf. preceding abstract).—When insulin is injected there is no storage of dextrose as phosphoric ester even when the inorganic phosphorus of the blood is kept high by intravenous injection of sodium phosphate. H. J. CHANNON.

Colour reactions attributed to vitamin-*A*. F. H. CARR and E. A. PRICE (Biochem. J., 1926, **20**, 497—501).—The following reagents give colour reactions with cod-liver oil: antimony trichloride in chloroform, a brilliant blue colour not undergoing perceptible change for 3 min.; stannic chloride in chloroform, a deep blue colour rapidly changing to purple; anhydrous ferric chloride, a fluorescent, reddish-violet colour (this reagent does not give uniform results); anhydrous aluminium chloride added in the form of a fine powder to the oil, reddish-violet colour fading to brown, if added to oil in chloroform purple in the presence of carbonyl chloride or of dry hydrochloric acid, red in the absence of these reagents; silicon tetrachloride, a rose-pink colour (not given by cholesterol); phosphorus oxychloride, a transient blue rapidly fading to red. The first of these reagents is the most suitable. Quantitative records can be obtained by matching the colour produced in a Lovibond tintometer. Pure trichloroacetic acid does not give a coloration with cod-liver oil, but will do so on the addition of carbonyl chloride and of methyl sulphate. S. S. ZILVA.

Antirachitic properties of irradiated sterols. O. ROSENHEIM and T. A. WEBSTER (Biochem. J., 1926, **20**, 537—544).—On irradiating cholesterol in an atmosphere of nitrogen and crystallising it out of hot absolute alcohol, an active fraction remains in the mother-liquor, part of which is soluble in light petroleum. If the fraction in the mother-liquor is taken up in alcohol and precipitated with digitonin, a very active fraction which protects rats from rickets in daily doses of about 0·01 mg. is obtained from the filtrate.

The following cholesterol derivatives and compounds have been irradiated: cholesteryl chloride, cholestene, cholestenone, cholesteryl acetate, cholesteryl palmitate, coprosterol, ergosterol, α-amyrol, and squalene. Of these, only ergosterol and cholesteryl acetate and palmitate became antirachitic. The secondary alcohol group and the unsaturated carbon linking of the sterol molecule must therefore be intact for the compound to be activated on irradiation. Cholesterol is rendered antirachitic on exposure to sunlight. S. S. ZILVA.

Antirachitic factor of cod-liver oil. E. LESNÉ and S. SIMON (Compt. rend., 1926, **182**, 1424—1426).—The content of antirachitic factor is influenced by the origin and method of preparation of the oil, and has no relation to colour. The only suitable means of defining the antirachitic activity of a specimen of oil is the biological test. H. J. EVANS.

Vitamins. II. H. VON EULER and I. LINDSTAL (Arkiv Kemi, Min., Geol., 1926, **9**, No. 12, 1—6).—Saponification of cod-liver oil in an atmosphere of hydrogen yields a residue having reducing properties and a high iodine number. An aldehyde is probably present, distillable at 0·03—0·05 mm. Among the distillation products of cod-liver oil is a fraction with strong reducing properties and a low iodine number. C. RIMINGTON.

Inter-relation of vitamin effects. H. VON EULER and H. WIDELL (Arkiv Kemi, Min., Geol., 1926, **9**, No. 15, 1—5).—The growth-promoting effect of cod-liver oil is inhibited by treating the oil with iodine. Addition of irradiated lemon juice to a diet deficient in fat-soluble factors resulted in slight growth improvement and good ossification. Not only the presence or absence, but also the relative quantity of each vitamin is important. C. RIMINGTON.

Relation of light to life and health. W. A. PRICE (Ind. Eng. Chem., 1926, **18**, 679—685).—A sufficiency of calcium and phosphorus in the diet is essential to health and growth of chicks, and in order to derive any benefit from the food, exposure to radiant energy, such as the sun's rays, or the presence of an antirachitic vitamin in the diet, is necessary. Exposure of cod-liver oil to bright sunlight for a short time increases its effect on calcium metabolism, but prolonged exposure is deleterious and in some cases results in the formation of poisonous substances. A. R. POWELL.

Inequality in content of water-soluble vitamin-*B* of yeast extracts of different origin. L. RANDOIN and R. LECOQ (Compt. rend., 1926, **182**, 1408—1410).—Extracts of yeast of different origin have by no means the same biological value as sources of vitamin-*B*. Some (brewer's yeast) promote metabolism and simultaneously prevent or cure polyneuritis; others (distiller's yeast) promote metabolism only. H. J. EVANS.

Is the water-soluble vitamin-*B* of brewer's yeast derived from the culture medium? L. RANDOIN and R. LECOQ (Compt. rend., 1926, **182**, 1564—1566; cf. preceding abstract).—Yes. Hops do not contain this vitamin. L. F. HEWITT.

Vitamins (*A*, *B*, and *C*) of papaya. C. D. MILLER (Biochem. J., 1926, **20**, 515—518).—The papaya (*Carica papaya*, L.) is only a fair source of vitamin-*B*, a good source of vitamin-*A*, and an excellent source of vitamin-*C*. S. S. ZILVA.

Action of reducing agents on the antiscorbutic factor inactivated by aëration. C. G. DAUBNEY and S. S. ZILVA (Biochem. J., 1926, **20**, 519—524).—Antiscorbutic solutions were inactivated by aëration and subsequently reduced (1) by means of platinum-black and hydrogen, (2) electrolytically. The antiscorbutic activity was not re-established by either treatment. S. S. ZILVA.

Bezssonoff's reagent for vitamin-C. E. LOEWY (Münch. med. Woch., 1925, **72**, 1780—1781; from Chem. Zentr., 1926, I, 741).—The colour reaction of Bezssonoff (Biochem. J., 1923, **17**, 420) gives results in good agreement with clinical observations and experiments with animals, and apparently corresponds with the actual vitamin-*C* content of the material. G. W. ROBINSON.

Accessory factors for growth. VIII. H. VON EULER and M. RYDBOM (Z. physiol. Chem., 1926, **155**, 270—278).—Yeast extract and muscle contain an accessory growth factor which is apparently not identical with any known vitamin. This "growth-factor *F*" may possibly be a substance of known chemical composition which is lacking in the basal diet. The total quantity of vitamins-*A* and -*D* required by the rat is greater than the experimental minimum present in a diet which just permits of normal growth, since the animal body is able, by various means, to synthesise or activate the sterols concerned. H. D. KAY.

Relation of the energy balance to the source of nitrogen in the medium in the growth of higher plants. G. VINCENT (Bull. Soc. Chim. biol., 1926, **8**, 330—340).—Young arachis plants were grown in the dark on media the only difference of which was that the same amount of nitrogen was provided as various ammonium salts in one case and as potassium nitrate in the other. The energy utilisation was 83% in the former case and 67% in the latter. H. J. CHANNON.

Labile modification of reserve-protein in plant cells. O. LOEW (Chem.-Ztg., 1926, **50**, 429—430).—In most actively growing cells of the epidermis of the colourless leaf-base of *Iris interregna*, a droplet is visible, having the appearance of a globule of oil, which gives the tests for protein with Millon's reagent and with nitric acid. On placing the cells in water at 60°, other similar but smaller drops appear and coalesce. Between 63° and 65°, the drops suddenly disappear, water being set free and a small coagulum remaining. Coagulation also takes place a short time after the death of the cell. It is concluded that the protein in the drops is present in a very labile form, and that it is probably concerned with the transport of nitrogen. C. T. GIMINGHAM.

Photochemical effect of chlorophyll and its significance for carbon dioxide assimilation. K. NOACK.—See this vol., 808.

Rate of absorption of sodium nitrate by oats and cotton when applied at different stages of plant growth. W. H. APPLETON and H. B. HELMS (J. Amer. Soc. Agron., 1925, **17**, 596—605).—Sodium nitrate (400 lb. per acre) applied to oats 14, 42, 70, and 92 days after planting was completely absorbed in 49, 20, 14, and 10 days, respectively; corresponding values for cotton (600 lb. per acre) after 14, 40, and 61 days were 30, 14, and 11 days, respectively. In both cases there was a close correlation between rate of growth and rate of nitrate absorption. CHEMICAL ABSTRACTS.

Nutrition of plants with aldehydes. VI. Polymerisation of formaldehyde by *Elodea canadensis* to higher carbohydrates. T. SABALITSCHKA and H. WEIDLING (Biochem. Z., 1926, **172**, 45—57).—*E. canadensis*, R. and M., can polymerise added formaldehyde to higher carbohydrates in the presence or absence of light. Light

does not influence the amount of this polymerisation. The optimum amount of formaldehyde in the culture medium is 0·024%. Higher concentrations adversely affect the enzyme of the plant, so that less starch is formed. Formaldehyde is an intermediate step in the formation of starch in plants under normal conditions. H. I. Coombs.

Mechanism of lactic acid formation in Phanerogams. II. C. Neuberg and G. Gorr (Biochem. Z., 1926, **173**, 358—362; cf. this vol., 761).—Lactic acid-forming enzyme is not only active in fresh seeds (*Vicia faba*, *Lupinus albus*), but also in dry acetone preparations and in aqueous extracts and alcohol–ether precipitates of the latter. The enzyme acts in presence of toluene. P. W. Clutterbuck.

Irradiation and chlorophyll. J. Amar (Compt. rend., 1926, **182**, 1353—1354).—When left exposed to light either in an empty tube or in a tube filled with water coloured with gentian-violet, spindle-tree leaves were discoloured, but those kept in a tube of water coloured with carmine-red remained unchanged. When a small amount of a solution of the pigment was added to a solution of egg-albumin, carmine-red diffused most, chlorophyll less, and gentian-violet least. L. F. Hewitt.

Cellular pigments and physico-chemical action. J. Amar (Compt. rend., 1926, **182**, 1566—1569).—The decolorising action of light of short wavelength on chlorophyll is ascribed to oxidation, since oxidising agents have a similar effect. When a solution of egg-albumin and chlorophyll is electrolysed, the pigment moves to the anode, presumably adsorbed on the albumin. L. F. Hewitt.

Variation of organic and mineral constituents, especially calcium, in leaves of trees during autumnal fading. R. Combes and R. Echevin (Compt. rend., 1926, **182**, 1557—1559; cf. this vol., 647).—In the case of nearly every tree examined, the dry weight, inorganic salt and calcium content of the leaves decreased during the autumnal fading, but the relative proportion of calcium in the leaves increased. L. F. Hewitt.

Comparison of various methods of obtaining ash-free pectin. A. M. Emmett (Biochem. J., 1926, **20**, 564—568).—The following methods of removing mineral impurities from pectin were compared: (1) dialysis against distilled water, (2) dialysis against 0·02*N*-hydrochloric acid, (3) electro-dialysis. The last method proved to be the most rapid and effective. The ash of a sample of pectin was reduced from 3·1% to 0·5% in 3 days. S. S. Zilva.

Stone cells of the pear. C. Dorée and E. C. Barton-Wright (Biochem. J., 1926, **20**, 502—506).—The "stone cells" of the pear, *i.e.*, the woody concretions found in the fleshy parenchyma, consist of 80% of a lignocellulose, 1·2% of extractives, 4·62% of mannan, and 12% of an alkali-soluble furfuroid, which yields 77% of its weight of furfuraldehyde and contains "uronic" acids. The lignocellulose contains 60 parts of cellulose and 20 parts of lignin. The cellulose fraction is made up of 73% of α- and 27% of β-cellulose. S. S. Zilva.

Determination of the hydrogen-ion concentration of the blood. L. E. Bayliss, P. T. Kerridge, and R. C. Verney (J. Physiol., 1926, **61**, 448—454).—No systematic differences have been found between the values determined by the hydrogen electrode, the glass electrode, and the colorimetric method of Dale and Evans. The probable errors of the mean reading on a given sample are stated to be 0·003 p_H for the hydrogen electrode, 0·008 for the glass electrode, and 0·011 for the colorimetric method. R. K. Cannan.

Colorimetric determination of bile salts in blood. P. Szilárd (Biochem. Z., 1926, **173**, 440—448).—Oxalated or citrated fresh blood is centrifuged, and the proteins are precipitated from a measured volume of plasma by adding it slowly to fifty times the volume of absolute alcohol. The mixture is boiled, the alcoholic solution filtered and evaporated to small bulk, and the bile salts are precipitated by adding ether in excess and keeping. They are filtered off and dissolved in a small quantity of water. A solution of ferric chloride in dilute hydrochloric acid is added, and precipitates the bile salts on keeping at 37°. The precipitate is centrifuged off, suspended in alcohol, an equal volume of chloroform added, and a trace of 20% sulphosalicylic acid. The iron compound is then shaken out with a measured quantity of acidified water, and compared in a colorimeter with a comparable amount of sodium glycocholate similarly treated. The rose colour finally obtained is proportional to the amount of iron in the ferric chloride precipitate, which is again dependent on the amount of bile salts originally present. H. D. Kay.

Strontium as a source of error in blood-calcium determinations. M. Fay (Amer. J. Physiol., 1926, **77**, 73—75).—Addition of strontium salts to blood-serum increases the blood calcium figure as determined by the oxalate precipitation method by about a third of the strontium added. It is not yet possible to decide whether the alleviation of parathyroid tetany by strontium is due to direct replacement of calcium in the blood. R. K. Cannan.

Necessity of assuring the absence of nitric acid in Marsh's toxicological test for arsenic. F. Schoofs (Bull. Soc. chim. Belg., 1926, **35**, 121—129).—If a Marsh test solution containing nitric acid is added to the hydrogen generator it liberates nitric oxide, which may cause an explosion. E. W. Wignall.

Detection and determination of tin in toxicological cases. E. Deussen (Arch. Pharm., 1926, **264**, 360—362).—Chiefly a review. W. A. Silvester.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1926.

POLITECHN... SLĄSKIE...

General, Physical, and Inorganic Chemistry.

General rules of optical spectra. K. BECHERT and M. A. CATALÁN (Z. Physik, 1926, **37**, 658—666; Anal. Fís. Quim., 1926, **24**, 222—233).—A relationship is exhibited between the separation of terms of the same k-grouping in arc and spark spectra of elements in the same horizontal series of the periodic system. Deviations from the interval rule affect corresponding terms in the same manner. E. B. LUDLAM.

Standard wave-lengths for use in the extreme ultra-violet. S. SMITH and R. J. LANG (Physical Rev., 1926, [ii], **28**, 36—45).—The wave-lengths of a number of lines, chiefly of carbon, lying between 900 and 1600 Å., have been measured in the third and second orders, using a vacuum spectrograph with a concave grating of 6 ft. radius ruled with 30,000 lines to the inch (cf. this vol., 649). The dispersion was approximately 4·5 Å. per mm. The carbon lines and the iron standard lines used as comparisons were obtained simultaneously by passing a condensed spark discharge between a carbon and an iron electrode. Details are given of a new method of obtaining curves to correct for (*a*) deviation of the spectra from normality, and (*b*) error in the tilt of the photographic plate. A. B. MANNING.

Simple vacuum tube demonstrating the Döppler effect on the Balmer lines of hydrogen. G. NAKAMURA (Mem. Coll. Sci. Kyōtō, 1926, **9**, 303—304).—The cathode consists of a hollow cylindrical tube of aluminium in a side tube attached to the bulb of a flask with the anode at the top of the neck. The hydrogen was supplied by heating sodium in a small side tube. Photographs are reproduced which show the doubling of the Balmer lines very clearly. The exposure was about 10 min., using a Hilger wave-length spectrograph with camera lens about 21 inch focus. E. B. LUDLAM.

Structure in the secondary hydrogen spectrum. IV. O. W. RICHARDSON (Proc. Roy. Soc., 1926, **A, 111**, 714—753; cf. A., 1925, ii, 1013).—A more detailed examination of the spectrum of the first type discharge, in which the strength in the red consists almost entirely of hydrogen and Fulcher's lines, has shown that there are a number of other lines which belong to the same system as Fulcher's bands. A rearrangement of these lines is proposed. A. B. MANNING.

Secondary hydrogen spectrum. O. W. RICHARDSON (Nature, 1926, **118**, 116).—The green and red bands have the same electron jump, but correspond with different sets of vibrational transitions. Two other less well-developed sets of bands in the infra-red and three on the violet side of the green have the same electron jump. There is an intercombination between the lines of all these bands. The blue bands have a different electron jump; there are less well-developed bands on the violet side of these, for the frequencies of the successive lines of which a Rydberg formula is given (cf. preceding abstract). A. A. ELDRIDGE.

Infra-red secondary spectrum of hydrogen. T. E. ALLIBONE (Proc. Roy. Soc., 1926, **A, 112**, 196—212).—About 320 lines of wave-length greater than H_α have been observed in the above spectrum. Fulcher's first band has been extended into the infra-red in all seven series, and it is found that for the satisfactory representation of these lines formulæ of the type $\nu=A+Bm+Cm^2+Dm^3$ are required. Application of a transverse magnetic field broadens all the lines without any selective reduction in intensity, but it is not possible to distinguish two separate components of any line. R. CUTHILL.

Reversal of the hydrogen series in the extreme ultra-violet. T. LYMAN (Nature, 1926, **118**, 156—157).—With an improved technique the first four members, 1215·6, 1025·8, 972·5, and 949·7 Å., of the hydrogen series in the extreme ultra-violet have been obtained sharply reversed. The first two members have been obtained with helium containing a trace of hydrogen. A. A. ELDRIDGE.

Spectral observations under special conditions [of lithium]. H. W. J. DIK (Arch. Néerland., 1926, IIIA, **9**, 29—67).—Unsuccessful attempts have been made to excite the theoretically important spark spectrum of doubly-ionised lithium. The method employed by Paschen in obtaining the Fowler series of helium and the high-intensity discharge used by Goldstein in obtaining the "fundamental" spectra of metals have been adapted to the requirements of the work. A number of lines of uncertain origin obtained under various conditions are tabulated, but the Li II spectrum calculated from the Bohr–Sommerfeld theory was not observed. A number of doubtful air lines are classified as due to oxygen or nitrogen. The electrodeless discharge has been used with potassium vapour, and an intense spectrum free from arc lines obtained which is considered to be the spark spectrum of singly-ionised potassium. R. A. MORTON.

Spark spectrum of lithium. S. WERNER (Nature, 1926, **118**, 154—155).—Further spark lines of lithium having been found, a series scheme has now been established of the terms of the lithium spark spectrum which are analogous to the terms of the singulet spectrum of helium. This is denoted the Li II *p*-spectrum. The author has confirmed Schüler's observation that the Li II *o*-spectrum (analogous to the orthohelium spectrum) is not a doublet spectrum, but is probably a triplet spectrum of a distinctive type. The *p*-spectrum is considerably weaker than the *o*-spectrum, as is also the case for helium. The ionisation potential for the Li^+ ion is estimated to be about 70 volts. The lines 2934 and 3715 Å. appear not to belong to the series of the ordinary lithium spark spectrum; lines, apparently of the same character, have also been observed at 4607·4 and 2337·0 Å. A. A. ELDRIDGE.

Resonance of lithium vapour. A. BOGROS (Compt. rend., 1926, **183**, 124).—The proof that the first doublet of the principal series of the alkali metals constitutes the resonance ray is extended to lithium, using a method analogous to that of Dunoyer (*ibid.*, 1913, **157**, 1068). A stream of lithium atoms, produced by vaporising the lithium in a vacuum, is illuminated by a ray of light from a lithium flame. A Wratten filter cuts off all but the supposed resonance ray (6708 Å.). At 540°, a resonance effect not produced by white light is observed which increases as the temperature rises. J. GRANT.

Spectrometry of the *K*-series of light elements. *K*-Discontinuity of fluorine. M. HOLWECK (Compt. rend., 1926, **183**, 48—51; cf. this vol., 552).—The critical potential method has been applied to boron trifluoride. A discontinuity occurs at 684·2 volts, but there is no fine structure here, due to the absence of free valency of fluorine in boron trifluoride. The accuracy of the critical potential method is discussed and previous results obtained by this method are collated. L. F. GILBERT.

Spectrophotometric investigation of the visible light of the negative glow in neon and helium. C. HEINRICH (Ann. Physik, 1926, [iv], **80**, 349—366).—Measurements are given of the intensity variations of helium and neon lines in "glow lamps" with change in current density. S. BARRATT.

Spark spectra of neon. L. BLOCH, E. BLOCH, and G. DÉJARDIN (J. Phys. Radium, 1926, [vi], **7**, 203).—Errata to an earlier paper (this vol., 766).

Doublets of stripped atoms of the potassium type. R. C. GIBBS and H. E. WHITE (Proc. Nat. Acad. Sci., 1926, **12**, 448—451).—It has been found possible to extend the regular and irregular doublet laws of stripped atoms to the *N*-doublets for K I, Ca II, Sc III, Ti IV, and V V. J. S. CARTER.

Spark spectrum of potassium. T. L. DE BRUIN (Z. Physik, 1926, **38**, 94—103).—The spectrum was excited in a "pyrex" glass bulb with a quartz window, using an electrodeless discharge. Lines from 7699 to 2190 Å. were measured and grouped, and compared with the observations of other workers. A tenfold *P* term was found. The *P* terms have the same inner quantum number as those of neon and their differences follow the same law. E. B. LUDLAM.

Series spectra of the first long period. R. J. LANG (Nature, 1926, **118**, 119).—The regular and irregular doublet laws are applied to some lines of the high-potential spark spectrum of scandium, titanium, vanadium, and chromium, and the first members of the *P* doublets of Sc III, Ti IV, V V, and Cr VI are tabulated. The intensities of the pairs decrease in this order, and the shorter line of each pair is always the more intense. It is supposed that when the two electrons in the *N* levels are removed, some of the *M* electrons may move out to take their places. A. A. ELDRIDGE.

Arc spectrum of copper under diminished pressure. G. WOLFSOHN (Ann. Physik, 1926, [iv], **80**, 415—435).—The arc spectrum of copper has been studied in the region 2100—5200 Å., at normal, and under diminished pressure. The pressure shifts of the lines are tabulated, and improvements suggested in the classification of the copper spectrum. S. BARRATT.

Structure of bromine lines. T. HORI (Mem. Coll. Sci. Kyōtō, 1926, **9**, 307—312).—The bromine was contained in a discharge tube arranged for end-on observation and a large bulb was sealed to the middle portion of the capillary to maintain a sufficient supply of bromine; thus a life of two days for the tube was obtained. Photographs were taken, using an echelon grating of twenty plates. The lines are described as regards multiplicity and wave-length, and appear to belong to the arc, and not to the spark type. The separation of the components of the multiplets is given, but no attempt is made to establish theoretical relationships. E. B. LUDLAM.

Spectra of tin, lead, antimony, and bismuth in a magnetic field. P. A. VAN DER HARST (Arch. Néerland., 1925, IIIA, **9**, 1—28).—The Zeeman effect has been measured for 35 tin lines, 23 lead lines, 27 antimony lines, and 16 bismuth lines. The work of Purvis (Nature, 1907, **76**, 166) is in some respects discrepant owing to lack of precision and to an error in the intensity of the field. Relations between the decompositions of various lines which have been proposed by Kayser and Runge and others do not appear to be valid. The separations are fairly regularly distributed between values 1—1·5 times the normal results. A number of lines attributed to antimony by Schippers (A., 1912, ii, 877) are not confirmed. R. A. MORTON.

Atomic states and spectral terms. J. C. MCLENNAN, A. B. MCLAY, and H. G. SMITH (Proc. Roy. Soc., 1926, **A**, **112**, 76—94).—An account of the method of application of the theory of Heisenberg and Hund to the computation of the spectra of the elements from their atomic structure (cf. Fowler and Hartree, this vol., 650). The spectral term corresponding with the most stable electronic configuration of the atom of each element has been calculated. R. CUTHILL.

Structure of the arc spectrum of gold. J. C. McLennan and A. B. McLay (Proc. Roy. Soc., 1926, **A**, **112**, 95—110; cf. preceding abstract).—It has been found possible by means of the theory of Heisenberg and Hund to predict practically all the known terms in the above spectrum. Absorption measurements have been made in the quartz spectral region, both by the method of vapour absorption and by that of the spark under water, and a few new wave-lengths have been recorded. R. Cuthill.

Series spectra of palladium. J. C. McLennan and H. G. Smith (Proc. Roy. Soc., 1926, **A**, **112**, 110—128; cf. preceding abstract).—All the lines in the arc spectrum of palladium predicted for the prominent electronic configurations by the theory of Heisenberg and Hund have been found, and there are in addition a large number of faint lines of shorter wave-length, probably belonging to a secondary series system, for which no place can be found. Analysis of the spark spectrum has not been wholly satisfactory.
R. Cuthill.

Explosion spectra of mercury, copper, and iron. T. Hori (Mem. Coll. Sci. Kyōtō, 1926, **9**, 379—403).—See this vol., 652.

Continuous spectrum of mercury vapour in relation to the resonance line 2536·52. Lord Rayleigh (Proc. Roy. Soc., 1926, **A**, **111**, 456—461; cf. A., 1925, ii, 738).—The continuous spectrum emitted by glowing mercury vapour distilling from the arc ends near the resonance line 2536·52, with which it appears to be closely associated. The continuous spectrum can be produced without the resonance line by fluorescent excitation of fairly dense mercury vapour with the aluminium spark. Under these conditions, it is found to end at 2535·9, the resonance line and the band at 2540 appearing sharply reversed on the continuous background. By lowering the density of the vapour, the line 2536·52 and the band 2540 appear in emission. The continuous spectrum can also be obtained in absorption, the limit then being measured as 2535·5. A. B. Manning.

Self-reversal lines of lead in explosion spectrum and the series relations between them. B. Arakatsu (Mem. Coll. Sci. Kyōtō, 1926, **9**, 451—459).—The spectra obtained from the flash produced on short-circuiting a.-c. circuits through lead filaments are examined. The lines reversed at 100, 300, and 760 mm. pressure, respectively, are tabulated; no lines belonging to the $2p_1$ term could be reversed. The effect of pressure on the reversals is explained by the rapidity of the expansion of the ionised vapour.
S. K. Tweedy.

Spectrography of *X*-rays of large wave-length. A. Dauvillier (Compt. rend., 1926, **183**, 193—195).—Using the method previously described (this vol., 649), the ray $K\alpha_2$ for boron has been found at 73·5 Å. Neither sulphur nor phosphorus gives an $L\alpha$ ray, but iron, chromium, and copper do. The ray $M\alpha$ has not been found for zirconium, molybdenum, or barium, but tantalum and tungsten give very strong rays. Lines of the N and O series have been found for barium. All the K, L, M, and N spectra so far found in the spectral region under investigation reduce to a single line. R. Cuthill.

***X*-Rays—internal absorption and "spark" lines.** H. Robinson (Nature, 1926, **118**, 224).—Secondary cathode rays emerging from a "target" irradiated by *X*-rays were drawn out into a magnetic spectrum and their energies measured. The corpuscular spectra show many lines which are due to internal conversion of the fluorescent *X*-rays or, alternatively, to radiationless readjustments within the atom which lead to the expulsion of photo-electrons of the second kind. These electrons evidently come from atoms which were already ionised. Direct evidence has been obtained of the fundamental difference between internal and external absorption.
A. A. Eldridge.

Zeeman effect in the palladium spectrum. (Frl.) M. Levitski (Ann. Physik, 1926, [iv], **80**, 397—407).—The transverse Zeeman effects for the lines of the palladium arc and spark are tabulated. Two main classes of line are distinguished, one showing resolution into triplets (of complex structure), the other giving four components. S. Barratt.

Stark effect for the anode rays of lithium. A. Poirot (J. Phys. Radium, 1926, [vi], **7**, 217—224).—With an auxiliary electric field and by utilising anode rays of lithium in place of the usual canal rays, Stark effect measurements have been made for the line 4602 Å., the second line of the diffuse series, in fields 30—108 kilovolts/cm. In strong fields, the orange-red, luminous region becomes bluish-violet, the colour and the intensity depending on the direction of the luminous radiation. The distribution of the electric field in the experimental tube is consistent with the known conditions for the emission of anode rays. J. S. Carter.

Compton effect and quantum mechanics. G. Beck (Z. Physik, 1926, **38**, 144—148).—The Compton–Debye formula for the scattering of *X*-rays can be deduced directly from quantum mechanics; the agreement of that formula with experimental results is not in itself a proof of the particular light-quantum theory on which it is based.
E. B. Ludlam.

Light-period of atoms of alkali metals with and without a magnetic field. E. Rupp (Ann. Physik, 1926, [iv], **80**, 524—532).—Alkali metal canal rays have been excited by bombarding with electrons from a glowing wire an anode containing a salt. Lines in the subordinate series of lithium and the principal series line 404 μμ of potassium have been measured by means of photo-electric photometry. The light-period T (in 10^{-8} sec.) for H_β is 2·0, for K 404 μμ 2·9, and for Li 460, 427, 413 μμ 5·2. An outer magnetic field of 12,000 gauss vertical to the canal ray was found to have no marked effect on the value of α $(= 1/T)$ for H_β. R. A. Morton.

Duration of radiation excited in hydrogen by 10·2-volt electron impacts. F. G. Slack (Physical Rev., 1926, [ii], **28**, 1—12).—Hydrogen atoms were bombarded by electrons accelerated under a fluctuat-

ing potential produced by superposing an alternating potential of about 2 volts peak value on to a constant potential of 10·2 volts. During the positive half of the alternating cycle, the energy of the electrons was just sufficient to excite the atoms to the $2P$ state, resulting in the emission of the first line of the Lyman series. The alternating potential was applied in phase to a second pair of electrodes in the tube, forming a photo-electric system, and the current produced in the latter by the radiation was measured. At high frequencies of alternation, the radiation persists into the negative half cycle due to its finite rate of decay and results in a decrease of current in the electrometer. The calculated decrease of current, assuming that, starting at the instant of impact, the radiation falls off exponentially, agrees well with the observed decrease. The exponential constant was $0{\cdot}83\times10^{8}$ sec.$^{-1}$, whence, assuming no lag in the photo-electric effect, the average duration of the radiation was $1{\cdot}2\times10^{-8}$ sec. A. B. MANNING.

Electrical excitation of metal vapours in King's resistance furnace. H. SCHULER (Z. Physik, 1926, **37**, 728—731).—By using graphite tubes, a low-voltage discharge is obtainable through vapours such as those of iron and chromium at a temperature of 2000°. The spectra resemble arc spectra, but are of greater intensity and are sharper in consequence of the very low intensity of the electric field. The method is applicable to measurements of electron-impact excitation. E. B. LUDLAM.

Spectroscopic studies on the luminous vapour distilled from metallic arcs. LORD RAYLEIGH (Proc. Roy. Soc., 1926, **A**, **112**, 14—29; cf. A., 1925, ii, 738).—The absence from the arc spectrum of certain lines which appear in the spectrum of the vapour distilled from it appears to be due to the lines being so much broadened at the high concentrations prevailing in the arc that they overlap. It has been found possible to render luminous the vapour of a metal by means of a luminous jet of the vapour of another metal introduced into it. The excitation potential of the observed lines of the arc spectrum is usually less than the ionisation potential of the exciting metal, so that it seems as if the excitation is due to single collisions with ionised atoms of the latter metal.

R. CUTHILL.

Ionisation of mercury vapour as a function of the intensity of the exciting light. G. W. GIDDINGS and G. F. ROUSE (Proc. Nat. Acad. Sci., 1926, **12**, 447—448; cf. A., 1925, ii, 919).—Ionisation of mercury vapour is produced by light of wave-length 2536 Å. The ionisation current varies with the light intensity according to the relation $C_0/C_1=(I_0/I_1)^n$, where C_0 and C_1 are the initial and final ionisation currents and I_0 and I_1 the corresponding light intensities. The variation of n with vapour pressure and temperature has been investigated. At constant temperature (300°), the value of n increases from 2 to 3 when the vapour pressure is increased from 1 to 30 mm.; at constant vapour pressure (2 mm.), n increases from 2 to 2·3 when the temperature is raised from 170° to 350°. J. S. CARTER.

Electron affinity of hydrogen. J. KASARNOVSKI (Z. Physik, 1926, **38**, 12—21).—The electron affinity is calculated from the lattice energy of the alkali hydrides by a cyclic process involving also knowledge of the heat of formation, dissociation, and ionisation. The calculation of the lattice energy involves a knowledge of the repulsive forces in the crystal, obtainable from data on compressibility and density, and as the former are lacking for the hydrides, they are deduced by analogy. A negative hydrogen ion has an electron shell of two, like a helium atom; a positive lithium ion will have a similar two-electron shell. Comparison shows that the lattice energy of the hydrides of the alkalis and alkaline earths is nearly equal to that of the corresponding halides of like molecular volume and crystalline form. Thus calculated, the electron affinity of hydrogen is −22 Cal.; although only an approximation, this value is negative; it follows that hydrogen acquires an electron with absorption of energy. E. B. LUDLAM.

Ionisation potential of silver. G. PICCARDI (Atti R. Accad. Lincei, 1926, [vi], **3**, 489—490).—For the ionisation potential of silver the author finds values between 7·37 and 7·67 volts, the mean, 7·46 volts, being in good agreement with the value 7·54 given by Foote and Mohler (" The Origin of Spectra "). Shenstone's value, 6 volts (A., 1923, ii, 605), must be regarded as erroneous. T. H. POPE.

Critical voltages of radon. F. STRUWE (Z. Physik, 1926, **37**, 859—860; cf. this vol., 552).—The value 10 volts for the ionisation potential of radon obtained by Glockler (A., 1925, ii, 1105) as compared with 8·0 and 9·5 volts, is criticised; deductions from the atomic radius of radon which has been calculated from the diffusion coefficient are regarded as untrustworthy. E. B. LUDLAM.

Photo-electric emission from platinum as influenced by heating. L. A. WELO (Phil. Mag., 1926, [vii], **2**, 463—473).—A reply to Herrmann (A., 1925, ii, 947). The author has repeated his own earlier work (Phil. Mag., 1923, [vi], **45**, 593) and now finds that, in agreement with Herrmann's results, the photo-electric sensitiveness of platinum diminishes as the temperature to which it is previously subjected increases. The readiness with which this takes place, however, varies markedly with the sample of platinum employed. Scraping the insensitive surface appears to restore the sensitiveness to some extent. A certain minimum appearing at low temperatures in the curve showing photo-electric sensitiveness as a function of the heating current is probably not due to mercury vapour, as suggested by Herrmann (*loc. cit.*), since it may be avoided even in the presence of mercury and obtained when mercury is not there. The results obtained by adding gases such as oxygen and hydrogen, after out-gassing by heating, are in general agreement with the observations of Herrmann, but they also depend on the sample of platinum used.

M. S. BURR.

Distribution in space of the directions of emission of photo-electrons. P. AUGER and F. PERRIN (Compt. rend., 1926, **183**, 277—280).—The law deduced

by the authors (A., 1925, ii, 730) for the distribution of the directions of emission of photo-electrons from low-frequency X-rays depends on two conditions: (*a*) for an incident polarised wave, the probability of the departure of a photo-electron in an elementary cone depends only on the angle made by the cone with the electric vector of the wave; (*b*) the distribution of the revolution round the direction of propagation of the waves is obtained by superposing the distributions of the directions of emission of two waves having the same direction, frequency, and intensity, and polarised in perpendicular planes. These conditions are deduced from the classical wave theory, but probably apply also to quanta. For high-frequency radiations, the first condition has to be modified owing to the high speed of the incident quantum, and the formula obtained in this way is verified by experiments carried out by Wilson's method. J. GRANT.

Photo-ionisation of a gas by a discharge in the same gas. F. L. MOHLER (Physical Rev., 1926, [ii], **28**, 46—56).—Critical potentials of cæsium, potassium, argon, and neon have been determined by an application of the space-charge method for measuring the photo-ionisation produced in a gas by the radiation from a thermionic discharge in the same vacuum tube (cf. A., 1925, ii, 919; this vol., 217). Screening electrodes were interposed between the two thermionic units in the tube to prevent passage of electrons and ions from one side to the other. Relatively little photo-ionisation is produced by arc radiation, whilst spark excitation and soft X-radiation give a strong effect. The curves of photo-effect against discharge voltage show critical potentials which have been interpreted as follows. Ionisation of n_2 rare gas shell: Cs 13·0, K 19·0; spark excitation: Cs 18·5, K 21·6, A 32·2, Ne 48·0; double ionisation: Cs 21·5, K 31·8, A 34·8, Ne, 54·9; ionisation of n_1 rare gas shell: Cs 39·0, K 48·0, A 39·6; the Ne II spectrum is excited at 55 volts. The photo-electric emission from the electrodes was at least ten times as great as that from the gas, whilst the current change produced by the space charge effect was more than 2400 times the ion current in argon and cæsium.

A. B. MANNING.

Ion-rays. G. C. SCHMIDT (Ann. Physik, 1926, [iv], **80**, 588—608).—The emission of ions from salts heated at about 500° has been investigated. Sodium, potassium, cæsium, and silver chlorides, potassium, lithium, and silver bromides, sodium, potassium, and silver iodides, and potassium fluoride emit positive ions exclusively at temperatures up to 500°. Above this point, negative ions also occur, and at still higher temperatures the salts dissociate directly into two ions. The chlorides of lithium, barium, and lead emit both positive and negative ions with approximately the same readiness. The emission changes with time. An increase may occur rapidly; in all cases, a rapid fall for a short period is followed by a slower rate of decrease until equilibrium is reached. The experiments confirm the relationship established earlier (A., 1925, ii, 251) between electrolysis and emission of ions. At moderate temperatures, those salts in which only positive or only negative ions wander in electrolysis emit exclusively positive or negative ions, respectively. The more rapidly wandering ion is more readily emitted. A direct connexion is established between the emission of ions and the loosening tendency (A., 1922, ii, 623) of the crystal lattice. Similarly, the emission of ions from different salts varies with the proportion of ions existing in the fused salt. The initial increase in emission is traced to enrichment of the mass of salt in halogen owing to exclusive emission of positive ions. Large aggregates of halogen ions are formed which later dissociate. The decrease is ascribed to polarisation. The retained negative ions form an increasingly thick surface layer which attracts the liberated positive ions and retards their emission. The whole mechanism of the selective emission of ions seems to depend on the power possessed by halogen ions of forming complexes and of being thus held fast by the undecomposed salt molecules.

R. A. MORTON.

Equations for thermionic emission. P. FREEDMAN (Nature, 1926, **118**, 193—194).

Determination of the mobility of ions in gases. M. LAPORTE (Compt. rend., 1926, **183**, 119—121).—The author's method (this vol., 449, 553) is applied to the measurement of the distribution of ions of various mobilities in certain moist and dry gases. The distribution curves for positive ions in dry or wet air, nitrogen, and oxygen are identical, except that in wet oxygen the mobilities are slightly increased. For negative ions the curve for nitrogen differs from those for air and oxygen, which coincide, and this explains the strong and weak electronegative affinities of oxygen and nitrogen, respectively. Moisture diminishes the mobilities in air and oxygen and increases them in nitrogen. The negative ions in air are therefore those due to oxygen. In argon normal curves are obtained for positive ions, but inconstant values for negative ions, owing to changes in purity of the gas. J. GRANT.

Mobility of negative ions and ionisation currents in pure argon. M. LAPORTE and M. A. DA SILVA (Compt. rend., 1926, **183**, 287—289).—Curves are plotted showing the relation between the voltage applied to two parallel plates and the current passing across them in pure and impure argon and in air. The voltage required to produce the saturation current depends on the ionic mobility, and it is shown that for pure and impure argon and for air this takes place at 50, 264, and 1760 volts, respectively. Complete purification thus eliminates the ions of low mobility (cf. this vol., 553). The use of ionisation chambers containing pure argon is thus suggested for measuring ionisation where saturation may be obtained at low voltages. These properties of argon are in accord with its behaviour as an inert gas. J. GRANT.

Mobility of ions in air. III. Air containing organic vapours. A. M. TYNDALL and L. R. PHILLIPS (Proc. Roy. Soc., 1926, **A**, **111**, 577—591; cf. this vol., 219).—The method of determining mobility previously described has been used to study the mobility of ions formed in air containing organic vapours (aliphatic alcohols, chloroform, carbon tetrachloride, etc.) at concentrations ranging up to

saturation. In every case, a reduction in mobility is observed on addition of the vapour. The mobility–vapour pressure curves for the negative ion show a steep gradient at low concentrations, which becomes less as the concentration increases. For the homologous series of aliphatic alcohols, the steepness increases with the mol. wt. of the vapour. Similar effects are observed with the positive ion, but the initial drop in mobility is much less marked. The results are discussed from the point of view of the "cluster" theory of gaseous ionic structure, and it is suggested that the relative effects of the various vapours depend on (*a*) a "clustering coefficient" determined by the combined effect of any permanent electric moment and an induced electric moment in the neutral molecule, and (*b*) the "effective diameter" of the cluster. The results accord with this view. The theory is further confirmed by the fact that the addition of saturated water vapour to air saturated with amyl alcohol raises the mobility, this being due to the replacement of some alcohol molecules in the cluster by water molecules. A. B. MANNING.

Influence of chlorine on the mobility of ions in pure oxygen. H. MAYER (Physikal. Z., 1926, **27**, 513—518).—The mobility of positive and negative ions in pure dry oxygen has been determined with and without the presence of chlorine by an alternating field method. For pure dry oxygen, the mean values $k_{pos.}$=1·38 cm./sec. volt/cm. and $k_{neg.}$=2·05 cm./sec. volt/cm. were obtained. $k_{pos.}$ falls gradually to 1·22 at 3—4% of chlorine, and $k_{neg.}$ to 1·38 with 1% of chlorine, and to 1·08 with 4·5% of chlorine. For pure chlorine at 80 mm. pressure, the mobility of the negative ion is smaller (about 0·5 cm./sec. volt/cm.) than that of the positive ion. The ratio $k_{pos.}$: $k_{neg.}$ is about 1·22. The relatively small mobilities are better explained by the cluster (complex ion) theory than by the alternative theory of electrical forces between simple ions. R. A. MORTON.

Quantum theory and the behaviour of slow electrons in gases. F. ZWICKY (Proc. Nat. Acad. Sci., 1926, **12**, 461—466; cf. Physikal. Z., 1923, **24**, 171).—The deviations from rectilinear motion which electrons undergo in the force-fields of atoms are considered. A formula representing the deflexion angle as a function of the potential and kinetic energies of the electron and of a resonance is given, the mathematical theory being promised later. Application of this formula to simple atomic models shows that it is capable of explaining the various types of effective area (absorption coefficient)–electron velocity curves obtained with various gases and vapours (Ramsauer, A., 1923, ii, 529, 749; Brode, *ibid.*, 1925, ii, 617, 1020). J. S. CARTER.

Transfer of energy from electrons to atoms. F. ZWICKY (Proc. Nat. Acad. Sci., 1926, **12**, 466—470; cf. preceding abstract).—Mathematical. The energy transferred to an atom by a passing electron is considered on the basis of the perturbation theory. It is shown that the calculated energy transfer is in complete contradiction to the experimental facts. J. S. CARTER.

Transference of energy in collisions between electrons. J. S. TOWNSEND and C. M. FOCKEN (Phil. Mag., 1926, [vii], **2**, 474—495).—The application of the theory of the transference of energy in quanta to explain the increase in electrical conductivity of a gas with increase in potential, when this is less than 100 volts, is discussed, and, in the form usually employed, which involves the supposed existence of large photo-electric effects resulting from the radiation from molecules, is found to be untenable. Previous experiments with neon and helium to determine the relative importance of the photo-electric effect and the effect of ionisation by collision (Townsend and McCallum, A., 1924, ii, 375; McCallum and Focken, *ibid.*, 1925, ii, 641) have been repeated with simpler apparatus giving a more direct comparison. A definite increase in current due to ionisation by collision may be obtained with potentials as low as 21 and 17 volts in helium and neon, respectively, the upper limit in each case of the ionising potential. The increase of current attributable to a photo-electric effect is relatively small. This confirms previous results. M. S. BURR.

Mechanism of conduction of electric current in metals. N. S. NASAROV (Physikal. Z., 1926, **27**, 455—458; cf. Höjendahl, A., 1924, ii, 647).—Theoretical. On the assumption that the conduction of the current in metals occurs through the agency of the valency electrons, which absorb electrical energy and then pass from atom to atom, the conductivities of the metals of the first group of the periodic classification have been calculated. The values obtained are much greater than the experimental values at the ordinary temperature, but at low temperatures the agreement is better. Increase of the thermal agitation of the atoms will make the passage of electrons between them more difficult, and from this consideration a relation between the conductivity and temperature similar to those proposed by Thomson and by Lorentz has been derived. If two metals are present together, the one with the higher nuclear charge will tend to take electrons from the other and form a system which ceases to transmit energy, thus increasing the resistance by an amount which is independent of the temperature. R. CUTHILL.

Structure of the atomic magnet. Its normal position in relation to the lattice and the permanent magnetisation. R. FORRER (Compt. rend., 1926, **183**, 121—123).—From the author's experimental results for iron and nickel (*ibid.*, **182**, 1530; this vol., 670) it is concluded that for single crystals it suffices to know the orientation of the crystal lattice with respect to the field in order to deduce the permanent magnetisation. Where a metal is composed of a number of small crystals having different orientations, the magnitude of the permanent magnetisation can be used to decide between the possible normal positions of the resultant of the constituents of the magnetic multiplet. For the magnetic doublet of nickel, the resultant may be parallel to the binary or quaternary axes of the crystal. The magnetic triplet of iron can exist in a symmetrical

and an unsymmetrical form, depending on the purity and mechanical treatment of the metal.

J. GRANT.

Atomic weight and isotope-ratio of silicon. F. M. JAEGER (Z. Elektrochem., 1926, **32**, 328—330).—Measurements of the density of tetraethylsilicane prepared from specimens of silica from various parts of the world and of meteoric origin yield values of d^{20} (0·76735±0·00005) which are approximately the same in all cases. There is therefore no detectable variation in the isotope-ratio. J. S. CARTER.

Radioactive and non-radioactive isotopes. T. HORI (Mem. Coll. Sci. Kyōtō, 1926, **9**, 371—378).—With the aid of several assumptions, the known isotopes are arranged in a series which is a continuation of the ordinary radioactive series. Isotopes of atomic masses $4n+2$ and $4n$ belong to the uranium and thorium series, respectively; those of atomic masses $4n+1$ and $4n+3$ to the actinium series. The arrangement in radioactive series does not necessarily imply that the common isotopes are disintegration products of elements of higher atomic weight. The existence of several isotopes is predicted. The assumptions do not hold entirely for elements below copper; the possible reasons for this are discussed.

S. K. TWEEDY.

Effect of the sun on the radioactivities of polonium and lead. (MLLE.) S. MARACINEANU (Compt. rend., 1926, **183**, 345—347).—Experiments on the effect of the sun on radioactive elements (A., 1925, ii, 348) are extended to polonium. A drop of a solution of polonium emitting only α-particles placed on a lead sheet 0·1 mm. thick produces from the opposite face of the lead a gradually increasing ionisation current, which attains a maximum after 25 days. If the solution is dried in the sun, the current increases more rapidly and attains a higher maximum value. In both cases, it falls off at the same rate. The effects produced on a zinc sulphide screen are of the same order. The phenomenon is not due to penetration of the lead by the polonium, and the ionisation curves agree with those obtained theoretically for the production of polonium from radium-*E*, except for a slight difference due to the radioactivity of the lead. It is suggested that the effect of the sun may be to produce a reversibility in the radioactive series by the production of radium-*E* from polonium. J. GRANT.

Polonium. J. ESCHER-DESRIVIÈRES (Ann. Chim., 1926, [x], **5**, 251—313).—To distinguish between the effects of adsorption and solid solution, determinations have been made of the proportion of polonium present in a solution which appears in various precipitates formed therein, the results being recorded in the form of partition coefficients between solid phase and mother-liquor, such coefficients being found to be approximately independent of the amount of polonium present.

When metals such as bismuth, copper, and mercury are precipitated as sulphides in acid solution, all the polonium present appears in the precipitate. A similar result is observed in the precipitation of bismuth and ferric hydroxides, but if excess of sodium hydroxide be present, a certain minimum amount of the precipitate must be produced before the removal of polonium is complete. On the other hand, precipitation of silver chloride or lead sulphate in acid solutions never removes the whole of the polonium, the amount so precipitated being in general less than one quarter of the whole. Figures are recorded showing the influence of a varying excess of hydrochloric acid or sodium hydroxide on the proportion of polonium precipitated with silver chloride or the hydroxides of bismuth and iron, respectively. The diminishing separation of polonium on the solid phase with increasing concentrations of hydroxyl ion is closely paralleled by the variation of the adsorption of polonium by animal charcoal from solutions containing increasing concentrations of alkali.

The results are discussed from the point of view of Fajans' theory. Precipitation with another element owing to chemical analogy with it may be distinguished from mere adsorption by the presence of the former element in the interior of the grains of precipitate. Confirmation of the view that polonium is only adsorbed on bismuth and ferric hydroxides is provided by the observation that the polonium can in this case be partly dissolved away by washing with solutions of sodium hydroxide.

Quantitative expressions are developed for the amounts of polonium precipitated in solid solution and also adsorbed, and their applicability is verified in the case of precipitation with bismuth, copper, gold, and tellurium sulphides from acid solutions. A method is thus provided which permits of the more accurate determination of the true chemistry of an element present in imponderable quantities.

Although polonium forms a sulphide analogous to that of bismuth, it is sharply differentiated from this element in its hydroxide. Polonium hydroxide is soluble in sodium hydroxide solutions, and electrolysis shows the polonium to be present as an anion; it is thus closely allied to tellurium. Precipitation with silver chloride is merely an adsorption effect.

G. M. BENNETT.

Stopping-power of some metals for α-particles. J. CONSIGNY (Compt. rend., 1926, **183**, 127—129).—Bragg's original law that the stopping-powers of metals are proportional to the square roots of their atomic weights does not take account of the speed of the incident α-particles. The mean stopping-powers of aluminium, copper, silver, and gold for α-particles having speeds of from $1·59\times10^9$ to $1·09\times10^9$ cm./sec. have been determined, and their logarithms plotted against those of the atomic numbers and weights. Straight lines are obtained, with angles of slope $\tan^{-1}0·552$ and 0·5, respectively. J. GRANT.

Retardation of α-particles by matter. S. ROSENBLUM (Compt. rend., 1926, **183**, 198—200).—The retardation of the α-particles from the active deposit of thorium produced by mica, aluminium, copper, silver, tin, gold, platinum, and lead has been determined by measuring the magnetic deviation (A., 1925, ii, 463). Except for platinum, the mass per unit area which reduces the speed of the particles

by the same fraction is a linear function of the atomic number, although this is probably not true for elements of low atomic number. R. CUTHILL.

Scattering of α-particles through small angles. D. C. ROSE (Proc. Roy. Soc., 1926, **A**, **111**, 677—690).—The single scattering of α-particles by gold foil through angles from 1·2° to more than 8° has been measured. The scattering curves indicate that the nuclear field obeys the inverse square law for distances from $0{\cdot}4\times10^{-10}$ to $1{\cdot}7\times10^{-10}$ cm. from the nucleus. These distances include the radius of the K shell of electrons for gold, but the results are not accurate enough to detect any shielding effect due to the K shell. The curves indicate, however, that the K shell is not ionised to any appreciable extent. Wentzel's criterion for single scattering (Ann. Physik, 1922, [iv], **69**, 335) has been made more precise. A. B. MANNING.

Anomalous scattering of α-particles. E. GUTH (Physikal. Z., 1926, **27**, 507—509; cf. this vol., 450).—The sub-normal scattering of α-particles by magnesium and aluminium has not been observed for the heavier metals. The phenomenon is, however, regarded as a general one, and it is assumed that the variation of scattering with the velocity of the α-particles and the scattering angle follows a qualitatively similar, anomalous course for all elements. This leads to the conception of conditions for sub-normal, normal, and super-normal scattering for all elements. Blackett's experiments on nitrogen–α-particle collisions are shown to support this view, and the bearing of the work on the mechanism of atomic disintegration is discussed. R. A. MORTON.

Absorption of β-particles by matter. G. FOURNIER (Compt. rend., 1926, **183**, 37—39; cf. A., 1925, ii, 622).—The type of equation used in connexion with the absorption of the β-radiation from radium-E is also valid for the absorption of the β-radiation from uranium-X by carbon, aluminium, copper, zinc, silver, and gold. It is now considered that dispersion, and not the existence of a radiation more easily absorbed than the principal radiation, is responsible for the complications previously observed, which occur also with uranium-X. A new method of studying absorption by powdered substances is described, and has been employed in an investigation of the absorption of the β-radiation from radium-E by a number of elements and compounds, of which sulphur alone does not follow the linear law. L. F. GILBERT.

Absorption of β-particles by matter. G. FOURNIER (Compt. rend., 1926, **183**, 200—203; cf. preceding abstract).—The absorption of β-rays by solid and liquid compounds and solutions has been examined. The absorption coefficients, μ/ρ, of many compounds are related to those of their constituent elements by the mixture rule, but for solutions, substances containing water of crystallisation, water, and certain other compounds the observed coefficients are greater than those calculated in this way. R. CUTHILL.

Investigation of the primary and secondary β-radiation from radium by the absorption method. (MME.) J. S. LATTÈS (Ann. Physique, 1926, [x], **6**, 102—182).—A method is described for the analysis of the complex β- and γ-radiation of radium. Using lead as absorbent, four principal groups of primary γ-rays, three of primary β-rays, and three of secondary β-rays were observed. The analysis was also made using gold, platinum (cf. A., 1925, ii, 465), silver, aluminium, and carbon. The mass coefficient of absorption μ/ρ for the primary β-rays, where μ is the ordinary absorption coefficient and ρ the density of the absorbent, is connected with the atomic number N of the absorbent by Fournier's relation $\mu/\rho=a+bN$, where a and b are constants for the same principal group (*ibid.*, 176, 622). An expression for the relationship between the secondary β-radiation and the γ-radiation producing it is developed theoretically and appears to be justified experimentally. The quantity of the secondary β-radiation varies with the absorbing substance; the quality depends only on the wave-length of the exciting γ-radiation. The various coefficients of transformation of the secondary β-rays included in the theoretical expression have been calculated. The radiations exerting a destructive action on living tissue are probably for the most part corpuscular, being the secondary radiations when γ- and X-rays are employed. There appears to be no definite limit to the wave-length of the γ-rays necessary to produce necrosis, provided the amount absorbed is sufficient. The biological and therapeutic significance of the work is discussed, especially with reference to the methods of filtration employed in radio-therapy. M. S. BURR.

Laws of scattering of canal-rays in their passage through solid bodies. E. HOMMA (Ann. Physik, 1926, [iv], **80**, 609—620).—The scattering of homogeneous canal-rays of hydrogen by gold leaf has been investigated. The most probable angle of deflexion is inversely proportional to the third power of the velocity of the canal-ray. For different thicknesses d of foil, the probable angle increases approximately as $d^{3/2}$. These laws are in good agreement with the laws governing multiple scattering of α-particles. Presumably multiple scattering obtains for the hydrogen particle traversing metal foil (cf. A., 1922, ii, 12). R. A. MORTON.

Existence of the sub-electron. J. MATTAUCH (Z. Physik, 1926, **37**, 803—815).—From an examination of the data the author concludes that they do not support the hypothesis of a sub-electron. E. B. LUDLAM.

Existence of the sub-electron. F. EHRENHAFT (Z. Physik, 1926, **37**, 816—819; cf. preceding abstract).—The author regards Mattauch's conclusions as incorrect and founded on a selection of only a portion of the available data. E. B. LUDLAM.

Models of the helium atom. U. CRUDELI (Atti R. Accad. Lincei, 1926, [vi], **3**, 666—672).—Further consideration of the hypothesis previously advanced (Rend. R. Accad. Lincei, 1924, ii, 242). T. H. POPE.

Constitution of the atoms scandium to nickel. R. SAMUEL and E. MARKOWICZ (Z. Physik, 1926, **38**, 22—32).—The analogy between the valencies and paramagnetism of the ions is studied and a scheme of sub-grouping of the electrons worked out. The 3_3 sub-group is sub-divided into two groups. If all the 3_3 electrons were interchangeable, there would be greater similarity between the tervalent ions of an element and the bivalent ions of the preceding element, such as exists between beryllium and aluminium, lithium and magnesium, etc. E. B. LUDLAM.

Spinning electrons. I. I. RABI (Nature, 1926, **118**, 228).—Unless in solid copper and silver these elements exist in a form very different from their normal atomic state, and unless the number of free electrons does not exceed 3% of the total number of atoms, the hypothesis of the spinning electron leads to difficulties in understanding the diamagnetism of these metals and of the alkali metals. Any considerable contribution by the spinning free electrons to the susceptibility should result in a temperature variation in the total diamagnetic susceptibility of a much higher order than that experimentally found.
A. A. ELDRIDGE.

Electromagnetic mass and momentum of a spinning electron. G. BREIT (Proc. Nat. Acad. Sci., 1926, **12**, 451—461).—A mathematical treatment of the spinning electron based on considerations of a simple model. It is shown that the calculated radius, angular momentum, peripheral speed, and attractive and repulsive forces between the "northern" and "southern" hemispheres are not of inconceivable orders of magnitude. Although the model is imperfect, the agreement in the order of magnitude of various effects suggests that the spinning electron has a deeper significance than its spectroscopic utility (Uhlenbeck and Goudsmit, this vol., 215; Bichowsky and Urey, *ibid.*, 447). Furthermore, the nature of the results suggests that Planck's constant, the electronic mass and charge, and the velocity of light have not accidental values, but must be definitely connected.
J. S. CARTER.

Difficulty in the theory of the rotating electron. G. WENTZEL (Z. Physik, 1926, **37**, 911—914).—The screening effect for the X-ray spectra is calculated on the assumption that the rotating electron possesses a magnetic moment and the result is a value more than 50% greater than that obtained by measurement of the doublets. E. B. LUDLAM.

Perihelion rotation of the orbit of the radiating electron in hydrogen-unlike atoms. B. WALTER (Z. Physik, 1926, **38**, 33—34).—A simplified form of the equation for the rotation of the orbit is given: $\Delta\varphi=2\pi C_1/k^2$, where k is the azimuthal quantum number and $C_1=c_1/a_1$, c_1 being a constant representing the interaction between the radiating electron and the others, and a_1 the radius of the first Bohr orbit of hydrogen. The rotation is dependent only on k, and is the same for all ellipses of the same k type. The equation is applicable only to orbits which do not penetrate into the interior of the atom.
E. B. LUDLAM.

Action of radiation on free electrons. E. O. HULBERT (J. Franklin Inst., 1926, **202**, 51—60).—Expressions are derived both from the classical theory and from the quantum theory for the effect of radiation on an electron stream in terms of the change in momentum. If the classical and quantum expressions become identical for the longer wave-lengths, the diameter of the quantum, it is shown, must be about one tenth of that of the electron. For wave-lengths less than 0·01 Å., the quantum expression predicts less total momentum transferred to the electrons than does the classical theory. The negative results obtained by H. A. Wilson and by Lapp for the effect of radiation on an electron stream would be expected from the quantum expression, whilst the number of collisions observed by C. T. R. Wilson in the cloud-drop experiment is consistent with the calculated value. C. J. SMITHELLS.

Intra-atomic condensation of matter. V. A. PLOTNIKOV (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 213—222).—A discussion of the law of whole numbers, the condensation of the atomic nucleus, the heat of radioactive disintegration, elements with atomic weights multiples of four, generation of energy by the artificial decomposition of atoms, loss of mass on radioactive disintegration, and the structure of proton. T. H. POPE.

Probable action of matter on radiation quanta. F. WOLFERS (Compt. rend., 1926, **183**, 276—277).

Frequency of atomic vibrations. H. SIRK (Z. Physik, 1926, **37**, 926; cf. *ibid.*, 1925, **33**, 894).—In answer to Rawlins (*ibid.*, 1926, **36**, 400), who directed attention to the importance of work on the physical constants of elements of very low m. p., the author points out that the experimental data necessary for the application of his formula are lacking. E. B. LUDLAM.

Simple derivation of the Planck–Einstein formula. M. KATAYAMA (Bull. Chem. Soc. Japan, 1926, **1**, 3—5).—A brief derivation of the Planck–Einstein equation for the mean energy of an atom in a monatomic solid is given, based on the assumption that the equilibrium between atoms having different quanta of energy can be treated as a special case of chemical equilibrium. S. BARRATT.

Characteristic vibration spectra of diatomic molecules, and wave mechanics. E. FUES (Ann. Physik, 1926, [iv], **80**, 367—396).

Secondary spectrum of hydrogen and the occurrence of H_3^+. H. D. SMYTH and C. J. BRASEFIELD (Proc. Nat. Acad. Sci., 1926, **12**, 443—447).—Since positive-ray analysis of the products of ionisation in hydrogen shows that under certain conditions H_3^+ ions are more numerous than H_2^+ ions (A., 1925, ii, 459; Hogness and Lunn, *ibid.*, 839), an attempt has been made to determine whether or not any part of the secondary spectrum is due to H_3^+. The direct method depending on the observation of the spectrum of a homogeneous beam of H_3^+ ions passing into an electron atmosphere yields no results, the light produced being too small to be photographed.

A method consisting of the correlation of spectroscopic and positive-ion concentration measurements in a glow discharge in hydrogen furnishes, however, evidence leading to the conclusion that the conditions which favour the production of H_3^+ favour the excitation of the Fulcher bands, particularly those in the red. It is, however, emphasised that the method is suggestive rather than conclusive. J. S. CARTER.

Configuration of the carbon dioxide molecule. A. EUCKEN (Z. Physik, 1926, **37**, 714—721).—The argument of Schaefer and Philipps in favour of a triangular shape for the molecule of gaseous carbon dioxide (this vol., 556, 658) is based on the measurements of the band spectrum in the infra-red. The author suggests a different interpretation of the spectrum which is possible on the assumption of a molecule with the carbon and oxygen atoms in the same straight line. In favour of the latter view is the *X*-ray spectrograph of solid carbon dioxide and the specific heat of the gas. On the other hand, carbon dioxide is supposed to possess an electric moment, although it is very small; its existence is a deduction from the temperature coefficient of the dielectric constant, involving a possible experimental error and a formula not rigidly applicable.

E. B. LUDLAM.

Absorption spectrum of carbon dioxide and the structure of the molecule. D. M. DENNISON (Z. Physik, 1926, **38**, 137—140; cf. this vol., 222, and preceding abstract).—Discussion of the infra-red absorption spectrum and its interpretation in terms of the moments of inertia of the molecule.

E. B. LUDLAM.

Ultra-violet absorption spectra and photochemical decomposition of gaseous hydrogen bromide and iodide. H. C. TINGEY and R. H. GERKE (J. Amer. Chem. Soc., 1926, **48**, 1838—1850).—The ultra-violet absorption spectra of hydrogen bromide and iodide are continuous; this is to be expected if the photo-chemical decomposition of these gases follows the mechanism suggested by Warburg (Sitz. Preuss. Akad. Wiss. Berlin, 1916, 314; 1918, 300), but not if the mechanism of Stern and Volmer is followed (A., 1920, ii, 461). The long-wave absorption limit is 2640 for hydrogen bromide and 3320 Å. for hydrogen iodide. Attempts to obtain an emission spectrum of hydrogen bromide and to detect photoelectric conductivity in the gas failed.

S. K. TWEEDY.

Dissociation of potassium iodide and the absorption spectra of iodine and potassium iodide. W. R. BRODE (J. Amer. Chem. Soc., 1926, **48**, 1877—1882).—The absorption spectra of iodine in alcohol, carbon tetrachloride, and aqueous potassium iodide solutions are recorded. The absorption spectrum of potassium iodide solution exhibits a satellite band which disappears when sodium thiosulphate is present. This band, which has the same frequency as the first band of iodine in aqueous potassium iodide solution, is shown to be due to the presence of free iodine. Exactly similar results are obtained with potassium bromide solutions. Iodine in carbon tetrachloride exhibits a spectrum similar to that of iodine vapour; such a solution is proposed for screening visible from ultra-violet light. A solution effect is apparent in the alcoholic and potassium iodide solutions. S. K. TWEEDY.

Band spectra of halogens. I. Absorption of iodine vapour. II. Analysis of the band spectrum of iodine, bromine, and chlorine. G. NAKAMURA (Mem. Coll. Sci. Kyōtō, 1926, **9**, 315—334, 335—369).—I. The effect of high temperature and addition of foreign gases on the individual lines of the absorption spectrum was studied using a grating spectrograph giving a dispersion of about 0·75 Å./mm. Raising the temperature increased the absorption in the red; this is explained as being due to activation or partial dissociation of the molecule. Absorption lines exist until practically the whole of the iodine vapour is dissociated, at variance with the results of Evans, who found that they disappeared when more than 80% had been dissociated, the reason being that he used small dispersion and was unable to resolve the lines which are diffuse at such high temperatures. The difference between the action of inert and chemically active gases is only slight, and is similar to that of iodine vapour itself. The effect is of two kinds, one of which is destructive of certain lines at low temperatures, but at higher temperatures these lines reappear; the other is a general blurring effect on some lines. The lines which are strengthened by raising the temperature in pure iodine vapour are the ones suppressed by the presence of foreign gas.

II. For iodine, a series of diffuse bands was measured in the extreme red and expressed by means of a formula of the Deslandres type. They are not covered by an extension of Mecke's formula. When, however, the vapour was heated at 1100°, some thirty bands appeared in addition to those measured by Mecke, but expressed by an extension of his formula. For bromine, about 180 heads of absorption bands were measured and grouped in sixteen series for which Deslandres' formulæ were calculated. At high temperature, several stronger absorption bands appeared at the red end which were absent at the ordinary temperature, but there was found to be an extension of one of the series observable in the cold. The emission bands were compared with those of absorption, and were not complementary. In the case of chlorine, tubes of various lengths up to 12·6 metres were used, seventy edges were measured from 480 to 576 μμ and grouped into four series. At 820°, new bands appeared in the yellow region, some of which formed a new series, others were an extension of the fourth series. The emission spectrum of chlorine shows a clear series from 474·8 to 448·2 μμ. Haziness in some of the bromine bands and waviness in some of those in heated chlorine are attributed to the presence of isotopes. E. B. LUDLAM.

Absorption spectra of some hydride compounds in the ultra-violet. E. HULTHÈN and R. V. ZUMSTEIN (Physical Rev., 1926, [ii], **28**, 13—24; cf. A., 1925, ii, 453; this vol., 107).—The absorption spectra of copper, silver, gold, and aluminium hydrides have been obtained by heating the vapour

of the metal at about 1700° in a carbon tube through which a slow current of hydrogen was passing. Attempts to obtain the absorption spectra of the hydrides of cadmium, calcium, boron, thallium, carbon, nitrogen, lead, and tin under similar conditions failed. The four bands found for copper hydride confirm the analysis of Frerichs (A., 1924, ii, 77). The eight bands of silver hydride have been arranged to show the n_1n_2 scheme. The five gold hydride bands, of which those at 3298·1 and 3170·0 are new, confirm and extend the work of Bengtsson (A., 1925, ii, 166). Three other new bands at 2773·9, 2612·3, and 2511·7 indicate a new excited electronic level of the AuH molecule. Three aluminium hydride bands were absorbed (cf. this vol., 107, 334). The OH absorption bands at 3064 and 2852 were observed on nearly all the plates. Some bands were found which may have been due to the oxides of calcium and silver. A. B. MANNING.

Optical and chemical investigation of solutions of alkali halides and halogen acids. A. HANTZSCH (Ber., 1926, **59**, [*B*], 1096—1119).—The alkali halides differ in optical and chemical behaviour from the other alkali salts. In contrast with the homogeneous acids of which the absorption increases with acidity in the sequence HCl < HBr < HI, the alkali salts are all transparent in the solid state and differ optically in aqueous solution, in which absorption increases in the order of the acidity of their acids, XCl < XBr < XI; this absorption is much weaker than that of the corresponding acids. The absorption of solutions of chlorides, like that of hydrochloric acid, is so feeble that it cannot be determined, whereas the bromides and iodides are identical with solutions of hydrogen bromide or iodide at moderate dilution. The optical identity of solutions of acids and their salts is due chemically to the conversion of the homopolar compound into the hydroxonium salt, $X[H_3O]$, whereas the transparent heteropolar salts suffer conversion of the halogen ions which are non-absorbent in the solid state into the absorbing aquo-ions. The effect of the water is discussed in some detail.

The strong selective absorption of the nitrate ion and of molten mixtures of alkali nitrates is very little altered by hydration. The optical anomaly of the halides corresponds with their chemical position in "neutral salt" action, since the alkali chlorides, bromides, and iodides reinforce the so-called catalytic actions of hydrogen chloride, bromide, and iodide by their dehydrating effect to an extent which is much greater than that of all other salts towards their corresponding acids. They are actually the only salts which accelerate this action in the hydrolysis of esters, since perchlorates, nitrates, and sulphates behave in this case as negative catalysts. In the last reaction, the activity of the halogen acids is in the sequence HI < HBr < HCl, this being the reverse of the order in processes depending on the intermediate formation of ammonium or oxonium salts; this is due to the production during ester catalysis of homopolar additive products resembling orthocarbonic acid in place of salts.

The existence of definite hydrates as the main components of hydrated solution equilibria of alkali halides is rendered probable by the occurrence of maxima of specific conductivity when 4, 6, or 8 mols. of water are present for each mol. of salt. In hydrochloric acid, $HCl,4H_2O$, all the water is chemically united (as in the cryoscopically-established compound, $HBr,4H_2O$), since only traces of sodium chloride are soluble in acid of this concentration. Hydrochloric acid, b. p. 110°/760 mm., contains as main component a salt-like octohydrate, $Cl(H_2O)_8H$, corresponding with the salt hydrates, $Br,I(H_2O)_8Na$. Such formulæ of the octohydrates are suggested as permit an explanation of the nearly equal velocity of migration of the chlorine, bromine, and iodine ions. The probability that the halogen ions in aqueous solution function as central atoms of co-ordination number 4, and hence combine with 4 mols. of water in the first sphere to yield tetra-aquo-ions, $[X(H_2O)_4]$, of almost equal mobility, is supported by the observation that hydrochloric, hydrobromic, and hydriodic acids in moderately dilute solution are of the same strength and conduct as well chemically as perchloric acid, the aquo-ions of which contain four oxygen atoms. H. WREN.

Absorption spectra of salt solutions of some rare-earth elements. T. INOUE (Bull. Chem. Soc. Japan, 1926, **1**, 9—13).—In addition to the bands in the visible, absorption bands are recorded in the ultra-violet for the following solutions: cerous chloride at 3350 and 2469, samarium chloride at 2600, and erbium chloride at 2470 Å. It is suggested that the concentration of certain rare-earth salts in solution may be determined by observing the minimum thickness of solution with which a characteristic absorption band can be detected. S. BARRATT.

Band series in infra-red absorption spectra of organic compounds. II. J. W. ELLIS (Physical Rev., 1926, [ii], **28**, 25—35; cf. this vol., 454).—The absorption bands in the infra-red spectra of methyl iodide, methylene chloride, methylene bromide, methylene iodide, chloroform, and bromoform have been analysed. In addition to the C–H bands previously described, a number of bands are accounted for on the basis of linear C–Cl, C–Br, and C–I series, starting at 16·8, 17·2, and 17·5 μ, respectively, and by simple additive combinations between these frequencies and those of the C–H series. Carbon tetrachloride and tetrachloroethylene behave anomalously, the corresponding bands, which should be well developed in these compounds, being very weak or absent altogether. An interpretation of the results in the light of the quantum theory leads to the conclusion that in the type of linking considered the iodine atom is held by the carbon atom more firmly than the chlorine or bromine atoms.
A. B. MANNING.

New type of absorption spectrum. Double rotational quantification in formaldehyde. W. HENRI and S. A. SCHOU (Nature, 1926, **118**, 225).—The ultra-violet absorption spectrum of formaldehyde vapour corresponds with a new type of rotational spectrum, with two quantifications. It consists of 32 bands between 3550 and 2500 Å., formed by numerous fine lines which are referred to two types,

the stronger lines being produced by rotation about the axis of symmetry passing through the carbon and oxygen atoms, with the smaller moment of inertia J_0, and the closely-grouped fine lines corresponding with rotations about a perpendicular axis with the moment $K_0(=L_0)$. The distance between the hydrogen atoms in the normal molecule is computed to be 1·30 Å., and between the carbon and oxygen atoms 1·0±0·1 Å. In the activated molecule, the distance between the hydrogen atoms is 1·37 Å. Similar results have been obtained for other "Y-molecules," *e.g.*, carbonyl chloride and thiocarbonyl chloride. A. A. ELDRIDGE.

Optical properties of isomeric ethylenic compounds. Ultra-violet absorption spectra of dihalogen derivatives of ethylene. J. ERRERA (J. Phys. Radium, 1926, [vi], **7**, 215–216; cf. A., 1925, ii, 1137).—The ultra-violet absorptive power of *trans*-dihalogen derivatives of ethylene is usually greater than that of the corresponding *cis*-compounds, the difference being more marked for short wave-lengths. Compounds containing iodine, however, show inversion when the wave-length of the absorbed light is increased above about 3000 Å., the *cis*-becoming more absorbent than the *trans*-compounds; inversion is possibly due to the presence of free iodine. Klingstedt (A., 1923, ii, 48) has shown that the absorptive power of *p*-substituted benzene derivatives is greater than that of the corresponding *o*-compounds, and hence the present measurements afford a further example of the parallelism between *cis*- and *trans*-ethylenic compounds and between the corresponding *o*- and *p*-derivatives of benzene (cf. Langseth, this vol., 116). J. S. CARTER.

Infra-red absorption spectra of cyclic derivatives. J. LECOMTE (Compt. rend., 1926, **183**, 27—29).—The absorption spectra of the following substances have been examined in the region 2·85—8 μ: *cyclo*hexane, methyl*cyclo*hexane, *m*- and *p*-dimethyl*cyclo*hexane, *cyclo*hexene, *o*-, *m*-, and *p*-methyl*cyclo*hexene, *cyclo*hexanol, *cyclo*hexanone, *cyclo*hexyl acetate, *cyclo*hexylallylene. The principal results are tabulated. L. F. GILBERT.

Absorption spectra of phenolphthalein, *iso*phenolphthalein, and of diphenylphthalide. W. R. ORNDORFF, R. C. GIBBS, and (MISS) S. A. MCNULTY (J. Amer. Chem. Soc., 1926, **48**, 1994—2002).—The absorption curves of phenolphthalein, *iso*phenolphthalein (*op*-dihydroxydiphenylphthalide), and diphenylphthalide in neutral alcohol have been determined by the procedure previously described (cf. A., 1925, i, 35). The introduction of the two hydroxyl groups markedly decreases the intensity of absorption and suppresses the weaker bands in the ultra-violet. In 93% sulphuric acid, diphenylphthalide shows the two prominent bands characteristic of triphenylmethane derivatives (*loc. cit.* and this vol., 733). The colour of freshly-prepared solutions of phenolphthalein and *iso*phenolphthalein in sulphuric acid is due to formation of quinonoid sulphates, but the colour fades owing to sulphonation, fading being complete in 1 day in the former case, but only in 3—4 days with *iso*phenolphthalein. The absorption curves of these two substances in alcohol containing hydrogen chloride are the same as in neutral solution, and it is considered, from observations on the effect on the absorption curves of adding potassium hydroxide to the alcoholic solutions, that salts of *iso*phenolphthalein have an *o*-quinonoid and of phenolphthalein a *p*-quinonoid structure. The absorption in 33% aqueous potassium hydroxide solution is in either case due to the colourless tripotassium salt of the carbinolcarboxylic acid. A table is given showing the frequency numbers of the peaks of the bands in the various solutions of the three substances examined. For diphenylphthalide in absolute alcohol, the peaks have the numbers 3531, 3620, 3711, 3769, 3861, 3960; for phenolphthalein, 3523 and 3613, and for *iso*phenolphthalein 3511 and 3606 in the same solvent. R. BRIGHTMAN.

Absorption spectra of benzeneazobenzene. W. R. BRODE (J. Amer. Chem. Soc., 1926, **48**, 1984—1988).—Determinations of the absorption spectra of benzeneazobenzene in alcohol, concentrated hydrochloric acid, benzene, and light petroleum by the relative transmission method show that there is no extensive shift of the centre of the absorption band with change of organic solvent, as is the case with benzeneazophenol. The absorption band consists of a smaller band on the lower-frequency side of the principal band, this weaker band having been overlooked by some earlier observers. R. BRIGHTMAN.

Absorption spectrum of *p*-benzoquinone vapour. I. LIFSCHITZ and E. ROSENBOHM (Z. Physik, 1926, **38**, 61—71).—Three regions of absorption were examined: (*a*) 4800—4200, attributed to the C^+ atom, very rich in lines, of which 300 were measured; (*b*) 3100—2600, attributed to oxygen, consisting of narrow absorption bands not resolvable into lines, grouped into two series, the second of which showed a maximum at 2848·5; (*c*) continuous, showing no band structure, due to the electrons, and explicable either as non-quantised jumps under the influence of the electric field of neighbouring molecules, or possibly as due to a pre-dissociation state, as on the hypothesis of Henri ("Structure des Molécules," 1925). E. B. LUDLAM.

Fluorescence of bromine vapour. P. DAURE (Compt. rend., 1926, **183**, 31—33).—Solar light causes bromine at low pressures (less then 1 mm.) to exhibit a green fluorescence. By interposing suitable filters, it has been found that the exciting radiations lie within the range 5000—5600 Å. L. F. GILBERT.

Parallelism between power of fluorescence and reaction velocity. J. PERRIN and (MLLE.) CHOUCROUN (Compt. rend., 1926, **183**, 329—331).—By combining the activated molecule theory of Arrhenius and the quantum theory of fluorescence, it is concluded that molecules are activated by absorption of a quantum of light or energy, and return to their normal states with the emission of fluorescence or loss of kinetic energy. It follows that the rate of destruction of fluorescence is proportional to the life of the active molecule, and that this is greatest when the dilution is a maximum. For methylene-blue in

glycerol, it is found that from concentrations of 1/200 to 1/1500 the brightness of the fluorescence is multiplied by 10·5 and the reaction velocity by 11. The law of mass action holds at concentrations c for which the power of fluorescence is constant, but at high concentrations the terms in c must be replaced by ce^{-kc} according to Perrin's law (cf. A., 1924, ii, 713 and following abstract). J. GRANT.

Radiochemistry of fluorescent substances. (MLLE.) CHOUCROUN (Compt. rend., 1926, **183**, 357—359).—With methylene-blue dissolved in glycerol, it has been found that the rate of reaction is decreased and increased by hydrogen and hydroxyl ions, respectively. By the addition of buffer solutions, progressive alteration of the p_H during the reaction is stopped, and the results obtained show that the reaction velocity increases with decrease in concentration, but attains its limiting value more quickly. This is in accord with Perrin's theory (cf. preceding abstract). J. GRANT.

Comparative study of the fluorescence of natural and artificial porphyrins. C. DHÉRÉ and E. BOIS (Compt. rend., 1926, **183**, 321—323).—The fluorescence spectra of protoporphyrin, uroporphyrin, coproporphyrin, hæmatoporphyrin, mesoporphyrin, ætioporphyrin, and *iso*ætioporphyrin in pyridine show three weak bands and one strong band in the red region of the spectrum. All the methyl esters possess similar spectra except that of protoporphyrin, which has only three bands. The change of the fluorescent colour of hæmatoporphyrin from orange to red on rendering the solution alkaline is shown by the other porphyrins. L. F. HEWITT.

Change of colour of barium platinocyanide under the action of *X*-rays and on heating. A. TRAPESNIKOV (Z. Physik, 1926, **37**, 844—858).—When the green barium platinocyanide is heated or subjected to *X*-rays, the colour changes to yellow and orange. Subsequent exposure to visible light restores the green colour. The kinetics of these changes has been studied; under *X*-rays, the colour change is proportional to the time until saturation begins to appear. At 37·3°, the heat reaction is slower than the influence of *X*-rays, at 52·3° it is faster; the temperature coefficient in the range 37·3—52·3° is about 3. There is, however, an induction period in the heat reaction. Reflexion curves of the differently coloured platinocyanide showed only one reflexion band, with a maximum about 520 μμ. The change from green to yellow is probably due to loss of water, and the change back to green to the return of the water. E. B. LUDLAM.

Additive colouring of alkali halide crystals. Z. GYULAI (Z. Physik, 1926, **37**, 889—894; cf. this vol., 225).—Crystals of the salt were coloured by heating in a hard glass test-tube with the alkali metal; synthetic crystals behave in the same way as natural crystals. Absorption curves are given and the absorption coefficients calculated for potassium chloride and bromide; they are in good agreement with those obtained for crystals coloured by *X*-rays. The influence of light of photo-electric wave-length on the form of the curves is also the same as when the colour has been produced by *X*-rays. E. B. LUDLAM.

Luminescence of water and organic substances subjected to γ-rays. L. MALLET (Compt. rend., 1926, **183**, 274—275).—Water exposed to a filtered radioactive source emitting 13% and 81% of soft and hard γ-rays, respectively, shows a white luminescence. Photographic experiments through screens of various materials indicate that the wave-length is less than 3000 Å. Alcohol, ether, chloroform, carbon disulphide, albumin, serum, oils, and fats show similar fluorescence. J. GRANT.

Phosphorescent sulphides of zinc. II. A. A. GUNTZ (Ann. Chim., 1926, [x], **5**, 363—420; cf. this vol., 558).—Accurate spectrographic observations are recorded of the effect (excitation or extinction) of light of various wave-lengths on zinc sulphide with a trace of copper and increasing proportions of cadmium sulphide, and of the resulting fluorescence and phosphorescence. The fluorescence is caused by all radiations of wave-length less than 4850 Å. The band of excitation becomes displaced in the direction of longer wave-length with increasing proportion of cadmium sulphide. The increasing red colour of the fluorescence is attributed to the shifting of emission bands due to copper. In general, in each case, the emission of phosphorescence is displaced to exactly the same extent as is the absorption and in the same direction, these results being in accord with the view (Walter, Physikal. Z., 1912, **13**, 6) that the diluent absorbs light largely and excites the phosphorescence. A detailed study is described of the limit of the band of excitability at temperatures from 212° down to −180°, and for mixtures of various compositions. No deviation from Stokes' law was detected even at 220°. The temperatures (varying between 100° and 360°) at which fluorescence of various wave-lengths and phosphorescence vanish are recorded.

Observations of the effect of infra-red radiation in producing the two opposite phenomena of extinction and restitution are in agreement with the theory of Lenard. The effects are described for various mixtures and at different temperatures. It is shown that the two theories of Lenard and Perrin concerning these effects are reconciled if an electron detached from the active metal according to Lenard's theory is assumed to be captured by a neighbouring sulphur atom, the change thus constituting a photochemical reaction. Perrin's theory is then applicable to the question of the reversal of this action under the influence of infra-red radiation. G. M. BENNETT.

Phosphorescence of metallic sulphides. A. A. GUNTZ (Bull. Soc. chim., 1926, [iv], **39**, 953—975).—A lecture.

Polarised and unpolarised phosphorescence of solid solutions of dyes. P. PRINGSHEIM and S. J. VAVILOV (Z. Physik, 1926, **37**, 705—713).—Solid solutions of dyes exhibit emission bands in the long wave-length region in addition to the fluorescence bands which are characteristic of them in liquid solu-

tions; they are comparatively weak in fluorescence, but in the phosphorescence at −180° they are the only bands observed. In contrast with the fluorescence bands, these phosphorescence bands are completely unpolarised, both at the moment of excitation and later. As the two kinds of emission are superimposed, the degree of polarisation of the total emission and of particular regions depends on the proportions in which each kind is present. With due regard to this fact, the results obtained with a variety of dyes in sugar and in gelatin solutions are explicable.
E. B. LUDLAM.

Photo-electric measurements on liquid surfaces. W. ZIMMERMANN (Ann. Physik, 1926, [iv], **80**, 329—348).—Photo-electric measurements have been undertaken to provide information as to the nature of the surface layers of liquids, particularly those of aqueous solutions. The source of the radiation was a mercury lamp, with a fluorspar window. Among the liquids examined were solutions of alkali chlorides, nitrates, sulphates, chromates, ferricyanides, ferric chloride, ammonia, ozone, bromine, alcohol, and formaldehyde. Freshly-prepared surfaces of these solutions gave no measurable photo-electric effect, and such positive results as were obtained could be traced to the formation of solid skins on the surface (*e.g.*, in formaldehyde solutions, owing to polymerisation to trioxymethylene). The only solutions giving a true photo-electric effect were those of ferrocyanides. The effect is ascribed to undissociated molecules in the surface layer. Solid salts were also examined, and here again the ferrocyanides proved unusually active. As salts gave positive results in the solid state which were quite inactive in solution, it is concluded that the surface layers contain fewer undissociated molecules than does the bulk of their solution.
S. BARRATT.

Dielectric constant of bromine. A. BRAMLEY (J. Franklin Inst., 1926, **202**, 23—33).—The variation of the dielectric constant of bromine with pressure is abnormal. No evidence of liquefaction or of association of the molecules even in a high electric field could be found. A theory is deduced which indicates that the variation from the values predicted from the refractive index is due to the temperature variation of the probabilities of an absorption transition in an external electric field for the energy states of the molecule which give rise to the infra-red spectra of the vapour.
C. J. SMITHELLS.

Dielectric constant of dipolar gases according to quantum mechanics. L. MENSING and W. PAULI, jun. (Physikal. Z., 1926, **27**, 509—512).—Mathematical. In this as in other fields, the newer quantum mechanics fits more closely with the classical mechanics than does the older quantum mechanics.
R. A. MORTON.

Magnetic susceptibilities and dielectric constants in the new quantum mechanics. J. H. VAN VLECK (Nature, 1926, **118**, 226—227).—It is shown that in the new theory the spatial quantisation relative to the applied field has no direct effect on the magnetic susceptibility or the dielectric constant. On calculation of the dielectric constant of a diatomic gas, it is found that only molecules in the state $j = 0$ of lowest rotational energy make a contribution to the polarisation attributable to the permanent moment of the dipoles. This accords with the fact that in the classical theory only molecules with energy less than μF contribute to the polarisation.
A. A. ELDRIDGE.

Rotatory power of quartz in the ultra-violet. J. DUCLAUX and P. JEANTET (J. Phys. Radium, 1926, [vi], **7**, 200—203).—The rotatory power of quartz increases continuously with decreasing wave-length of light over the range investigated, 3000—1850 Å. For light of wave-length 3088, 2568, 1990, and 1854 Å., the values of $[\alpha]^{20}$ are 91·2, 144·1, 295·7, and 370·9, respectively. The variation of rotatory power with wave-length follows no known law.
J. S. CARTER.

Rotatory power of tartaric acid. R. LUCAS (Compt. rend., 1926, **183**, 29—31).—The influence of calcium chloride, carbamide, and of boric and tungstic acids on the rotatory power of tartaric acid is consistent with the presence of a third form of this substance, the proportions of the three forms being altered by the above-named compounds.
L. F. GILBERT.

Rotatory dispersion. T. M. LOWRY (J. Chim. phys., 1926, **23**, 565—585).—A lecture describing the historical development of views on normal and abnormal dispersion.
J. W. BAKER.

Dispersion of carbon disulphide and the Ketteler–Helmholtz formulæ. G. BRUHAT and M. PAUTHENIER (Ann. Physique, 1926, [x], **5**, 440—469).—Previous attempts to determine the constants in formulæ of the Ketteler–Helmholtz type have failed to represent the dispersion of carbon disulphide in the ultra-violet region 2500—4000 Å. with sufficient accuracy. This is attributed to the presence of a complex absorption band at 3200 Å. Much better agreement between theory and experiment is obtained by the use of a formula consisting of the sum of five terms, corresponding with the central wave-lengths of five groups of rays in the absorption region obtained from Pauer's measurements on carbon disulphide vapour. In the regions of transparence on each side of the absorption maximum, it is still possible to employ a formula having a single term with considerable approximation. The slight deviations between theory and experiment may be due to the nearness of the complex band between 2000 and 2500 Å.
C. H. D. CLARK.

Anomalous dispersion and absorption of electric waves. III. S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 115—123).—The experiments previously described were repeated on some aliphatic alcohols, using a wave-length of 9·5 metres (this vol., 560, 778). Propyl, *iso*propyl, *iso*butyl, and amyl alcohols behave, in general, like glycerol. Ethyl and methyl alcohols probably behave like the other alcohols at sufficiently low temperatures. The results indicate that a very strong wave-absorption occurs where the dispersion is most anomalous.
S. K. TWEEDY.

Method of determining the dispersion of double refraction and the thickness of a crystalline plate (*e.g.*, mica). T. HORI (Mem. Coll. Sci. Kyōtō, 1926, **9**, 313—314).—A beam of polarised light is passed through a plate of mica half-silvered on both sides and observed through a spectroscope. The continuous spectrum is crossed by interference fringes which reduce to a single system by suitable arrangement of the polarising Nicol. The thickness, d, can be calculated from the formula $2d(\mu_m/\lambda_m-\mu_0/\lambda_0)=m$, where μ is the principal index and the band corresponding with λ_m is the mth towards the violet, counting from the one corresponding with λ_0. Knowing the thickness, the values for the two indices of refraction can be calculated throughout the range of the spectrum.

E. B. LUDLAM.

Magnetic rotatory and electric double refraction dispersion. R. DE MALLEMAN (Compt. rend., 1926, **183**, 33—35).—The expression previously deduced (this vol., 111) for Verdet's constant has been directly tested, with satisfactory results, with optical data for carbon disulphide and for camphor dissolved in hexane. A second test, also satisfactorily applied, depends on the theorem, now enunciated, that the ratio of the magnetic rotatory dispersion to the electric double refraction dispersion is equal to the ratio of the corresponding wave-lengths. The necessary magnetic and electric dispersion data for carbon disulphide were redetermined experimentally.

L. F. GILBERT.

Determination of the Kerr effect in liquefied gases. Oxygen. H. WALCH (Arch. Néerland., 1925, IIIA, **9**, 175—206).—The electric double refraction is investigated for liquid oxygen. The results are represented by the equation $\delta/\lambda=BH^2l$, where δ is the displacement, l the distance between the electrodes, and H the field, which is applicable to other liquids. For liquid oxygen $B_{520\mu\mu}$ is $2{\cdot}0\times10^{-8}$ c.g.s.u., which is less than that for carbon disulphide ($\pm3{\cdot}35\times10^{-7}$). The Kerr effect produces dispersion, which increases in the neighbourhood of the absorption band at 480 μμ. Exact values of the indices of refraction are required before the different theories can be tested.

C. J. SMITHELLS.

Kinds of chemical linkage. H. LUX (Z. physikal. Chem., 1926, **121**, 456—462).—Possible positions taken up by valency electrons on the formation of simple chemical compounds are discussed, with special reference to the polarity of the compounds.

L. F. GILBERT.

Phenomenon of valency. R. DE (J. Sci. Assoc. Maharajah's Coll. Vizianagaram, 1926, **2**, 114—119).—The group displacement law relating to the expulsion of a β-particle from a radioactive element is applicable to the process of ionisation. A substance ionises by the transference of an electron from one radical to the other; the radical losing an electron shows an increment of one in valency, whilst the radical acquiring an electron exhibits a decrement of valency. The apparent increase in the valency of nitrogen by two in the formation of ammonium chloride is accounted for by the loss of an electron by nitrogen, which then becomes quadrivalent, unites with hydrogen, and remains attached to the chlorine ion electrostatically. Optical isomerism in ammonium and phosphonium compounds is explained by the space-model of a tetrahedron. In sulphonium salts, the valency of sulphur is three, the halogen being attached by an electrostatic linking; oxonium salts are similar, and water is regarded as forming an additive compound of this type with hydrogen chloride. The hitherto supposed hydrogen ion is really H_3O^+. The line of reasoning employed is also applicable to boron, active triatomic hydrogen, and compounds of helium.

R. A. MORTON.

Rôle of magnetism in valency. E. H. WILLIAMS (Physical Rev., 1926, [ii], **28**, 167—173; cf. Taylor, this vol., 566).—Magneto-chemical theory leads to the hypothesis that a symmetrical arrangement of electrons tends to produce diamagnetic and an unsymmetrical arrangement paramagnetic properties in an atom or molecule. A change from paramagnetic to diamagnetic properties would therefore be expected in related compounds in which a change in valency is accompanied by a change from an odd to an even number of electrons in the molecule, *e.g.*, in cupric and cuprous oxides. Results show that the compounds of copper, bismuth, lead, and tin of odd molecular number are paramagnetic, whilst those of even molecular number are diamagnetic. On the other hand, the oxides MnO (odd) and Mn_2O_3 (even) are both paramagnetic, the former slightly more so. The oxide CoO (odd) is strongly ferromagnetic, whilst Co_2O_3 (even) is paramagnetic. Silver oxide and suboxide (Ag_2O) are both diamagnetic, suggesting that possibly silver oxide is of the form Ag_2O_2.

A. B. MANNING.

Electronic nature of isomeric transformations. F. I. BEREZOVSKA (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 121—142).—In continuation of the work of Pisarshevski ("The electron in chemical energetics," Jubilee J. [Russian] Mining Inst.), the author shows that the influence of an alkyl residue introduced into a molecule depends on the position of the alkyl group. When the alkyl enters in place of hydrogen, it influences both the distribution of the electrons at the position of linking and the intensity of their motions, these finding expression in a change of the acidic properties of the molecule and of its stability. The motion of the electrons at the double linking of the molecules of maleic and fumaric acids creates a magnetic moment in the molecule, this conditioning a turning of the circular current formed by the motion of the electrons at the double linking and leading to the transformation of maleic into fumaric acid, and inversely, in a constant magnetic field. The effect of the action of a magnetic field depends on the magnitude of the magnetic moment, which, in its turn, depends on the strength of the current (in this case, on the velocity of movement of the electrons) and on the area surrounded by the current (in the present case, on the separation of the components of the molecules).

From the strength of an external magnetic field giving a similar effect, it may be possible to judge of the magnitude of the magnetic moment and con-

sequently of the work of the current on the area round which the electrons flow. Moreover, if one of these magnitudes is taken as constant, an idea of the comparative magnitudes of the other in different molecules may be formed.

The effect of a constant magnetic field on oxalic acid indicates the existence of a magnetic moment in the molecule of this acid, and hence of the movement of the electrons at the position where the carbon atoms are united. T. H. POPE.

Polarisation of the hydrogen atoms in organic compounds. A. E. VAN ARKEL and J. H. DE BOER (Z. physikal. Chem., 1926, **122**, 101—112).—An extension to a consideration of refractivity data of the previously expressed view (A., 1925, ii, 758, 1141) that hydrogen in such compounds as methane and ethane and their halogen derivatives plays the part of an electronegative element. On this assumption, accumulation of hydrogen atoms would be expected to increase their atomic refractivity, owing to mutual polarisation, and this proves to be so. This effect is accompanied by increase in the value of van der Waals' coefficient a, and of the mol. vol. at the b. p. R. CUTHILL.

Molecular fields of hydrogen, nitrogen, and neon. J. E. LENNARD-JONES and W. R. COOK (Proc. Roy. Soc., 1926, **A**, **112**, 214—229).—The effective forces between the molecules of the gases under consideration are assumed to be a force of attraction and a force of repulsion, the former predominating at large distances, the latter at small. It is further supposed that both of these are representable by inverse power laws, and that the field is spherically symmetrical. Application of this theory to the isotherms of neon gives results in good agreement with those derived from the experimental data and from thermal conductivities and viscosities. With nitrogen and hydrogen, too, the form of the isotherms is satisfactorily accounted for; from this it is concluded that the molecular fields of these gases can be regarded as spherically symmetrical. With both nitrogen and argon, however, the results of the application of the theory are not in very good agreement with the values derived from viscosity and thermal conductivity data, which latter are probably the more accurate, as they are supported by crystallographic measurements. R. CUTHILL.

Forces between atoms and ions. II. J. E. LENNARD-JONES and (MISS) B. M. DENT (Proc. Roy. Soc., 1926, **A**, **112**, 230—234; cf. this vol., 11).—The forces between the molecules of the inert gases and between uni- and bi-valent ions of the inert gas type have been calculated on the assumption that the field of force is spherically symmetrical, and consists of both a repulsive and an attractive component, each of which can be expressed in terms of an inverse power law. R. CUTHILL.

Stereochemistry of platinous salts. H. REIHLEN (Annalen, 1926, **448**, 312—316).—Arguments are brought forward to show that co-ordinated, quadrivalent platinum occupies no special position in stereochemistry, but that for platinum, nickel, and all other co-ordinated, quadrivalent elements the tetrahedral arrangement of van 't Hoff holds good. These ideas are applied to ethylenethiolacetatoplatinum (A., 1914, i, 384), ββ′β″-triaminotriethylamineplatinous iodide, and tristriaminotriethylaminenickelous iodide (this vol., 387), for which space diagrams are drawn. J. S. H. DAVIES.

Born's dipole theory of anisotropic liquids. G. SZIVESSY (Z. Physik, 1926, **38**, 159—160; cf. A., 1925, ii, 1123; Kast, this vol., 779).—If the theory were correct, the sudden change in the electrical state of the surface of a liquid on applying a magnetic field could easily be measured; also, as soon as a double layer had been formed, the $P.D.$ would remain as long as the dipoles were kept in position. E. B. LUDLAM.

Determination of the size, mass, and charge of sub-microscopic spheres of radius from 4×10^{-5} to 5×10^{-6} cm. F. EHRENHAFT and E. WASSER (Z. Physik, 1926, **37**, 820—843).—The spheres were produced by spraying a saturated solution of potassium mercuric iodide and barium mercuric iodide, and their motion between the plates of a condenser was observed. Ultra-violet photomicrographs were taken of colloidal particles of gold and of selenium, which were spherical, and of antimony sulphide, which were not. E. B. LUDLAM.

Alkali perchlorates and a new principle concerning the measurement of space-lattice cells. A. E. H. TUTTON (Proc. Roy. Soc., 1926, **A**, **111**, 462—491).—The optical constants of crystals of the perchlorates of potassium, rubidium, cæsium, and ammonium have been determined for all parts of the spectrum, in spite of the very small size of the available crystals. The optic axial angles, the molecular and specific refractions and dispersions of the three salts all show a regular progression following the order of the atomic numbers. The corresponding refractive indices do not show this progression; they are, however, exceptionally close to one another, differing only in the third place of decimals. The ammonium salt differs as regards the position of the optic axial plane, which is c (001) instead of a (100), and its optic axial angle is larger than for the metallic salts. The refractive index and the specific refraction are also larger. The molecular refraction of ammonium perchlorate is nearly the same as that of rubidium perchlorate. A complete goniometrical measurement of the crystals has also been carried out, and the values obtained by Barker (Z. Krist., 1907, **43**, 529; 1908, **45**, 17) have been confirmed and amplified. The topic axial ratios have been calculated on the basis of the setting indicated by X-ray analysis; the unit cell has edges parallel to the crystal axes and has the axis a double the length given by the Groth–Barker setting. A new principle has been used to convert these relative cell measures into absolute lengths of the cell edges. It states that in a well-established isomorphous series, if any one member be thoroughly worked out by X-ray analysis, the crystals being large and perfect enough to permit, not only of spacing determinations, but also of intensity measurements, so that the space-lattice unit-cell

dimensions and character are fixed with certitude, then the absolute cell-dimensions of all the other members of the series may be obtained by calculation from the topic axial ratios, which express the relative measures exactly, the crystal structure being strictly analogous throughout the series. The perchlorates (and permanganates) form such an isomorphous series with the barytes group of minerals, and the cell dimensions of barytes, the structure of which has been thoroughly worked out by *X*-ray analysis, have been used to calculate those of the alkali perchlorates. The results are confirmed by their close agreement in the case of potassium perchlorate with the values of James and Wood, obtained by *X*-ray analysis (this vol., 13). A. B. MANNING.

Symmetry of sylvine and the nature of the etching figures. K. F. HERZFELD and A. HETTICH (Z. Physik, 1926, **38**, 1—7).—The lack of symmetry in the etching figures is caused by traces of impurity which are observable through a microscope. With sylvine carefully freed from organic impurities, iron oxide, etc., the etching figures are holohedral. The hemihedral structure assigned to a number of other crystals may prove to be erroneous for the same reason. E. B. LUDLAM.

Structure of beryl, $Be_3Al_2Si_6O_{18}$. W. L. BRAGG and J. WEST (Proc. Roy. Soc., 1926, **A**, **111**, 691—714).—The structure of beryl has been analysed by making use of careful quantitative measurements of the absolute intensity of *X*-ray reflexion. Beryl belongs to the holosymmetric class of the hexagonal system, $c=9{\cdot}17\pm0{\cdot}01$, and $a=9{\cdot}21\pm0{\cdot}01$ Å.; the unit cell contains two molecules; the space-group is D^2_{6h}. The observed intensities of *X*-ray reflexion have been used to determine *F*, the scattering factor (cf. Hartree, A., 1925, ii, 735), for a number of crystal planes, and the atomic positions have been directly deduced from these values. The method of analysis developed by Duane (Proc. Nat. Acad. Sci., 1925, **118**, 489), involving the Fourier analysis of electron distribution in sheets parallel to a set of crystal planes, has also been applied to beryl, and the scope of the two methods compared. In the beryl structure every silicon atom is surrounded by four oxygen atoms arranged tetrahedrally, every aluminium atom by six oxygen atoms at the corners of an octahedron, and every beryllium atom by four oxygen atoms on a distorted tetrahedron. The silicon and oxygen atoms form rings of the composition Si_6O_{18}. These rings have a hexagonal axis and equatorial plane of symmetry, and are arranged around tho hexagonal axes. They are composed of SiO_4 groups, each group joined to its neighbour on either side in the ring by an oxygen atom held in common. The rings are stacked on each other along the hexagonal axes, forming a series of open channels, for no atomic centre is nearer than 2·55 Å. to a hexagonal axis. The rings are linked together by the aluminium and beryllium atoms. A. B. MANNING.

Crystal structure of magnesium plumbide. J. B. FRIAUF (J. Amer. Chem. Soc., 1926, **48**, 1906—1909).—*X*-Ray examination indicates that magnesium plumbide has a face-centred cubic structure; the unit cell contains four molecules and has an edge of 6·78 Å. These results confirm those of Sacklovski. S. K. TWEEDY.

X-Ray examination of aluminium silicates [and pseudobrookite]. P. ROSBAUD [with H. MARK] (Z. Elektrochem., 1926, **32**, 317—319).—Disthene forms triclinic-pinacoidal crystals having the space-group C_i^1; $a=7{\cdot}18$, $b=8{\cdot}00$, $c=5{\cdot}55$ Å.; four molecules in unit cell. Andalusite forms rhombic bipyramidal crystals with the space-group B_h^{12}; $a=7{\cdot}90$, $b=7{\cdot}90$, $c=5{\cdot}50$ Å.; four molecules in unit cell. The rhombic crystals of sillimanite have the space-group B_h^{16}; $a=7{\cdot}25$, $b=7{\cdot}65$, $c=5{\cdot}88$ Å.; four molecules in unit cell. Mullite forms rhombic bipyramidal crystals having the space-group B_h^9; $a=7{\cdot}25$, $b=7{\cdot}65$, $c=2{\cdot}94$ Å.; two molecules in unit cell. Pseudobrookite, Fe_2TiO_5, forms rhombic bipyramidal crystals; space-group B_h^{12}; $a=9{\cdot}78$, $b=9{\cdot}80$, $c=3{\cdot}65$ Å.; four molecules in unit cell. Mullite has the composition Al_2O_3,SiO_2, not $3Al_2O_3,2SiO_2$ (cf. Bowen, Grieg, and Zies, A., 1924, ii, 416). J. S. CARTER.

Copper hydride and its crystal structure. H. MÜLLER and A. J. BRADLEY (J.C.S., 1926, 1669—1673).—A modification of Wurtz's method has been used to prepare copper hydride, the Cu : H ratio in the purest product obtained being 1 : 0·97. When submitted to *X*-ray analysis by the Debye powder method, spectra corresponding with the atomic arrangement of the hydride CuH were obtained. Less pure specimens showed in addition the spectrum of copper. The crystal structure of the hydride may be considered as hexagonal close-packed with an axial ratio of 1·59—1·60, the side of a unit rhomb being 2·89 Å. By obtaining one electron from hydrogen, the substance assumes the hexagonal symmetry of zinc, the size of the elementary hexagon of which ($a=2{\cdot}67$ Å.) is slightly smaller than that of copper hydride. The space occupied by one hydrogen atom is nearly the same as that corresponding with the lattice expansion of palladium–hydrogen alloys. The hydride may be prepared, under certain conditions, by electrolysis of a dilute solution of a copper salt, and then appears black. Evidence is submitted to show that the cupric hydride described by Bartlett and Merrill (A., 1895, ii, 268) consists of a mixture of finely-divided copper and cuprous oxide. A. B. MANNING.

Crystal structure of red mercuric iodide. J. M. BIJVOET, A. CLAASSEN, and A. KARSSEN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 529—546).—Red tetragonal-holohedral mercuric iodide has been examined by the rotating crystal and powder methods. The unit cell has $a=4{\cdot}38$, $c=12{\cdot}43$ Å. and contains two molecules; $d_{calc.}$ 6·28 agrees with the experimental value. The variations in the intensity of reflexion indicate the space-group D_{4h}^{15}. The mercury ions are in a body-centred lattice, each being surrounded nearly tetrahedrally by four iodine ions. The shortest distance between two iodine ions in successive layers is 4·18 Å., which is very near to the similar value (4·21) in crystals of stannic and cadmium iodides. No evidence was obtained of pseudo-tetragonality. G. M. BENNETT.

Crystal structure of lead iodide. P. TERPSTRA and H. G. K. WESTENBRINK (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 431—442).—Crystals of lead iodide, in the form of very thin hexagonal plates, have been examined goniometrically and also by the *X*-ray spectrograph by several different methods. The crystal appears to be trigonal, of rhombohedral symmetry, with a fundamental structure, characterised by a hexagonal translational group. The unit cell contains one molecule; only three space-groups, in simple and two-fold equivalent positions, are possible: D^1_3, D^2_3, and D^3_{3d}, and, under certain conditions, D^2_3 and D^3_{3d} may become identical. The structure is analogous to that attributed by Aminoff to ditrigonal-scalenohedral minerals, pyrochroite, $Mn(OH)_2$, and brucite, $Mg(OH)_2$, and also to that of cadmium iodide (Bozorth, A., 1922, ii, 851). All measurements give the ratio $a:c$ in the neighbourhood of 1 : 1·5, a and c determined by the Debye–Hull method being 4·59 and 6·78, respectively, and by the Bragg method 4·54 and 6·86 Å. For lead iodide, d^{15} is 6·18. M. S. BURR.

Crystal forms of derivatives of ethoxy- and trimethyl-benzophenones. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 410—416).—A detailed crystallographic investigation has been made of the following derivatives of benzophenone: 4-ethoxy-, m. p. 42—46·5°, 3-bromo-4-ethoxy-, m. p. 102·2°, 3 : 5-dibromo-4-ethoxy-, m. p. 83·5°, 4-nitro-2′ : 4′ : 6′-trimethyl-, and 3 : 5-dibromo-2′ : 4′ : 6′-trimethyl-benzophenone, and 4 : 4′ : 4″ : 4‴-tetrabromobenzpinacone (+1Et·OAc).

M. S. BURR.

Crystal forms of some organic nitrogen compounds. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 417—430).—Crystallographic details are given for the additive product of carbon disulphide and triethylphosphine, PEt_3,CS_2, m. p. 122°, and also of the following compounds: *p*-aminoacetophenone, m. p. 106°; acetylphenylurethane, m. p. 59°; 2-acetamidopyridine, m. p. 71°; 2-pyridylurethane, m. p. 105·5°; acetylquinine, m. p. 116°; tartronamic acid, m. p. 160° (decomp.); *d*-tartramidic acid, m. p. 172°; aminosulphonic acid; phthalimidine, m. p. 150°; ammonium phthalimidine acetate; ethylenediamine hydrochloride; *p*-nitro-*n*-propylaniline; methyl benzoylcyanoacetate, m. p. 75·2°; methyl *m*-nitrobenzoylcyanoacetate; and the trihydrazide hydrochloride of tricarballylic acid.

M. S. BURR.

***X*-Rays and long-chain organic compounds. Spectrographic study of structure and orientation.** J. J. TRILLAT (Ann. Physique, 1926, [x], **6**, 5—101).—The molecular orientation of palmitic acid on different surfaces, or on the same surface under different conditions, has been studied by the *X*-ray spectrograph. The carboxyl groups attach themselves to an alkaline surface and the hydrocarbon chains are all inclined at the same angle to the surface, giving a sharply-defined spectrum. An acid surface repels the carboxyl group and results in a very diffuse spectrum showing ill-defined orientation. If the surface is moistened with water, the orientation is quite different, the molecules apparently lying flat on the surface. The stratification of the acid is more complete the slower the rate of crystallisation on the given surface. The spectrum becomes more and more diffuse as the thickness of the layer increases, showing that the orienting effect of the surface diminishes until, at a distance of the order of 0·005—0·01 mm., it disappears completely (cf. A., 1925, ii, 195). The behaviour with metal surfaces indicates in some cases chemical reaction between the metal and the acid (cf. *ibid.*, 752). The physical interpretation of the behaviour observed is discussed (cf. de Broglie and Trillat, *ibid.*, 640). On water, as on moist glass, the molecules appear to be flat, so that the maximum distance is not found perpendicular to the surface. Traces of an orientation similar to that found on unwetted glass have also been observed, and suggest that directly in contact with the water is a layer in which the chains rise up from the water, being only attached to the latter by their acid radicals, thus producing on the solid acid a surface which can be wetted by water. A comparison of the behaviour of acids with different numbers of carbon atoms, and also of dibasic acids has been made (cf. *ibid.*, 489). *X*-Ray spectrography is applicable to the analysis of organic compounds, *e.g.*, an equimolecular mixture of two acids, margaric acid, may be distinguished from a pure compound, daturic acid, of the same percentage composition, or indications may be obtained of the structure of different natural fats and waxes (cf. *ibid.*, 752). The process of oxidation of unsaturated fatty acids has also been followed (cf. *ibid.*, 1127), an approximately constant lengthening of the chain being observed with each molecule of oxygen taken up. It is suggested that, by the use of organic compounds with sufficiently long chains, a study may be made of long-wave *X*-rays nearer to the ultra-violet than has hitherto been approached. During the process of lubrication, *X*-ray examination of the grease indicates, by the production of intense orientation spectra, that stratification has taken place, forming layers which glide over one another (cf. Compt. rend., 1925, **180**, 843). M. S. BURR.

Imperfect crystallisation of common camphor. W. G. BURGERS (Nature, 1926, **118**, 116—117).—Like behenolic acid (Müller, this vol., 665), Japan camphor provides an example of imperfect crystallisation. *X*-Ray examination of thin, hexagonal plates, obtained by slow sublimation at the ordinary temperature, gave the spacings d_{0001} 5·80, $d_{10\bar{1}1}$ 5·42, $d_{10\bar{1}0}$ 6·06 Å., axial ratio 1·656; reflexion from $(11\bar{2}0)$ was not observed. Spots were always observed in positions bearing no definite relation to the setting of the crystal. Apparently good crystals are therefore actually conglomerations. True powder photographs could not be obtained; when camphor is rubbed in a mortar, orientation of the crystal elements is effected with the basal planes more or less parallel to the surface of the pressed substance. Possibly the crystals are not truly hexagonal, but are intergrowths of biaxial lamellæ, a supposition which necessitates the presence of an artificial spiral of lamellæ. The imperfection of the crystals is ascribed to temperature changes during their growth. A. A. ELDRIDGE.

Effect of torsion on certain elastic properties of wires. E. EDWARDS, I. BOWEN, and S. ALTY (Phil. Mag., 1926, [vii], **2**, 321–340).

Plastic deformation of single metallic crystals. F. S. GOUCHER (Nature, 1926, **118**, 157).—Polemical (cf. Millington and Thompson, this vol., 666).

A. A. ELDRIDGE.

Molecular weights of proteins in phenol. E. J. COHN and J. B. CONANT (Proc. Nat. Acad. Sci., 1926, **12**, 433—438).—Estimates based upon a simultaneous consideration of the contents of sulphur, sulphide sulphur, and of various individual amino-acids yield minimal mol. wts. of 34,000, 72,000, 96,000, 150,000, and 192,000 for egg-albumin, gliadin, zein, gelatin, and casein, respectively (cf. Sörensen, A., 1919, i, 178). These numbers are in complete disagreement with the remarkably low mol. wts. (200—600) calculated from measurements of f.-p. lowering in phenol (Troensegaard and Schmidt, A., 1924, i, 581; Herzog and Kobel, *ibid.*, 1007). The suggestion that these small values represent the mol. wts. of the units of a large aggregate, stable in water but dissociated in phenol, appears rather improbable. The mol. wts. of gelatin, zein, casein, and gliadin in phenol solution have therefore been reinvestigated, using materials free from other proteins and from electrolytes. Preliminary experiments showed the enormous influence of small quantities of moisture on the magnitude of the apparent mol. wt. Thus, a specimen of zein, dried at 100° in a vacuum for 3 hrs., gave a f.-p. lowering corresponding with a mol. wt. of 1800—2200. Further drying by grinding under absolute ether and subsequent evacuation at a pressure of 0·001 mm. for 4 hrs. raised the apparent mol. wt. to 4250. In view of the difficulties attending the complete removal of water, the usual experimental procedure was modified by the addition of freshly-powdered anhydrous calcium chloride. So long as the system contains the solid anhydrous salt in equilibrium with its hydration products, the f. p. is independent of added water. The system has a much sharper f. p. than pure phenol. This procedure is analogous with that used for the determination of mol. wts. in nitrobenzene solutions, sodium sulphate being the added solid phase (Roberts and Bury, J.C.S., 1923, **123**, 2037). When proteins are added to the system, no discernible alteration of the f. p. occurs. The added protein remains in solution during the determination, and hence the measurements show that there is no dissociation of protein molecules into units of low mol. wt. and that the true mol. wts. in phenol, as in water, are those revealed by the analytical method. J. S. CARTER.

New conductivity effect by the simultaneous action of blue and red light and a case of more than proportional increase in conductivity with light intensity at low temperatures. F. KÄMPF (Z. Physik, 1926, **38**, 104—115).—Mercuric iodide, made conducting by exposure to bluish-green light at the temperature of liquid air, showed a diminution in conductivity in red light. At the ordinary temperature, both effects probably co-exist, but the red effect is too small to be noticed. When light of wave-length 555—650 $\mu\mu$ acted alone, the conductivity did not increase in proportion to the intensity of the light, but when, simultaneously, light in the red and infra-red of constant intensity was added, the increase in conductivity was more than proportional to the increase in the light. E. B. LUDLAM.

Superconductors. H. K. ONNES (Arch Néerland., 1925, IIIA., **9**, 143—170).—Experimental results on superconductivity obtained by the use of liquid helium are described. Measurement of the mutual forces due to electric currents in two rings of lead in the superconducting state showed that the current decreased by less than 1 in 21,000/hr. over a period of 6 hrs. From this, the resistivity appears to be 10^{-12} times the value at 0°, which is less than one tenth of the value obtained previously. A similar experiment, in which a hollow lead sphere was surrounded by a lead ring in such a manner that the inclination of its axis could be changed, indicated that the current in the sphere persisted in the original direction, as though its path in the superconductor was fixed. The Hall effect is absent in superconductors, but can be restored by increasing the field above the threshold value. It is suggested that the path is ruptured by the increased field and that this condition is necessary for the transference of electrons from one atom to another. Measurements between 1·85° and 3·42° Abs. show that a linear relation exists between the threshold value of the field and the temperature of the form $B_T=H_0+C_{HT}T$, where C_{HT} is a universal constant and H_0 a constant of the material. *X*-Ray photographs of lead in the normal and superconducting states show no difference in structure. Langevin's suggestion of a phase change is rejected, and it is suggested that a change in the trajectory of the electrons without alteration of the nuclei occurs. A number of metals have been tested for superconductivity. Indium shows a sharp discontinuity at 3·41° Abs.; sodium and potassium show no effect down to 1·5° Abs.; the results with cadmium, germanium, and gallium are uncertain. It is suggested that superconducting metals form a special class, like the ferromagnetic materials. Attention is directed to their unusually wide atomic spacing, giving a large free path for the electrons. C. J. SMITHELLS.

Magnetostriction in "permalloy." L. W. MCKEEHAN and P. P. CIOFFI (Physical Rev., 1926, [ii], **28**, 146—157; cf. A., 1925, ii, 945).—The magnetisation and magnetostriction of iron, nickel, and seven nickel–iron alloys ("permalloys") of varying nickel content have been measured in fields up to 40 gauss. The magnetostriction of the alloys containing 74, 80, and 84% of nickel were measured also under an applied tension of 3600 lb./sq. in. The metal, in the form of wire 1 mm. in diameter, was stretched vertically within a solenoid 52 cm. long. Brass sleeves were clamped to the wire, leaving a central portion 12 cm. in length on which the determinations were made. The change in length was measured by a combination of a mechanical lever, an optical lever, a multiple slit, and a photo-electric cell, giving a magnifying power of about 2×10^6. The magnetostriction–magnetisation curves have an initial slope of zero in all cases. The magnetostriction

approaches a limiting value when the field is sufficient to produce magnetic saturation. Permalloys with more than 81% of nickel show a contraction, and those with less than 81% an expansion on magnetisation. The limiting values of magnetostriction, when plotted against composition, fall on a smooth curve. Tension increases the contraction and diminishes the expansion occurring on magnetisation. It causes a reversal in the sign of magnetostriction in permalloy with 80% of nickel, a small contraction preceding the final small expansion. A. B. MANNING.

Significance of magnetostriction in "permalloy." L. W. MCKEEHAN (Physical Rev., 1926, [ii], **28**, 158—166; cf. preceding abstract).—The results of the preceding paper are in qualitative agreement with the author's theory of atomic magnetostriction (A., 1925, ii, 944). The effect of tension on magnetostriction and on other magnetic properties of the alloys is explained on the assumption that mechanical stresses produce an orientation of the magnetic axes of iron and nickel atoms similar to that produced by a magnetic field. A connexion between magnetic hysteresis and mechanical hysteresis is suggested, and the molecular field postulated by Weiss is interpreted as the integrated effect of local mechanical stresses. A. B. MANNING.

Variation of paramagnetism with temperature. B. CABRERA and J. PALACIOS (Anal. Fís. Quim., 1926, **24**, 297—317).—Mathematical. The classical theory of Langevin, although otherwise successful, does not give a satisfactory interpretation of the influence of temperature. Cabrera has already (A., 1925, ii, 1107) suggested a possible mechanism of the temperature effect. Extending this suggestion, it is assumed that the magnetic axis can occupy only a limited number of positions determined by atomic configuration and environment. Statistical methods lead to a general formula for the magnetic moment, which reduces to the classical Langevin formula when the magnetic axis can take up any position whatsoever, and under certain conditions is identical with the Curie–Weiss law. J. S. CARTER.

Spectral emissivities of tantalum, platinum, nickel, and gold as a function of temperature, and the m. p. of tantalum. A. G. WORTHING (Physical Rev., 1926, [ii], **28**, 174—189; cf. A., 1925, ii, 759).—The spectral emissivities of tantalum have been determined by (*a*) the tubular filament, (*b*) the reflectivity, and (*c*) the comparison at contact methods. For 0·665 μ, the smoothed values at 300°, 1500°, and 2700° Abs. are 0·493, 0·438, and 0·394, respectively; for 0·463 μ, 0·56, 0·50, and 0·43. The present values at incandescence are lower than those previously recorded. Probable sources of error in emissivity determinations, however, are such as to indicate that these lower values are the more trustworthy. The results have been used to construct a temperature scale for tantalum, *i.e.*, the difference between brightness temperature and true temperature as a function of the former. Two determinations of the m. p. of tantalum by the contact method, using tungsten as the known material, gave 3300° Abs. The spectral emissivity of platinum increases linearly with temperature; that of nickel remains constant. The spectral emissivity of gold for 0·665 and 0·535 μ increases with temperature, whilst that for 0·460 μ remains constant. A. B. MANNING.

Physical properties of well-seasoned molybdenum and tantalum as a function of temperature. A. G. WORTHING (Physical Rev., 1926, [ii], **28**, 190—201).—The specific resistance, radiation intensity, and thermal expansion of molybdenum and tantalum have been measured over a wide range of temperature up to about 2800° Abs., making use of their known temperature scales (A., 1925, ii, 759, and preceding abstract). The metals were in the form of well-seasoned filaments in highly-evacuated lamps. The molybdenum used was of a high degree of purity, as shown by its average temperature coefficient of resistance between 0° and 100° (cf. Geiss and van Liempt, A., 1923, ii, 866). For tantalum, a lamp was made from the same wire used in determining the spectral emissivity (preceding abstract). The logarithm of the specific resistance is nearly a linear function of the logarithm of the temperature, the value of $T/\rho \cdot d\rho/dT$ being 1·145 for molybdenum (above 1000° Abs.) and 0·785 for tantalum (1500—2800° Abs.). The thermal expansion of molybdenum is given by $\Delta L/L = 5{\cdot}00\times10^{-6}(T-300)+10{\cdot}5\times10^{-10}(T-300)^2$, and of tantalum by $\Delta L/L = 6{\cdot}60\times10^{-6}(T-300)+5{\cdot}2\times10^{-10}(T-300)^2$. A number of related physical quantities (emissivities, brightness temperatures, etc.) have been calculated from the data obtained. Comparison measurements on moderately pure and very pure molybdenum showed no appreciable variation in radiation properties, but appreciable differences appeared in their specific resistances. A. B. MANNING.

Temperature scale for tungsten. H. A. JONES (Physical Rev., 1926, [ii], **28**, 202—207).—The specific resistance of tungsten and the rate of radiation from a tungsten filament have been determined over a range of temperature from 273° to 3655° Abs. For the range from 273° to 1500° Abs., measurements were made of the resistance of tungsten filaments placed in a constant-temperature compartment of an alundum resistance furnace, through which a stream of pure dry hydrogen was passed. The temperatures were measured by a chromel–alumel thermocouple. For the higher range, 1200—3655° Abs., tungsten filaments were mounted in lamp bulbs and their resistances measured, temperatures being determined by an optical pyrometer. The specific resistance varied from $5{\cdot}00\times10^{-6}$ at 273° Abs. to $117{\cdot}1\times10^{-6}$ ohm/cm. at 3655° Abs. Lamps of the same type were used to measure the rate of radiation from the filament. This varied from 0·000016 watt/cm.^{2} at 300° to 399·4 at 3655° Abs. A. B. MANNING.

Reflecting powers of some metal sulphides. K. ASAGOE and N. KUMAGAI (Mem. Coll. Sci. Kyōtō, 1926, **9**, 439—450).—The reflecting powers of seven metal sulphides were examined in the ultra-violet region, the angle of incidence being 45°. Galena and stibnite had the highest reflecting power. The reflecting powers of zinc blende and galena decreased after 4 months' storage in a desiccator. These two minerals,

and also chalcopyrite, showed a maximum reflexion near 2500 Å. No relationship between the photo-electric activities of the sulphides and the reflecting powers was apparent. S. K. TWEEDY.

Physical properties of tungsten at high temperatures. C. ZWIKKER (Arch. Néerland., 1925, IIIA, **9**, 207—339).—A number of physical properties of tungsten have been re-determined as a function of the temperature, and the values compared with those of other workers (cf. Forsythe and Worthing, Astrophys. J., 1925, **61**, 146). The results include measurements between 1200° Abs. and the m. p. of specific resistance, total radiation intensity, brightness, spectral emissivity, colour temperature, thermionic emission, rate of vaporisation, thermal conductivity, and Thomson effect. Measurements of the brightness of a black body between 1300° and 2600° Abs. are also given. End losses due to the cooling of a filament by the lead-in wires have been determined. Values are given for filaments of various dimensions between 1800° and 2800° Abs.
C. J. SMITHELLS.

International low-temperature scale. W. H. KEESOM and H. K. ONNES (Arch. Néerland., 1925, IIIA, **9**, 114—142).—A detailed account of the present position concerning low-temperature standards. Among matters discussed are: reduction of gas-thermometric scales to the international scale, correction of the international helium scale, the international hydrogen thermometer and its correction. Provisionally the basis of the Kelvin scale is accepted as $\alpha_A=0{\cdot}0036617^4$ ($\alpha_{i\,He}=0{\cdot}0036614$), and thus $0°=273{\cdot}09^4$ or more approximately 273·09° Abs.
R. A. MORTON.

Specific heat of ferromagnetic substances. W. SUCKSMITH and H. H. POTTER (Proc. Roy. Soc., 1926, **A**, **112**, 157—176).—The specific heats of nickel and Heusler's alloy have been determined by the method of Nernst and Eucken at temperatures up to 410°, and simultaneously the magnetisation has been measured by the ballistic method. In each case, the specific heat reaches a maximum at the critical point, but, contrary to the requirements of the Weiss theory of ferromagnetism, beyond that point it falls continuously, not discontinuously. Quenching the alloy from about 400° raises the critical temperature by 8°. R. CUTHILL.

Solid helium. W. H. KEESOM (Compt. rend., 1926, **183**, 26—27).—A brass tube connected with two German-silver tubes was filled with helium under pressure and placed in a bath of liquid helium, the German-silver tubes projecting partly therefrom. The (absolute) temperatures and pressures at which the system became blocked were taken to be points on the fusion curve, and are approximately as follows: 1·1°, 2·6 atm.; 2·2°, 50 atm.; 3·2°, 86 atm.; 4·2°, 150 atm. Helium was also frozen in a glass tube. In one experiment, both the solid and liquid were present together, but no boundary surface between these phases could be observed; probably the indices of refraction of solid and liquid helium are very close to each other. L. F. GILBERT.

Fusion curve of helium. W. H. KEESOM (Compt. rend., 1926, **183**, 189—190; cf. preceding abstract).—The above curve has been followed over the range of pressures 140·5—25·3 atm., corresponding with a temperature range of 4·21—1·13° Abs.
R. CUTHILL.

Active nitrogen. I. Its nature and heat of formation. E. J. B. WILLEY and E. K. RIDEAL (J.C.S., 1926, 1804—1812).—The heat of formation of active nitrogen has been determined by causing a current of the activated gas to react with nitric oxide in a calorimeter and measuring the heat evolved and the amount of nitrogen peroxide produced. A second method was used also, in which the heat developed in the calorimeter when the activated nitrogen reacts with nitric oxide is compared with that produced when it undergoes catalytic decay in the presence of oxygen. The mean value obtained for the heat of formation, 42,500 cal./g.-mol. (about 2·0 volts), supports the hypothesis that active nitrogen is nitrogen in a metastable molecular form. Observations of the effect of various gases in extinguishing the fluorescence of active nitrogen indicate that only those for which the critical increments are less than a value approximately equal to the above heat of formation have a positive effect. A. B. MANNING.

Thermal study of electrolytic lead. Allotropy of lead. A. TRAVERS and HOUOT (Compt. rend., 1926, **183**, 359—361).—From the dilatometric study of electrolytic lead of purity 99·79%, it is concluded that some of the impurities (*e.g.*, tin) are in solid solution in the metal. If the lead is heated, a transition occurs from the two- to the one-phase zone, the latter corresponding with a solid solution; the dissolved constituent is then precipitated as the alloy contracts. Breaks in the temperature–dilatation curves at 60° and 180° indicate the existence of three allotropes of lead, ordinary lead being a mixture of two of these.
J. GRANT.

Precision measurements of heats of vaporisation at low pressures and temperatures. E. DONATH (Z. Elektrochem., 1926, **32**, 316—317).—An apparatus is described for the measurement of heats of vaporisation or sublimation at low temperatures and pressures with an accuracy of about 0·1%. Preliminary measurements have been made with carbon dioxide and ammonia and the data used to calculate values of C_p. The value of C_p for carbon dioxide at 155° Abs. is $7{\cdot}0\pm0{\cdot}4$, and for ammonia at 178·5° Abs. $8{\cdot}25\pm0{\cdot}55$. The results are discussed briefly. J. S. CARTER.

Calorimetric researches. Determination of the heats of combustion of volatile substances in the calorimetric bomb. P. E. VERKADE and J. COOPS (Rec. trav. chim., 1926, **45**, 545—551; cf. A., 1925, ii, 490).—Complete combustion of the substance under investigation is ensured by placing it in a thin glass bulb, on the outside and in the short neck of which 80—90 mg. of paraffin oil are dropped. The whole is placed in the bomb in a deep platinum crucible, and ignited by means of a weighed cotton

thread connecting the bulb to the ignition spiral. The increase in pressure on admitting the oxygen and the downward direction of the explosion lessen the chance of evaporation of the liquid, and complete combustion is ensured by the bursting of the bulb in the middle of the flaming paraffin. The remains of the bulb, and sometimes a little unburnt carbon, are left in the crucible, and the carbon is determined from the difference in weight after ignition. The method gives results agreeing with those of Richards and Davis (A., 1920, ii, 589), and may also be applied to readily oxidisable or saponifiable substances, and to hygroscopic and solid substances of low m. p.

J. GRANT.

Vapour pressure and heat of evaporation at low temperatures. J. E. VERSCHAFFELT (Arch. Néerland., 1924, IIIA, 8, 109—135).—A discussion at length of the accuracy at low temperatures of the equation connecting vapour pressure and molecular heat of evaporation: $d \log p/dT=\lambda/RT^2$ in view of its importance in the calculation of the chemical constant from data obtained at very low temperatures.

C. J. SMITHELLS.

Vapour pressure of anhydrous oxalic acid. W. A. NOYES, jun., and D. E. WOBBE (J. Amer. Chem. Soc., 1926, 48, 1882—1887).—The vapour pressure of anhydrous oxalic acid, determined between 60° and 105° by a dynamic method, is given by the equation $\log p(\text{mm.})=12{\cdot}22292-(4726{\cdot}9499/T)$. The molar heat of sublimation is thus nearly constant at 21,650 cal. The specific heat of the vapour is believed to be not very different from that of the solid.

S. K. TWEEDY.

Variation of pressure with temperature in evacuated vessels. N. R. CAMPBELL (Phil. Mag., 1926, [vii], 2, 369—383).—Vessels, both of glass and metal-coated glass, after being well exhausted at a temperature of not less than 380°, have been repeatedly subjected to three operations: (*a*) heating at a temperature T_a between 50° and 200°; (*b*) cooling to T_b between 13° and 20°; (*c*) "clean-up" or reduction of pressure to p_c by the passage of a thermionic discharge from a heated tungsten filament to a nickel anode. The results are of importance for high vacuum technique, and indicate that it is impossible to make a vessel with bare glass walls in which the pressure will remain permanently as low as 10^{-6} mm. in such conditions as usually prevail in practice. The pressure can be reduced to 10^{-8} mm. by the clean-up, but a very moderate rise of temperature will restore the original value. This behaviour is attributed to the diffusion of gas through the walls of the vessel. On the other hand, by coating the walls with evaporated metal, and taking care that the pressure during evaporation is as low as possible, it is easy to obtain vessels in which the pressure at 20° is permanently less than 10^{-7} mm. and not more than 10^{-6} mm. at 120°,

M. S. BURR.

Phenomena in dilute gases. T. SEXL (Ann. Physik, 1926, [iv], 80, 515—523).—Mathematical, extending the work of Baule (A., 1914, ii, 425).

R. A. MORTON.

Isotherms of hydrogen, of nitrogen, and of hydrogen–nitrogen mixtures, at 0° and 20°, up to a pressure of 200 atm. T. T. H. VERSCHOYLE (Proc. Roy. Soc., 1926, A, 111, 552—576).—Previous determinations of the isotherms of hydrogen and nitrogen are critically discussed. The apparatus used for the present determinations is based on that used at Leiden (Comm. Phys. Lab., Leiden, 97A etc.). The piezometer was of steel and was of the divided pattern, designed primarily for use at low temperatures. It was permanently mounted, the normal volume being determined in a volumenometer. The position of the mercury was determined by measuring the resistance of a fine platinum wire stretched down the centre of the tube, the relation between volume and resistance being obtained by compressing a known volume of hydrogen and measuring the resistance at several pressures. The accuracy of determination of the isotherms is estimated at 1 in 1000. The results are expressed by the equation $pv=A+Bp+Cp^2$. When p is expressed in international atm. and v in terms of the normal volume, the values of A, B, and C for hydrogen at 0° are 0·99937, $0{\cdot}6263\times10^{-3}$, and $0{\cdot}168\times10^{-6}$, respectively; for nitrogen at 0°, 1·00049, $-0{\cdot}4961\times10^{-3}$, and $3{\cdot}334\times10^{-6}$; and for the 50% mixture at 0°, 0·99969, $0{\cdot}3067\times10^{-3}$, and $1{\cdot}147\times10^{-6}$. The corresponding figures at 20° for hydrogen are 1·07257, $0{\cdot}6505\times10^{-3}$, and $0{\cdot}069\times10^{-6}$; for nitrogen, 1·07370, $-0{\cdot}2798\times10^{-3}$, $2{\cdot}800\times10^{-6}$; and for the 50% mixture, 1·07291, $0{\cdot}3979\times10^{-3}$, and $0{\cdot}933\times10^{-6}$, respectively. There is no justification for assuming the pv values for a mixture to be a linear function of the composition, at least when the critical temperatures of the component gases are widely different.

A. B. MANNING.

Equation of state of solid substances in connexion with the general expression for the energy. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1926, 29, 497—514; cf. this vol., 570).—Mathematical. The equation of state valid at high temperatures is modified so that it may be applicable to matter at moderately high and at very low temperatures. The cases of copper at 1083° and 20° and of benzene at its f. p. are discussed, and finally that of copper near the absolute zero, the coefficient of expansion and specific heat being calculated at about −253°, in good agreement with the observed values.

G. M. BENNETT.

Molecular association and the equation of state. M. F. CARROLL (Phil. Mag., 1926, [vii], 2, 385—402).—Theoretical. An attempt is made to show that all substances are associated, even the inert gases, provided the temperature is low and the pressure high. It is assumed that the discrepancy between van der Waals' equation as applied to actual fluids and the true equation of state depends entirely on association. Considering only the simple case of association to double molecules, a modified equation is derived and various applications of it are discussed.

M. S. BURR.

Density of carbonado and lustre carbon, W. A. ROTH, G. NAESER, and O. DÖPKE (Ber., 1926. 59, [*B*], 1397—1399).—A specimen of carbonado had

$d^{16\cdot85}$ 3·457 and, judged from density and heat of combustion, appeared to consist of about 3·5% of amorphous carbon and 96·5% of white diamond. The values d 1·878 and 2·02 were found for black and grey lustre carbon; the latter specimen was prepared at the higher temperature. Homogeneous specimens are very difficult to prepare.

H. WREN.

Measurement of the viscosity of pure liquids. J. DUCLAUX and J. ERRERA (Bull. Soc. chim. Belg., 1926, **35**, 198—203).—Further work with the apparatus previously described (A., 1925, ii, 1048) shows that constant results are obtained with the same liquid, that the duration of flow is inversely proportional to the pressure, and proportional to the viscosity referred to that of ether for acetone, carbon tetrachloride, xylene, and amyl alcohol.

J. M. GULLAND.

Method of measuring viscosity at higher temperatures. H. M. MERCER.—See B., 1926, 653.

Rate of flow of various gases through a porous wall. J. SAMESHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 5—8).—The rates of effusion of several gases through a porous plate 0·15 cm. thick have been measured. With a plate of this thickness, the simple diffusion laws do not hold, and an expression involving both the viscosity of the gas and its mol. wt. is necessary to express the results. The simple law was found to apply when the earthenware plate was replaced by a perforated platinum plate.

S. BARRATT.

Surface tension of liquid metals. I. Tin and lead. L. L. BIRCUMSHAW (Phil. Mag., 1926, [vii], **2**, 341—350).—The surface tensions of liquid tin and lead have been determined by the method of maximum bubble pressure, at temperatures from the m. p. to approximately 1000°. The values at the lower temperatures agree very well with those found by Hogness (A., 1922, ii, 29), but the temperature coefficient for the surface tension of tin obtained by him has not been confirmed. The increase with temperature of the relationship $\gamma^{\frac{1}{3}}/D$, where γ is the surface tension and D the density, indicates that both these metals in the liquid state may be highly associated (cf. Sugden, A., 1924, ii, 153).

M. S. BURR.

Elasticity coefficients and the thermodynamic integration factor for the solid state. A. PRESS (Phil. Mag., 1926, [vii], **2**, 431—436).—Mathematical. Supplementing the work of Grüneisen and Ratnovski (cf. Andrews, *ibid.*, 1925, [vi], **50**, 667).

M. S. BURR.

Methods of physico-chemical research at very high temperatures. F. M. JAEGER (Bull. Soc. chim. Belg., 1926, **35**, 211—228).—A lecture delivered on May 2, 1926.

Diffusion of helium and hydrogen through quartz glass at the ordinary temperature. H. M. ELSEY (J. Amer. Chem. Soc., 1926, **48**, 1600—1601).—Clear quartz glass is permeable to helium under a pressure of 100 atm. at the ordinary temperature. Under the same experimental conditions, no permeability to hydrogen was detected.

M. CARLTON.

Temperature of maximum density of alcohol–water mixtures. J. P. MCHUTCHISON (J.C.S., 1926, 1898—1899).—The influence of methyl, ethyl, *n*-propyl, *iso*propyl, and *n*-butyl alcohols on the temperature of maximum density of water has been investigated by Wright's method (*ibid.*, 1919, **115**, 119). Ethyl and *n*-propyl alcohols produce first a rise and then, with increasing concentration, a fall of temperature of maximum density. The others cause a fall, but, contrary to the requirements of Despretz's law, there is no proportionality between the lowering of the maximum-density temperature and the concentration of alcohol.

M. S. BURR.

Miscibility of quaternary mixtures of water and alcohols. P. BRUN (Compt. rend., 1926, **183**, 207—210; cf. A., 1925, ii, 769).—The system water–*iso*butyl alcohol–*iso*amyl alcohol has been studied, and miscibility is found to occur over two ranges of concentration separated by a range of immiscibility. Data have also been obtained for the quaternary system consisting of the above liquids with ethyl alcohol.

R. CUTHILL.

Diffusion of solids. P. HENRY (Bull. Soc. chim., 1926, [iv], **39**, 836—841; cf. Weiss and Henry, A., 1922, ii, 207, 487).—The relationship $V=Ka^T$, where V is the rate of formation of a homogeneous binary alloy from a heterogeneous alloy at temperature T, K and a being constants, is confirmed for an alloy of copper (51·7%) and nickel. The quenching of a solid solution in the liquid state, which varies with the temperature of the alloy and the rate of cooling, may be characterised by measuring the time taken for the heterogeneous quenched alloy to become homogeneous at the solidification temperature. Alloys of antimony were examined by depositing electrolytically silver or copper on crystals of antimony, the whole being heated in a vacuum and a polished section examined microscopically. With the copper alloy, the extent of interpenetration, which is decreased by hammering, is very regular perpendicular to the cleavage planes, and less regular, but twice as great, parallel to these planes. Preliminary experiments carried out in the same way with isomorphous sodium and silver chlorides and potassium perchlorate and permanganate yielded positive results.

S. K. TWEEDY.

Intermetallic compounds, with special reference to compounds of tin. I to V. W. HUME-ROTHERY (J. Inst. Metals, 1926, **35**, 295—361).—See this vol., 356.

Mixed crystals. T. BARTH and G. LUNDE (Z. physikal. Chem., 1926, **122**, 293—334).—The structure of various mixed crystals has been investigated by the X-ray method previously described (this vol., 114). Although similarity of lattice structure is a necessary condition for the formation of mixed crystals, the permissible difference is greater than was formerly supposed. In no case have the interference lines which would result from a regular distribu-

tion of the two components in the mixed crystal (cf. Laue, Ann. Physik, 1918, [iv], **56**, 493), been observed. Cuprous iodide and silver iodide form a continuous series of mixed crystals, the lattice dimensions of which can be represented by putting $n=2$ in Grimm and Herzfeld's equation (Z. Physik, 1923, **16**, 79): $r^{n-1}=a^{n-1}.x+b^{n-1}(1-x)$, where r is the lattice constant of a mixed crystal containing x g.-mol.% of a constituent of lattice constant a, and $1-x$ g.-mol.% of a constituent of lattice constant b, and n is the index of repulsion. Thallous bromide and thallous iodide form a continuous series of mixed crystals of the crystalline form of cæsium chloride, the lattice constant of the iodide being increased by addition of small quantities of the bromide. The systems cuprous bromide–silver bromide and cuprous chloride–silver chloride manifest only very slight miscibility. Silver iodide and silver bromide form a continuous series of mixed crystals, for which, however, the above equation is not valid. The iodide can crystallise in the bromide lattice, which is of the sodium chloride type, in amounts up to 50%, whilst, on the other hand, the bromide can be present as an isomorphous admixture in both the zinc blende and the wurtzite types of the iodide. Silver bromide and thallous bromide are only slightly miscible, but a *compound*, 2AgBr,3TlBr, has been isolated. Silver iodide, even in the form of natural argyrodite, appears to contain crystals of both the wurtzite and the zinc blende type. R. CUTHILL.

Relation between colour and structure of alloys. II. M. CHIKASHIGE, I. KURIYAMA, T. MIYOSHI, C. TEISCHÔ, J. NOSÉ, R. TAKEUCHI, and S. KAO (Z. anorg. Chem., 1926, **154**, 333—352; cf. A., 1923, ii, 30).—The intensity of reflexion of an alloy bears a closer relation to its structure than does its colour. In general, compounds are indicated by maxima on the intensity curve and eutectics by minima, but the latter may be displaced in the direction of the less lustrous metal. The whiteness of alloys of copper with antimony increases with the antimony content to a maximum at Cu_3Sb, after which it falls slightly. The intensity of reflexion is depressed by antimony. A maximum is found at Cu_3Sb and a minimum for the alloy which contains 10% more copper than the eutectic; there is, however, no break at Cu_2Sb. Addition of aluminium to copper increases its whiteness up to 40% of aluminium, after which the whiteness falls slightly. The intensity curve has maxima at 5% of aluminium and at Cu_3Al and $CuAl_2$. Alloys of magnesium and zinc are less lustrous than their components; there is a slight maximum corresponding with the compound Mg_2Sn and a minimum on the tin side of the eutectic. The whiteness of copper is steadily increased by the addition of silver; the lustre of silver is diminished by the addition of copper to a minimum at the eutectic. Alloys of copper with 10% of zinc are yellow, with 35% red, with 70% white, and with more zinc grey. The intensity curve has maxima at 10, 50, and 80% of zinc. The intensity curve for alloys of tin and antimony has minima at 8 and 89 at.-% of antimony, corresponding with saturated mixed crystals, and a sharp maximum at 57 at.-%; the colour curve is substantially parallel to the intensity curve. A. GEAKE.

Separation of supersaturated mixed crystals. W. FRAENKEL [with P. SCHALLER and (FRL.) QUINCKE] (Z. anorg. Chem., 1926, **154**, 386—394).—When a silver-copper alloy (92% Ag) is quenched from 700—750° and subsequently tempered, the hardness increases, and this is ascribed to the gradual separation of copper from mixed crystals which are supersaturated at the lower temperatures. Thus at 205° the hardness rises from 50 to 95 and then remains constant, at 287° it rises to 107 and then falls, and at 350° it rises to 78 and subsequently falls. Increasing hardness is accompanied by decreasing electrical resistance, whether measured at the ordinary or at the tempering temperature. The alloy "aeron" (aluminium with 1% Si and 4% Cu), which may be hardened at 175°, shows a similar decrease in resistance at this temperature. A. GEAKE.

Formation of deformation twins in eutectics. R. VOGEL (Z. anorg. Chem., 1926, **154**, 399—404).—The growth of crystals in the eutectic alloy containing 18% of zinc and 82% of cadmium may be either dendritic or spherolithic. When the growth is dendritic, the areas of growth are separated by parallel lines, and after working, twinning planes appear as parallel lines, the direction of which changes at the boundaries of the areas of growth. When the growth is spherolithic, similar changes in direction occur, resulting in spiral lines. A. GEAKE.

Influence of small additions of lead to gold. L. NOWACK (Z. anorg. Chem., 1926, **154**, 395—398).—Gold containing 0·7 or 0·06% of lead is brittle and cannot be rolled; this is due to a fine network of the brittle compound Au_2Pb between the primary gold crystals. Ignition at 380°, 412°, 650°, or 900° in air or hydrogen increases the size of the crystals, but does not render the gold workable. Gold containing 0·006% of lead behaves normally. Coinage gold, containing 10% of copper, is similarly affected by lead. A. GEAKE.

Behaviour of the platinum metals towards silver and gold during cupellation at 1100—1200°. W. TRUTHE (Z. anorg. Chem., 1926, **154**, 413—428).—500 Mg. of silver or 250 mg. of gold were cupelled with 3 g. of lead for 6 or 7 min. at 1150° with the addition of amounts of platinum metals from 0·01 to 200% of the weight of silver or gold, respectively. The loss of silver alone was 10·6 mg. and of gold alone 1·52 mg. and the loss of mixtures of these was approximately as would be expected. In the presence of considerable amounts of osmium, the loss of weight is greatly increased. The other platinum metals have the reverse effect, due to the retention of lead, and this is most strongly marked with palladium. Thus when an equal weight of palladium is added to the above weights of silver or gold, the excess weights of the resulting beads are 244 and 129 mg., respectively. A. GEAKE.

Limits of resistance of tungsten-molybdenum mixed crystals. J. A. M. VAN LIEMPT (Rec. trav. chim., 1926, **45**, 508—521).—Examination of the

corroding effects of various mixtures of acids on pure tungsten and molybdenum and of mixed crystals of these metals shows that for a definite proportion of tungsten in the mixed crystal corrosion commences rapidly. It is suggested that the critical value depends on the reagent, and that where an oxidising acid is used the effect is due to the production of an oxide, which then dissolves in one of the other components. The results cannot be explained by Tammann's theory, especially as no apparent analogy exists between the effect of cold-working and mixed crystallisation on the electrical and optical properties and on the corrodibility of the metals. A method for the analytical separation of the metals by selective dissolution is indicated. J. GRANT.

Change of volume of cast iron on solidification and a criticism of the double diagram of the system iron-carbon. K. HONDA and H. ENDO (Z. anorg. Chem., 1926, **154**, 238—252).—The specific volume of a cast iron containing 4·1—4·3% of total carbon, 2·8—3·0% of graphite, and 0·8—2·3% of silicon varies nearly linearly with the temperature, from 0·1480 at 1300° to 0·1433 at the m. p. (1130°). Cast iron containing 4·3% of total carbon, 3·08% of graphite, and 2·03% of silicon contracts 1·65% on solidification. When the total carbon content is kept constant, and the silicon and graphite contents are diminished, the contraction on solidification diminishes, and becomes zero for 0·38% of silicon, 2·06% of graphite, and 4·1% of total carbon. When the silicon is further diminished to 0·08% and the graphite to 1·17%, the cast iron expands 1·76% on solidification. The percentage change of volume varies nearly linearly with the graphite content, and by extrapolation the expansion is about 3·6% when this is zero. It is calculated that pure iron contracts 4·4% when solidified. It is also concluded that the solid phase separating from cast iron contains only cementite, and that graphite is formed by a secondary reaction. The volume change on solidification is the difference between the contraction due to formation of solid and the expansion due to decomposition of cementite. The latter is calculated to be 11·8% of the volume of cementite, and volume changes on solidification are calculated which are in reasonable agreement with the observed values. A. GEAKE.

Vapour pressure of solid sodium and solid potassium amalgams. F. E. POINDEXTER (Physical Rev., 1926, [ii], **28**, 208—228).—The vapour pressures of eight sodium amalgams ranging in concentration from 1 to 15 mols. of mercury to 1 mol. of sodium, and of three potassium amalgams, of 5, 10, and 21 mols. of mercury to 1 mol. of potassium, have been determined at temperatures between −56° and 90°. For each amalgam the logarithm of the pressure, which varied from about 10^{-8} mm. to 10^{-3} mm., is an approximately linear function of the reciprocal of the absolute temperature. The heats of reaction, calculated by means of the van 't Hoff isochore, varied from 15,000 cal. for sodium amalgams rich in mercury, to 14,000 cal. for the 2 : 1 amalgam, indicating that most of the heat of reaction between sodium and mercury is liberated in the formation of the initial compounds. The heats of reaction for the potassium amalgams were calculated to be 25,500 cal. The relation of the heats of reaction to the changes in free energy and the temperature gradients of the *E.M.F.* of concentration cells (cf. Richards and Conant, A., 1922, ii, 340) is discussed. The results have been used to calculate the efficiency of a sodium mercury vapour trap (cf. A., 1925, ii, 818, 895). A. B. MANNING.

Rhythmic crystallisation of potassium alum in the metastable state. K. HRYNAKOWSKI (Rocz. Chem., 1926, **6**, 150—154).—Crystals of alum placed at the boundary of a supersaturated and a saturated solution of alum grow in a rhythmic manner, determined by the structure of the successive layers. The first is oriented perpendicularly to an edge of the octahedron, and is followed by a layer containing vacuoles, without any apparent arrangement, then a dendritic layer, next a layer containing pear-shaped vacuoles, and finally a bipolar layer. All these zones, with the exception of the first vacuole zone, are oriented perpendicularly to the edge of the octahedron, and their relative breadths are respectively as $2^{-5} : 2^{-6} : 2^{-4} : 2^{-3}$. R. TRUSZKOWSKI.

Volume changes on dissolution in the light of the internal pressure theory of G. Tammann. F. DREYER (Z. anorg. Chem., 1926, **154**, 253—260).—From the equation of Tammann, $\Delta v=\Delta v_1+\Delta v_2+\Delta\Sigma v$, where Δv is the change in volume on dissolution, Δv_1, Δv_2 the changes in volume of the solvent and solute, respectively, corresponding with the changes in internal pressure, and $\Delta\Sigma v$ the sum of the volume changes when solvent and solute at the internal pressure of the solution are mixed, the quantities $\Delta\Sigma v$ are evaluated for the dissolution of alkali halides in water at 15°. The values of Δv are taken from the data of Happart, the internal pressures of solution are deduced from the temperatures of maximum density, and the corresponding values of Δv_1 taken from the compressibility data of Amagat. The internal pressure of water at 15° is calculated to be 7008 atm., and those of salts are calculated from Herz's values at the b. p. to be 113, 84, 61, 80, 65, and 47×10^3 for sodium chloride, bromide, and iodide, and potassium chloride, bromide, and iodide, respectively. The volume change $\Delta\Sigma v$ is proportional to the concentration of the solution, and for 1% solutions of the above salts is 0·82, 0·78, 0·85, −0·05, 0·15, and 0·29 c.c. per 1000 c.c. of solution, respectively. At 20°, the values for sodium chloride, potassium bromide and iodide are 0·47, −0·10, and 0·23, respectively. A. GEAKE.

Solubility of iodine in aqueous hydrogen iodide and the electrolytic dissociation of hydrogen tri-iodide. M. HLASKO and M. KADENACÓWNA (Rocz. Chem., 1926, **6**, 228—235)—In concentrated solutions of hydriodic acid saturated with iodine, the proportion of hydrogen tri-iodide exceeds that of hydrogen iodide; in solutions of the latter below $N/16$, these two values are approximately equal. Conductivity measurements indicate that the iodide and tri-iodide are dissociated to the same extent, viz., $\alpha=0\cdot92$ in $N/10$ solution. R. TRUSZKOWSKI.

Equilibrium in the system potassium oxalate-water. N. WOSKRESSENSKAJA (Z. anorg Chem., 1926, **155**, 115—120).—Measurements of the solubility of potassium oxalate have been made between the eutectic temperature (−6·34°) and the b. p. at 760 mm. (107°). A monohydrate separates out at or near the eutectic point. M. CARLTON.

Solubility of cholesterol in ethyl and methyl alcohol at different temperatures. L. ERLANDSEN (Biochem. Z., 1926, **174**, 53—54).—The solubility of cholesterol in methyl and ethyl alcohol has been measured between 0° and the b. p. of the solvent. The methyl alcohol solution contains 0·34 g. per 100 at 0° and 5·32 at 64·9°. The ethyl alcohol solution contains 0·68 g. per 100 at 0°, and 27·7 at 78·8°. E. C. SMITH.

Solubility of lead iodide in solutions of sodium chloride at 25°. L. J. BURRAGE (J.C.S., 1926, 1896).—The solubility of lead iodide varies from 0·758 g. per 100 g. of solution to 1·79 g. for concentrations of sodium chloride from zero to 29·80 g., respectively. A further increase in concentration of sodium chloride causes a change in solid phase from lead iodide to one containing chlorine.
M. S. BURR.

Effect of salts on the solubility of glycine and tyrosine. K. ANDO (Biochem. Z., 1926, **173**, 426—432).—Cations increase the solubility of glycine in water at 22° in the order Rb, K, Na, Li, Ba, Ca. The influence of anions is scarcely perceptible in the case of glycine, but with tyrosine, anions in the series SO_4, Cl, Br, I have increasing influence in lowering the solubility of this amino-acid. Whereas with tyrosine the univalent cations have practically no action, calcium and barium diminish the solubility.
H. D. KAY.

Compounds of solute and solvent from partition coefficients. N. R. DHAR (Z. anorg. Chem., 1926, **155**, 42—48).—The partition coefficients of substances such as lithium chloride, silver perchlorate, dimethylammonium chloride, citric and tartaric acids, etc., between water and a non-aqueous solvent are much greater than the ratio of their solubilities. Similar results have been obtained with caffeine, strychnine, and atropine for water and chloroform. The relations are explained by assuming the formation of a compound of solute and solvent. The tendency to form such compounds is the greater the greater the solubility of the substance concerned.
M. CARLTON.

Adsorption of water vapour on a plane fused quartz surface. Isosteric heats of adsorption of water on silica and platinum. S. LENHER (J.C.S., 1926, 1785—1792).—The adsorption of water vapour on a plane quartz surface, at temperatures from 290·8° to 313° Abs., has been measured by a method previously described (McHaffie and Lenher, A., 1925, ii, 854). The pressure coefficient of adsorption is greater than the temperature coefficient of de-adsorption, since adsorption increases when pressure and temperature are raised simultaneously. No adsorption appears to take place until a definite pressure, rather near to saturation pressure, has been reached. The results show that the silica content, as well as the alkali content, plays a part in the formation of the water film on a glass surface. The free energy changes accompanying the adsorption have been calculated. It is suggested that, at low pressures, a gas layer of unimolecular thickness is built up, and that the adsorption values obtained at comparatively high pressures refer to the formation of a multimolecular liquid layer. The isosteric heats of adsorption of water vapour at constant pressure on quartz and platinum, at different temperatures and for different amounts adsorbed, have been calculated. These do not refer to the firmly held unimolecular layer, since the temperatures reached are not high enough to remove this. The heat of adsorption of this layer is probably much greater than the latent heat of condensation. M. S. BURR.

Adsorption of gases on glass and silver powder. F. DURAU (Z. Physik, 1926, **37**, 419—457).—The object of the work was to determine the number of layers of molecules in the adsorbed film and, in particular, to test Regener's hypothesis, which is found not to be supported by the results. Full precautions were taken to avoid all likely sources of error. Nitrogen, hydrogen, and probably dry air are not absorbed by common glass at 18°. Carbon dioxide is adsorbed reversibly and to an extent at 760 mm., which corresponds with 16% of a unimolecular layer. On powdered silver at 18° and 760 mm., nitrogen and hydrogen form a layer equivalent to 18% and 5·7% of a unimolecular film, respectively, whereas air gives a value 44% and the effect is irreversible, probably due to chemical action. E. B. LUDLAM.

Adsorptive powers of charcoal. I. OGAWA (Biochem. Z., 1926, **172**, 249—261).—Sodium chloride is hydrolytically adsorbed by sugar charcoal, the solution becoming alkaline. Blood charcoal is inactive, but can be activated by heating strongly. Chemical analysis failed to show any difference between activated and inactive charcoal, and no difference could be detected by Röntgen rays.
C. RIMINGTON.

Adsorption from solution by ash-free adsorbent charcoals. I. Purification of adsorbent charcoals. E. J. MILLER (J. Physical Chem., 1926, **30**, 1031—1036; cf. Firth and Watson, A., 1924, ii, 542; Bartell and Miller, A., 1922, ii, 741).—Adsorbent charcoals are readily purified by two or three extractions with hydrofluoric acid alone or admixed with hydrochloric or sulphuric acid. The ash content is reduced to a few hundredths or less of 1%, the size of particle determining the limit of purification possible. The results obtained in adsorption experiments using these purified charcoals are free from the contradictions shown by unpurified materials. Prolonged heating removes most of the nitrogen in the charcoal. L. S. THEOBALD.

Absorption of iodine by various substances. A. LOTTERMOSER and L. HERRMANN (Z. physikal. Chem., 1926, **122**, 1—27).—The absorption of iodine from solutions of iodine and potassium iodide by basic

lanthanum acetate gels possesses all the characteristics of a true adsorption effect. With increasing age the specific adsorptive power of the gels decreases, but no further ageing occurs after iodine is adsorbed. The product obtained from freshly-prepared gels is brown in colour, but with older gels it is blue or green. Potassium iodide is taken up only to a small extent, and is readily displaced by iodine, so that the colour is not due to the iodide. The absorption of iodine by wheat gliadin is a closely similar process, but is complicated by swelling effects. In the case of cholic acid, the absorption is apparently largely determined by the crystalline form; this supports the view that in the substance formed the iodine is present as iodine of crystallisation only (cf. Küster, A., 1895, i, 322). Contrary to the statement of Wilks (J.C.S., 1912, **101**, 366), the absorption of iodine from carbon tetrachloride solutions by calcium hydroxide involves a chemical reaction, the amount of iodine taken up increasing with increase in the water content of the hydroxide. Using the oxide instead of the hydroxide, however, the effect is purely one of adsorption, whilst with the carbonate no absorption of any kind occurs. R. CUTHILL.

Adsorption of iodine by precipitated magnesia. A. HAMY (Compt. rend., 1926, **183**, 129—131).—The reversible formation of a reddish-brown coloration by the action of iodine on magnesia is assisted if the latter is freshly precipitated and if the mixture is stirred. The precipitate is rapidly decolorised by alcohol, the colour being due to adsorption of I_2 molecules, in a quantity (q) which varies with the concentration (C) of iodine in the solution according to $q=\alpha C/(\beta+C)$, where α and β are constants. Since molecules of tri-iodide may be present in solutions containing more iodine, this equation must be modified. It is shown that the adsorbed iodine forms an incomplete unimolecular layer around the adsorbing substance. The curves connecting the concentrations of iodine in the solution and in the precipitate are straight lines for concentrations of iodine in the liquid of more than $0{\cdot}69\times10^{-3}$ g. per litre. J. GRANT.

Adsorption and reaction. I. Setting of plaster of Paris. H. A. NEVILLE (J. Physical Chem., 1926, **30**, 1037—1042; cf. Cavazzi, A., 1913, ii, 136; Traube, A., 1919, ii, 499; Ostwald and Wolski, A., 1921, ii, 47).—The setting of plaster of Paris has been studied thermometrically, the maximum shown on the time–temperature curves being taken as the time of setting. Setting occurs in two stages, (*a*) adsorption, accompanied by a contraction in volume and a slight heat effect, and (*b*) a resulting exothermic chemical reaction between the adsorbed liquid and the adsorbent (*i.e.*, formation of crystals of gypsum), with an attendant increase in volume. The accelerating effect of the addition of 20 common inorganic substances on the time of setting has also been studied. The order of accelerating effect of cations is $K>NH_4>Na>Li$; $Zn=Cu>Mg$; the slight limiting effect of the anions is $I>NO_3>Br>Cl$. Contrary to Rohland (A., 1908, ii, 842), the accelerating effect is due, not to the increased solubility of calcium sulphate, but to the colloidal nature of the mixture of plaster of Paris and water. L. S. THEOBALD.

Adsorbent properties of cellulose nitrate. J. DUCLAUX (Rev. gén. Colloïd., 1926, **4**, 137—142).—Cellulose nitrate of about 11·5% nitrogen content, soluble in ether–alcohol, is best applied as an adsorbent in the form of sheets of calico impregnated with the nitrate. Basic dyes, especially, are strongly adsorbed from aqueous solutions; thus methylene-blue is taken up to the extent of 5% by weight of the adsorbent. Caramel and alizarin, although acidic, are also readily adsorbed. Impregnated filters as described may be superposed in any number, and are useful for adsorbing dyes from large volumes of dilute aqueous solution; subsequently the adsorbed material may be recovered by extraction with alcohol. W. A. CASPARI.

Adsorption of dissolved substances. I. A. CHARRIOU (J. Chim. phys., 1926, **23**, 621—647).—The effect of concentration, temperature, washing, and other factors on the adsorption of various inorganic substances from aqueous solution has been studied, more especially with a view to the elimination of adsorption errors from analytical processes. The amount of lime adsorbed by ferric hydroxide precipitated by the addition of ammonia to a solution of an iron salt in the presence of calcium salts depends on the quantity of calcium hydroxide produced in accordance with the equation, $CaCl_2+2NH_3+2H_2O \rightleftharpoons 2NH_4Cl+Ca(OH)_2$, since it increases with increase in the concentration of calcium chloride present, at first rapidly, and then more slowly, but does not approach a limit; whilst addition of ammonium chloride causes a continual decrease in the adsorption. Increase in the concentration of ammonia causes initially an increase in adsorption, due to the normal mass action effect in the above equation, followed by a decrease, since larger concentrations of ammonia combine with the calcium chloride and so displace the equilibrium in the reverse direction. The adsorption cannot be represented by Freundlich's formula.

Aluminium hydroxide precipitated by ammonia in the presence of either potassium chromate or ammonium sulphate adsorbs the chromic or sulphuric acid produced by hydrolysis, the amount adsorbed increasing with the concentration of the salt, exponentially in accordance with Freundlich's equation, $x=kc^{0\cdot41}$. The washed, precipitated aluminium hydroxide also adsorbs chromic acid from a solution of potassium chromate, but much more slowly than at the moment of precipitation. It is not possible to remove all the adsorbed acid by washing with boiling water.

Humic acid, prepared from sugar by the method of Berthelot and André (A., 1891, 1089), adsorbs potassium hydroxide from its solutions, the amount adsorbed following Freundlich's law, $x=kc^{0\cdot235}$. Less potassium hydroxide is adsorbed from equivalent solutions of potassium carbonate and hydrogen carbonate, and very little from a solution of potassium chloride, owing to the smaller amount of potassium hydroxide produced by hydrolysis, but in the last case the amount of adsorption is greatly increased by the addition of chalk, which removes the hydrochloric acid and thus increases the hydrolysis.

The incomplete separation of iron and aluminium

from calcium and magnesium by the nitrate method of Deville (Ann. Chim. phys., 1853, **38**, 5) is due to adsorption of lime and magnesia by the iron and aluminium oxides, which adsorption is greater the higher the temperature employed to decompose the nitrates, and is still considerable at 150°, the lowest temperature at which decomposition is possible. Exact results may be obtained, however, if the precipitation of the sesquioxides is carried out in the presence of at least 2 g. of ammonium nitrate, the whole evaporated to dryness at 150°, and the insoluble oxides washed by decantation with boiling water. J. W. BAKER.

Adsorption of salts by the colloidal substances of certain micro-organisms. P. N. PAVLOV (Ukraine Chem. J., 1926, **2**, 48—63; cf. A., 1925, ii, 958).—According to Ostwald, the poisonous action of salts on organisms is dependent on adsorption (A., 1907, ii, 981; 1910, ii, 592). Equations are derived expressing the relation between the duration of life (T) of an organism, the concentration of the substances in the surrounding medium, the volume of the solution, and the density of population of the organisms. Experiments with *Artemisia salina*, at 25—26° in the water in which it grows naturally and in this water diluted or concentrated to varying amounts, c, gave results expressed by an equation of the type $\log 1/T=ac^n$. For the diluted solutions this becomes $\log T=2{\cdot}13\,.\,c^{0{\cdot}35}$, and for the concentrated solutions $\log T=50{\cdot}28\,.\,c^{1{\cdot}24}$. Observations with *Gammarus pulex* var. at 17·5° in sodium chloride solutions of varying concentration gave results in accord with the equation $\log T=5{\cdot}738\,.\,c^{0{\cdot}54}$. The results given by Ostwald for *Daphnia magna* (*loc. cit.*) are in agreement with $\log T=1{\cdot}71\,.\,c^{0{\cdot}3}$. T. H. POPE.

Adsorption of soluble constituents by insoluble precipitates and the formation of mixed crystals. G. F. HÜTTIG and E. MENZEL (Z. anal. Chem., 1926, **68**, 343—358).—Precipitation of lead sulphide from solutions of lead nitrate containing sodium bromide under the most favourable conditions for the formation of mixed crystals of lead sulphide and sodium bromide yielded a mixture of lead sulphide and lead sulphobromide, $PbS,PbBr_2$, containing only traces of sodium bromide. Investigation of the system lead sulphide–sodium bromide in the fused and solid states showed no tendency to mixed crystal formation. Fusion of equimolecular mixtures of silver and sodium chlorides followed by leaching of the fused mass and thorough washing of the silver chloride with hot water invariably left 0·26% of sodium chloride in the silver chloride residue, but, by altering the ratio of the two chlorides in the fusion, amounts varying from 0·21 to 1·68% of sodium chloride were retained. Potassium and rubidium halides when fused with the corresponding silver halide were almost completely removed by washing the fused mass; lithium halides, on the other hand, were retained to about the same extent as the corresponding sodium salt. The greater tendency of sodium and lithium salts to form mixed crystals is due to the closer similarity of their lattice constants to those of the corresponding silver salts. Precipitation of silver chloride in the presence of sodium chloride gave products containing only 0·02% of sodium chloride. Again, only traces of permanganate were occluded by freshly-precipitated barium sulphate, although, by prolonged keeping of the solution before filtration, mixed crystals containing up to 40% of potassium permanganate have been obtained by Grimm. It is concluded, therefore, that in most analytical operations involving precipitation of an insoluble salt from a solution containing an isomorphous soluble salt, the precipitate is never in equilibrium with the solution; in some cases, prolonged keeping of the precipitate in contact with the solution results in an enrichment of the precipitate in one of the salts in solution (*e.g.*, barium sulphate in potassium permanganate and calcium oxalate in magnesium oxalate), and in other cases in the slow solution of some of the salt originally occluded due to a change in the surface energy of the precipitate caused by slow crystallisation or closer packing in the lattice (*e.g.*, the adsorption of phosphoric acid by metastannic acid). A. R. POWELL.

Adsorption and swelling. I. V. KUBELKA and I. TAUSSIG (Koll. Chem. Beihefte, 1926, **22**, 150—190; cf. B., 1924, 225).—The connexion between the swelling of hide-powder in acid solutions and its adsorptive power has been investigated. The adsorption of chloroacetic, formic, butyric, acetic, and propionic acids is related to the equilibrium concentration of acid by a simple exponential formula, and for equivalent concentrations decreases in this order. With di- and tri-chloroacetic acids, however, the adsorption curves are convex to the axis of concentration. A similar difference in behaviour occurs in the swelling of the powder in the aqueous solutions of the acids. With all three chloroacetic acids, the amount of swelling increases rapidly with the acid concentration at first, then passes through a sharp maximum, and drops finally to a constant value, which for di- and tri-chloroacetic acids is less than the value for pure water. In the case of the other acids, the maximum is very flat, and is not succeeded by any appreciable fall. If now the adsorption data are corrected for swelling, the isotherms for di- and tri-chloroacetic acids prove to be of the normal type, corresponding with an exponential equation, whereas for the other acids the amount of acid taken up is directly proportional to the concentration, and is the greater the greater the dissociation constant of the acid. R. CUTHILL.

Rates of evaporation of water adsorbed on metals and their oxides. S. S. BHATNAGAR and S. L. BHATIA (J. Chim. phys., 1926, **23**, 515—552).—The rates of evaporation of water from iron, cobalt, and nickel, and from one oxide (not named) of each metal, are linear functions of the time, and are correlated with the magnetic susceptibilities and Bohr's magneton values of the metals. L. F. GILBERT.

Polonium. J. ESCHER-DESRIVIÈRES.—See this vol., 879.

Variation of surface tension of sodium chloride solutions with time. E. KLEINMANN (Ann. Physik, 1926, [iv], **80**, 245—260).—A delicate technique has been devised for investigating the time

factor exhibited by the surface tension of solutions of sodium chloride in respect of variations in concentration and temperature. The effect of concentration on the ageing phenomenon depends on the Kohlrausch degree of dissociation, whilst the effect of temperature depends on the temperature coefficient of the ionic mobilities. The maximum capillary rise is as yet too difficult for satisfactory analysis. A preliminary interpretation of the experimental results is put forward in which the work of Lenard on the formation of electrical double layers at water surfaces is used. R. A. MORTON.

"Inter-traction." (SIR) A. E. WRIGHT (Proc. Roy. Soc., 1926, **A**, **112**, 213—214; cf. *ibid.*, 1921, **B**, **92**, 118).—The method used by Adam and Jessop (A., 1925, ii, 772) to prove that pseudopodial streaming can take place only when the lighter is superposed on the heavier fluid, and not when the fluids are placed side by side, is criticised, and a simple technique is described whereby horizontal streaming effects may readily be observed. L. L. BIRCUMSHAW.

Relation between the chemical constitution of organic liquids and the translucency of paper dipped in them. I. S. S. BHATNAGAR, N. A. YAJNIK, M. PRASAD, and B. AHMED (Z. physikal. Chem., 1926, **122**, 88—100).—The translucency of unsized paper wetted with various organic liquids has been determined by measurements with a spectrophotometer. Liquids such as water and solutions of inorganic salts which do not readily spread over the surface of paper do not increase its translucency. With increase in the amount of liquid per unit area of paper, the increase in translucency rises to a constant value, which is characteristic of the particular liquid used. This value increases regularly on ascending a homologous series, except in the case of the aromatic hydrocarbons, and is in general greater for the normal members than for the corresponding *iso*-compounds. When the paper contains this critical amount of liquid, its refractive index is very nearly equal to that of the pure liquid. R. CUTHILL.

Electrical properties and ionic permeability of membranes. IX. Dried collodion membranes. L. MICHAELIS and K. HAYASHI (Biochem. Z., 1926, **173**, 411—425).—For the individual characterisation of a collodion membrane the following measurements are recommended: (*a*) The concentration potential, which is the number of millivolts *P.D.* given when 0·01*N*-potassium chloride solution is on one side, and 0·1*N*-solution is on the other side of the membrane. (*b*) The chemical potential, which is the number of millivolts *P.D.* given between a 0·1*N*-sodium chloride solution and a 0·1*N*-potassium chloride solution separated by the membrane. Membranes with a concentration potential equal to or greater than 45 are absolutely impermeable to hydrochloric acid if pure water is on the other side, but if potassium chloride solution is there, an exchange of cations occurs. The *P.D.* between two solutions of the same electrolyte with the concentration ratio 1 : 10 approaches the theoretical maximum value of about 55 millivolts the more nearly the smaller the absolute concentration of the solutions. H. D. KAY.

General colloid chemistry. XXI. Stability and constitution of Bredig silver sols. W. PAULI and F. PERLAK (Kolloid-Z., 1926, **39**, 195—208).—Pauli's theory of the source of the electrical charge on noble metal colloid particles is discussed in the light of the results of other investigators in this field. The testing of the theory is here extended to Bredig silver sols. In a search for the optimum preparation conditions, it was found that in pure water it is impossible to prepare a stable sol, but that in the presence of 1×10^{-5} to $5\times10^{-4}N$-potassium hydroxide perfectly stable sols result, whilst in the presence of silver hydroxide, stable sols are formed only when its concentration is near $1\times10^{-5}N$ and when an average current (about 3·6 amp.) is passed for a short time (about 30 min.); even then the highest silver concentration obtainable, viz., 12 mg./litre, is only about half that obtained with the same concentration of potassium hydroxide. By progressive dialysis of sols prepared with potassium hydroxide, it was found that, as with the gold and silver sols studied, the conductivity first decreased and then increased and became constant, at the stage where only the cations paired with the negative complex colloid particles remained. The concentration of these cations calculated from the conductivity on the assumption that they are all hydrogen ions does not agree with the hydrogen-ion concentration found by titration. This is attributed to the incomplete replacement of potassium by hydrogen ions, and could probably be corrected by electrodialysis as was done in the case of Graham's silicic acid sol (Pauli and Valkó, A., 1925, ii, 521). The results show that Bredig's method cannot be regarded as a purely thermomechanical dispersion of the metal, but that this must be accompanied by electrolysis, the total effect being to form the ionogenic complexes demanded by the theory. On the basis of the theory, it is shown why stable sols cannot be obtained in pure water and only under very limited conditions in the presence of silver hydroxide.

N. H. HARTSHORNE.

General colloid chemistry. XX. Interpretation of the physico-chemical analysis of colloids by means of the theory of electrolytes. W. PAULI and E. VALKÓ (Z. physikal. Chem., 1926, **121**, 161—179; cf. this vol., 574).—An application of Bjerrum's theory (A., 1925, ii, 111) to colloids. The results of previous electrochemical measurements have suggested that only part of the ionisable molecules in a colloid particle yield free ions. Conductometric titration has now, however, shown that, *e.g.*, chloride ions in an aluminium hydroxide sol can be completely replaced by nitrate ions by means of silver nitrate; this indicates that all the ionisable molecules must be in the reactive state, *i.e.*, on the surface of the colloid particle, and not in its interior. Assuming now that the freedom of the ions is restricted by the interionic forces, it is shown that the conductivity and *E.M.F.* data for various sols lead to activity values which agree to within the limits of error. Treating colloids in this way as ordinary electrolytes, the application of Stokes' law to determine the magnitude of the charge leads to values which, for the higher charges,

are much lower than those obtained from the directly observed radii of the particles. This may be due to variations in the dispersity of the systems, or to a dipole effect of the water molecules (Born, A., 1920, ii, 527). R. CUTHILL.

Colloidal gold. P. P. VON WEIMARN (Kolloid-Z., 1926, **39**, 278—281).—An answer to the criticisms of Zsigmondy (Zsigmondy and Thiessen, "Das Kolloide Gold," Leipzig, 1925) of the author's modification of the preparation of gold sols by means of formaldehyde (A., 1925, ii, 198). N. H. HARTSHORNE.

Colloidal solutions and the second law of thermodynamics. H. ELBERTZHAGEN (Kolloid-Z., 1926, **39**, 217—218).—It is suggested that the walls of a vessel containing a sol must, in contradiction to the second law of thermodynamics, always be at a higher temperature than the sol itself, for the colloid particles cannot be conceived to be perfectly elastic, as are molecules, and must therefore in their collisions with the wall give up more heat to it than they receive from it. Another apparent contradiction would appear to be furnished by a vertical column of a sol in which metal plates are placed at the top and bottom. Since the concentration of the sol would be greater at the bottom than at the top, more particles would strike the bottom than the top plate in unit time, and the charge conferred on the former would be greater than that on the latter. Hence by connecting the two with a wire, a current would flow continuously the energy of which would be derived from the heat content of the solution.
N. H. HARTSHORNE.

Surface tension of colloidal solutions and the determination of molecular dimensions. P. LE COMTE DU NOÜY (Third Colloid Symposium Monograph, 1925).—Measurements of the time-drop in the surface tension of sols (*e.g.*, rabbit serum) show at least one minimum; absorption occurs on the glass surfaces as well as on the free surface. Using sodium oleate, Avogadro's number was determined as $6{\cdot}004\times10^{22}$. The dimensions of the "phantom shape" of the molecule of egg-albumin are considered to be $41{\cdot}7\times30{\cdot}8\times30{\cdot}8$ Å., corresponding with a mol. wt. of 30,000. The presence of colloids causes rhythmic crystallisation of sodium chloride at certain concentrations. CHEMICAL ABSTRACTS.

I. Colloid chemistry of urine. II. The making visible of albumin molecular aggregates and other subvisible structures. H. BECHHOLD (Kolloid-Z., 1926, **39**, 275—277).—Polemical against criticisms of previous research of the author and his co-workers by von Hahn (cf. this vol., 352), and by Liesegang (Kolloid-Z., 1926, **38**, 183—184).
N. H. HARTSHORNE.

Colloid chemistry of protoplasm. L. V. HEILBRUNN (Third Colloid Symposium Monograph, 1925, 135).—The viscosity of *Cumingia* egg protoplasm is maximal at 15°; slime moulds show the same phenomenon. Coagulation of protoplasm is not identical with that of proteins; lipins appear to be associated with the former. Anæsthetics reduce protoplasmic viscosity and may cause coagulation, especially in fertilised eggs. CHEMICAL ABSTRACTS.

Physical and colloid chemistry of salvarsan. II. Alkalinised solution of salvarsan. A. S. HUNTER and W. A. PATRICK (J. Lab. Clin. Med., 1925, **10**, 446—456).—On acidification, the conductivity of a solution of sodium salvarsan continuously increases, but when a freshly-alkalinised solution is acidified the conductivity is minimal after the addition of 1—2 c.c. of 0·1*N*-hydrochloric acid per 0·1 g. The changes are the reverse of those occurring during alkalinisation. There is a physical difference between the acid and alkaline solutions, the abnormal conductivity of the latter indicating that salvarsan is a colloidal electrolyte. An isotonic salvarsan solution shows no minimal conductivity either on alkalinisation or on subsequent acidification. In explanation of these results, and possibly of the differences in toxicity, the ionic micelle theory is employed.
CHEMICAL ABSTRACTS.

Colloidal characters of cellulose. R. O. HERZOG (Pulp and Paper Mag., 1926, **24**, 699—703).—A review. The particle size of cellulose, as deduced from the coefficient of diffusion of the nitrated material in acetone, is in reasonable concordance with that deduced from *X*-ray measurements. By treatment with sodium hydroxide in the absence of air, the particle size first falls and then slowly rises; in the presence of air a continuous fall occurs. Other chemical reactions, *e.g.*, with dilute sulphuric acid, do not diminish the particle size. In the ripening of viscose a rapid fall is followed first by a slow rise, and then by a rapid rise and jelly formation. When cellulose swells in an electrolyte, one or several C_6-groups are in stoicheiometrical relation to each mol. of the electrolyte, and a compound of the Werner type may be assumed. In such cases water enters the fibre by the attraction of the ions on the surface of the crystalline or colloidal particle, as an envelope around ions similarly attracted, and in chemical combination with the complex compound of the cellulose and electrolyte. A. GEAKE.

Viscose solutions. R. O. HERZOG, R. GAEBEL, and W. JANCKE (Kolloid-Z., 1926, **39**, 252—262).—An amplification and extension of previous work on the ultramicroscopic observation, micro-diffusion, and viscosity of viscose solutions (Herzog and Gaebel, *ibid.*, 1924, **35**, 193), and a description of experiments on the double refraction of stretched viscose films.
N. H. HARTSHORNE.

Determination of the size and charge of colloidal particles by means of Donnan's membrane equilibrium. J. STRAUB (Rec. trav. chim., 1926, **45**, 535—539).—Donnan's theory is applied to the case of, *e.g.*, sodium chloride solutions of unequal concentration, one of which contains a colloidal sodium salt. An expression is deduced connecting the amount of sodium chloride in the true solution and the percentage difference in chlorine between the two solutions, with the valency of the colloid anion (the charge on the particle). Another expression connects the two first-named quantities with the percentage difference in f.-p. depression between the two solutions. The equations take the form of series in ascending powers of percentage

chlorine difference. They may be used to calculate the charge on the particles and, from the f.-p. depression data, the weight of the colloid particles (mol. wt. of the anion). The equations are not wholly applicable in practice owing to the difficulty of obtaining exact experimental data. J. GRANT.

Diffusion velocity of egg-albumin in different aqueous media. J. GRÓH (Biochem. Z., 1926, **173**, 249—257).—Increase or decrease of p_H from the precipitation optimum causes a decrease of the diffusion velocity of egg-albumin, to the same extent on either side. The presence of sodium chloride increases the diffusion velocity, and variation of p_H has then but a slight effect on diffusion velocity. In distilled water (water free from buffer substances), the diffusion velocity is greater, the values being increased on addition of sodium chloride.

P. W. CLUTTERBUCK.

Diffusion researches on solutions of cellulose in copper ammonia solution. R. O. HERZOG and D. KRÜGER (Kolloid-Z., 1926, **39**, 250—252).—Cotton wool, alkali-cellulose, and cellulose regenerated from Schweitzer's reagent were dissolved in this solvent and the particle radius was determined by measurements of the diffusion coefficient and application of the Stokes–Einstein equation. In all cases, the result was between 47 and 53 Å. and was independent of the relative concentrations of cellulose, ammonia, and copper. The addition of a small amount of sucrose was also without effect. The results appear to show that in Schweitzer's reagent cellulose is dispersed not merely to crystallites the size of which depends on the kind and previous history of the cellulose, but rather to primary particles. Viscosity measurements of such solutions are in agreement with this view. The equal diffusion velocity of the particles in the different solutions is explained on the basis of a theory due to Stark.

N. H. HARTSHORNE.

Viscosity and hydration of dye solutions. S. LIEPATOV (Kolloid-Z., 1926, **39**, 230—236).—The viscosity of certain substantive dye solutions of an emulsoid nature has been measured, and the influence of temperature and of the addition of electrolytes examined. The degree of hydration of the colloid particles has been calculated from Hatschek's formula $\eta'=\eta A^3/(A^3-1)$, where η is the viscosity of the dispersion medium, η' that of the solution, and A the ratio of the total volume of the solution to that of the disperse phase. The degree of hydration is greatest with geranin-G and least with diamine-fast-red-F. It increases with concentration and in the case of geranin-G (particularly) and benzopurpurin-4B tends to assume a constant value at about 1%. Temperature influences greatly the viscosity of geranin-G solutions, and for a given temperature is not changed by previous heating. The addition of electrolytes greatly increases the viscosity in all cases. The action of the cations of the first group is in the order Li< Na<K. Sodium and potassium salts in sufficient concentration gelatinise the solutions to a macroscopically homogeneous mass which on shaking breaks up into small particles which, however, do not settle. Tannin strongly dehydrates geranin-G solutions, and this is accompanied by a colour change to a dark raspberry-red. By means of the above equation, an approximate value for the size of the geranin-G particles and the thickness of the adsorbed water shell is calculated. The connexion between viscosity, the size of a particle, and its charge is discussed.

N. H. HARTSHORNE.

Ultrafiltration of colloidal solutions of organic chromium compounds in ethylene bromide. F. HEIN and R. SPÄTE (Kolloid-Z., 1926, **39**, 236—237).—A description of the ultrafiltration of an ethylene bromide solution of chromium penta-*p*-bromotriphenylene bromide (this vol., 628) and of ethylene bromide solutions of other organic chromium compounds. The first compound is very much more dispersed in nitrobenzene, as would be expected from the higher dielectric constant of this solvent as compared with ethylene bromide.

N. H. HARTSHORNE.

Structure of gels. Organogels obtained with benzoic acetal from sorbitol. P. THOMAS and (MLLE.) M. SIBI (Compt. rend., 1926, **183**, 282—284).—Organogels have been prepared from crude benzoic acetal dissolved in organic solvents by a method analogous to that used in the preparation of hydrogels (this vol., 353). They are opalescent and isotropic, but sometimes show signs of incipient crystallisation. Alcoholic solutions of a number of dyes diffuse through the gel prepared from ethyl alcohol at equal rates. The crude acetal may be separated by boiling water into two fractions differing considerably in their solubilities in hot alcohol and acetone. Gels are obtained by cooling a hot solution of the water-soluble fraction in an organic solvent, but the water-insoluble fraction crystallises out normally. These fractions are considered to be stereoisomerides, the formation of the organogel being due to the presence of the isomeride soluble in boiling water.

J. GRANT.

Microscopical study of the freezing of gel. (SIR) W. B. HARDY (Proc. Roy. Soc., 1926, **A**, **112**, 47—61).—Three types of freezing, described as circles, rays, and disseminated, were distinguished. In the first two types the freezing is intermittent, and instead of pure ice, a solid solution of gelatin and ice separates. As the result of a large number of observations, the following conclusions were reached: (1) In gels from 2 to 40%, exposed to temperatures from −6° to −13·5°, freezing is intermittent. (2) Freezing is disseminated and very rapid, with separation of many crystals of pure ice, in gels of less than 2%; this type of disseminated freezing may occur in stronger gels, but it takes some days to appear. (3) In gels between 15 and 40% at −19°, freezing is disseminated and only minute spheres of ice separate. (4) At −2·6° to −3°, no spontaneous freezing occurs. The mechanism of the formation during intermittent freezing of membranes of dehydrating gel, separating zones of optically homogeneous material, is discussed. An investigation of the behaviour of gels on slow or rapid thawing showed that two distinct processes may occur: (1) a separation of solid solution into ice and

concentrated gel at about −6° and (2) a rapid transference of water from the sponge of concentrated gel so formed to the surrounding gel at about 0°.

It is stated that the current conception that the spongy structure found on thawing is due to crystals of ice is false. The phase equilibrium described by Moran (cf. following abstract) is considered theoretically, and it is shown that Moran's suggestion that the ice phase is a mixture of ice crystals and particles of dehydrated gel is not supported by the optical properties of the gel, nor by its behaviour on thawing.

L. L. BIRCUMSHAW.

Freezing of gelatin gel. T. MORAN (Proc. Roy. Soc., 1926, A, **112**, 30—46).—The behaviour of gelatin gels on freezing and thawing was examined from the point of view of the microstructure produced on freezing, the quantity of ice which separates, and the volume changes. A study of the structure of 38% gels, 12% gels, and gels weaker than 12% at −3°, −11°, −19°, and at the temperature of liquid air, showed that the disposition of ice in the frozen gel depends on the rate of freezing and on the gel concentration. From observations with gels of 12% and weaker, it is found that there are two groups of possible centres of crystallisation, external and internal, and that ice formation is confined to the former when the degree of overcooling is not too great. The external centres may be supposed to be situated in a layer of insensible thickness of very dilute gelatin solution covering the surface. With gels above a concentration of 12%, a regular disposition of shells of alternate ice and gel, arranged concentrically about the original centre of crystallisation, was observed so long as the rate of cooling was not too low. If frozen at −3°, however, ice separated only at the surface, and this fact was used to determine the ice–gel phase equilibrium at various temperatures. At concentrations of gelatin between 12% and 40%, with gels at the isoelectric point, it was found that on slow freezing in air at −3°, water passed into the external shell of ice until the gel had reached a constant composition of 54·3% gelatin. Some of the gelatin was now transferred to lower temperatures, when more water moved from the core to the shell. The curve obtained in this way reaches a constant level at a concentration of 65—66% of gelatin; gels of higher concentration than this could not be made to freeze. It is inferred that at this concentration, all the water in the gel is bound chemically to the gelatin. Dilatometric measurements are recorded and discussed.

L. L. BIRCUMSHAW.

Precipitates with a stratified structure. E. UNGERER (Kolloid-Z., 1926, **39**, 238—239).—If ammonia solution is allowed to diffuse into an agar gel containing cupric chloride, periodic layers of cupric hydroxide are formed. The phenomenon is explained on the basis of Ostwald's diffusion wave theory (A., 1925, ii, 530) as follows. The ammonia first forms the copper–ammonia complex and ammonium chloride. As the diffusion proceeds, the ammonia concentration decreases, and this and the presence of the ammonium chloride cause the partial (?) decomposition of the complex and the precipitation of copper hydroxide, forming the first ring. This adsorbs cupric chloride from the adjacent part of the gel, which is also precipitated and the layer thus strengthened. The layer also retards the diffusion. The adsorption frees the gel from cupric chloride beyond the layer. Through this zone, more copper–ammonia complex eventually diffuses until the ammonia concentration again falls and it encounters more cupric chloride, when the second layer is formed and so on. In gelatin gels, the layers are not so sharply defined. This is due to the presence of glycine, formed by the hydrolysis of the gelatin, which itself forms a soluble complex with copper salts and stabilises the copper–ammonia complex towards dilution and the action of ammonium chloride.

N. H. HARTSHORNE.

Concentric coloured rings of the beetroot, and the Liesegang phenomenon. S. S. BHATNAGAR and J. L. SEHGAL (Kolloid-Z., 1926, **39**, 264—268).—The connexion between the Liesegang phenomenon and similar periodic occurrences in the growth of living matter is discussed. The concentric coloured rings observed in a section of coloured beetroot are spaced in a similar manner to the rings obtained artificially by the interaction of mercuric chloride and potassium iodide in gelatin and in silica gel. Rings may be formed in white beetroot sections by soaking in dilute sulphuric acid and then placing some of the extract of a coloured beet in the centre, and in a similar fashion with mercuric chloride and beet soaked in potassium iodide or silver nitrate and beet soaked in potassium dichromate. The shape of the rings is not necessarily circular; it depends on the shape of the ring source.

N. H. HARTSHORNE.

Endosmotic investigation of the influence of dissolved electrolytes on the electrical charge of sparingly soluble powders. K. HAYASHI (Kolloid-Z., 1926, **39**, 208—216).—The influence of a large number of electrolyte solutions, mostly 0·02*N*, on the electrical charge of mercurous chloride, copper ferrocyanide, aluminium hydroxide, thorium hydroxide, asbestos, talc, and glass powders has been investigated by making the powders the diaphragms in endosmosis experiments. The adsorption potential was calculated from the amount of water transported in unit time by means of the equation of Helmholtz and Smoluchowski. The results show that no general rule for the process can be formulated, but in different cases the electrolyte ions fall into different series as regards relative effect. Thus with the silicate powders the valency is determinative except for hydrogen and hydroxyl ions which have a peculiar action. With mercurous chloride, copper ferrocyanide, and aluminium hydroxide, univalent cations fall into the lyotrope series. The solubility series (cf. Paneth, Physikal. Z., 1914, **15**, 924) was found only for the anions and then not in all cases. Hydrogen and hydroxyl ions almost always act more strongly positive and negative, respectively, than indicated by the above three generalisations, and this is especially the case with the silicate powders. In amphoteric powders, *e.g.*, aluminium hydroxide, the charge and even its sign depend greatly on the hydrogen-ion concentration. In some cases, it was noted that ions related to the powder had a stronger action than

foreign ions, *e.g.*, copper ferrocyanide, with potassium ferrocyanide. N. H. HARTSHORNE.

Validity of Traube's rule for the coagulation of hydrophile sols. H. FREUNDLICH and V. BIRSTEIN (Koll. Chem. Beihefte, 1926, **22**, 95—101).—The coagulation of arsenious sulphide sols by salts of amines and of ferric oxide sols by sodium salts of the fatty acids in general obeys Traube's rule, although the activity factor is less than 3 (cf. Frumkin, A., 1925, ii, 109). It would therefore seem that such processes are dependent on capillary action. In accordance with this view, it is found that of two isomerides such as sodium maleate and sodium fumarate, the less soluble, which shows the greater capillary activity, has the stronger coagulative power. That hydrogen-ion concentration plays only a subordinate part is shown by the fact that the effectiveness of the fatty acids in coagulating gold sols increases on ascending the series, whereas the hydrogen-ion concentration decreases. R. CUTHILL.

Velocity of the sol–gel transformation of concentrated iron oxide sols. H. FREUNDLICH and A. ROSENTHAL (Z. physikal. Chem., 1926, **121**, 463—483).—An extension of previous work (A., 1925, ii, 967). The retarding effect of amino-acids on the coagulation of concentrated ferric oxide sols is due probably to the formation of complex inner iron salts on the surface of the colloid particles. Experiments with amino-acids of widely different tendency to form complex inner salts, viz., α-amino*iso*valeric acid and δ-amino-*n*-valeric acid, gave results in accordance with this theory. The ζ potential of the particles is probably raised thereby, as the velocity of cataphoresis of the sols is increased by the presence of glycine. The rates of coagulation of thixotropic and of ordinary sols are expressed by similar equations. L. F. GILBERT.

Colloid chemistry of rennin coagulation. L. S. PALMER and G. A. RICHARDSON (Third Colloid Symposium Monograph, 1925, 112).—Rennin exerts no detrimental effect on the protective action of lactalbumin in the clotting of milk. Gelatin accelerates rennin coagulation, but lactalbumin is without influence on rennin coagulation of calcium caseinate. Mothers' milk coagulates with rennin when the soluble calcium is increased 135%; potassium caseinate inhibits the coagulation of calcium caseinate unless much soluble calcium is present. Evidently rennin, acting on an incompletely-formed calcium caseinate in colloidal dispersion at the p_H of milk, converts it into a much less completely formed calcium paracaseinate, the chemical binding capacity of which for both base and acid is permanently altered. The casein colloids appear to be intermediate between suspensoids and true emulsoids. Colloidal calcium phosphate mixed with casein forms a gel when acted on by rennin. CHEMICAL ABSTRACTS.

Existence of two regions of instability in the coagulation of certain suspensions by electrolytes with ter- and quadri-valent cations. A. BOUTARIC and (MLLE.) G. PERREAU (Compt. rend., 1926, **183**, 205—207).—A suspension containing 0·435 g. of gamboge per litre is precipitated by all concentrations of aluminium chloride above $7\times10^{-6}N$ except those lying between 23×10^{-6} and $5\times10^{-3}N$. Increase in the concentration of the gamboge, or addition of hydrochloric or sulphuric acid or potassium chloride, reduces the upper range of ineffective concentrations, whereas increase in size of the colloid particles or addition of barium chloride has the reverse effect. Rise in concentration of the colloid or addition of potassium hydroxide is accompanied by a rise in the minimum concentration necessary to produce coagulation, whilst addition of sulphuric acid, hydrochloric acid, barium chloride, or potassium chloride produces the opposite result. The use of chromic, ferric, thorium, or cerium salts as precipitants, or of gum mastic as the colloid, gives similar results. R. CUTHILL.

Peptisation of pyroxylin. M. L. BYRON (J. Physical Chem., 1926, **30**, 1116—1124).—"Pyroxylin" is not peptised by anhydrous ether at the ordinary temperature or at the temperature of liquid air. At the temperature of a carbon dioxide–ether freezing mixture, alcohol peptises pyroxylin, and when warmed to the ordinary temperature the sol becomes viscous and sets to a jelly. The change is reversible. Peptisation is due to the adsorption of polymerised alcohol. L. S. THEOBALD.

Hysteresis in sedimentation. I. B. ILIIN (Z. physikal. Chem., 1926, **122**, 137—148).—The rate of sedimentation of aqueous suspensions of rice starch on centrifuging is increased by the addition of sodium hydroxide or an ammoniacal solution of cuprammonium hydroxide by an amount which gradually increases to a maximum with increase in the time that the mixture is kept before centrifuging. Addition of ethyl alcohol to aqueous suspensions of blood-albumin has a similar effect, but the rate here ultimately falls again. Analogous observations have been made for sedimentation under the influence of gravity alone. It appears probable that adsorption plays a part in producing this phenomenon. R. CUTHILL.

Effect of gelatin on the decomposition of boiling aqueous solutions of hydrogen peroxide. V. KUBELKA and J. WAGNER (Koll. Chem. Beihefte, 1926, **22**, 102—149; cf. Bürki and Schaaf, A., 1921, ii, 389).—The rate of decomposition of hydrogen peroxide in boiling neutral or acid solution decreases with increasing acidity of the solution, but for a given acidity is a constant, independent of the time or concentration. Addition of gelatin reduces the value of this constant somewhat, but the nature of the reaction is otherwise unchanged. In pure alkaline solution, the rate of decomposition increases with the time, but here also gelatin has a retarding effect, although this is opposed by the accelerating effect of the alkali, and itself falls off after a time. The effect of the gelatin in neutral and acid solutions appears to be due to its forming adsorption compounds with both reactant and resultants, which break up rather slowly. This view is supported by the facts that such solutions contain much more oxygen than corresponds with the undecomposed hydrogen peroxide, and that the residue obtained by evaporating them liberates iodine from potassium iodide. In alkaline solutions, this effect is complicated by the probable

formation of metallic peroxides, and by hydrolysis of the gelatin to form substances which render the solution acid. R. CUTHILL.

Molecular condition of sucrose in aqueous solution. M. I. NAKHMANOVICH (Zapiski [Russia], 1924, **1**, 184—200).—Discrepancies between experimental and theoretical values of the osmotic pressure of sucrose solutions indicate that the formula is probably $C_{12}H_{22}O_{11},nH_2O$, where n is 5 or 6 in aqueous solutions of medium concentration below 25°. CHEMICAL ABSTRACTS.

Cryoscopic test-tube method for determination of molecular weights. E. FROMM and A. FRIEDRICH (Z. angew. Chem., 1926, **39**, 824—826).—A rapid method involving the use of 0·03—0·05 g. of substance and 3 g. of solvent is described in detail. The solvents used are: naphthalene (69); phenol (72); acetic acid (39); the numbers in parentheses are the respective constants. The apparatus consists of a test-tube fitted with a cork carrying a glass stirrer and a suitable thermometer. The liquid is slightly supercooled and then stirred. Crystal separation occurs with rise of temperature, the maximum temperature observed being taken as the f. p. J. S. CARTER.

Molecular association of benzoic acid in benzene. J. A. WILCKEN (Phil. Mag., 1926, [vii], **2**, 287—288).—The slope of the line obtained when the results of the partition of benzoic acid between water and benzene are plotted logarithmically deviates appreciably from unity. The assumption of the formation of double molecules in the benzene is said to be insufficient to explain the variation of distribution coefficient, and it is suggested that the process of association may pass through a metastable and a labile state. A. B. MANNING.

Interpretation of the dielectric polarisation of aqueous solutions. L. EBERT (Z. physikal. Chem., 1926, **122**, 28—38; cf. A., 1925, ii, 14).—Experimental data on the dielectric polarisation of solutions have been analysed by using the mixture formula of Lorenz and Lorentz, and values deduced for the relative effects of the solutes considered on the specific polarisation of water. In general, it appears that for solutions of non-electrolytes no definite conclusions as to the magnitude of the dipole moment can be reached from the variation of the dielectric constant of the solution with its concentration. R. CUTHILL.

Rotatory power of solutions of quinine salts as a function of their hydrogen-ion concentration. Rotatory power of asparagine and the effect of added salts. (MLLE.) J. LIQUIER (Compt. rend., 1926, **183**, 195—198; cf. A., 1925, ii, 743).—The rotatory power of solutions of the sulphates of quinine varies continuously with the p_H of the solution. On the curves connecting α with the p_H, there are two flat portions corresponding with the basic sulphate, $2C_{20}H_{24}O_2N_2,H_2SO_4$, and the normal sulphate, respectively, and from these the dissociation constants of quinine are calculated to be about 2×10^{-6} and $1\cdot8\times10^{-10}$. Hydrogen-electrode measurements have also been made with solutions of asparagine. These show that the addition of neutral salts to such solutions does not alter the hydrogen-ion activity, whilst salts of weak acids depress it. R. CUTHILL.

Determination of double ions in solutions of ampholytes. L. EBERT (Z. physikal. Chem., 1926, **121**, 385—400).—New approximate methods of determining the proportion of "double ion" or inner salt furnished by amino-acids in solution are described (cf. Bjerrum, A., 1923, i, 444), and illustrative examples of their employment are given. This proportion is considerably less in alcoholic than in aqueous solution, the aromatic amino-acids giving scarcely any double ion in alcoholic solution. L. F. GILBERT.

Possibility of the existence of free electrons in solutions. J. DOCHMANN (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 157—164).—Theoretical considerations lead to conclusions which are to be tested experimentally. T. H. POPE.

Reaction provinces. [Composition of explosive mixtures.] W. P. JORISSEN (Chem. Weekblad, 1926, **23**, 355—358; cf. *ibid.*, 79; also this vol., 246, 690, 909).—A *résumé* of work on the limits of composition of explosive ternary and quaternary systems. S. I. LEVY.

Theory of electrolytes. L. ONSAGER (Physikal. Z., 1926, **27**, 388—392).—A theoretical discussion of certain difficulties in the Debye–Hückel theory. An assumed invalidity of Stokes' law in the immediate neighbourhood of the ions does not affect the limiting value law of electrical conductivity. R. A. MORTON.

Theory of concentrated solutions. E. WILKE (Z. physikal. Chem., 1926, **121**, 401—428).—An expression for the *E.M.F.* of hydrogen and chlorine electrodes in solutions of hydrogen chloride (to $5N$) and sodium chloride (to $4\cdot5N$) (cf. A., 1925, ii, 795) has been derived by a method which takes account of interionic forces. The treatment is that of Ghosh rather than of Debye. For the hydrogen electrode, an equation corresponding with the van der Waals equation for compressed gases is used. For the chlorine electrode, it is necessary to consider, in addition to the electrostatic effects, the decrease in size of the chlorine-ion radius with increase in chlorine-ion concentration in the hydrogen chloride solutions. The ion radius is taken as the distance from the nucleus of the electrons in the outermost shell, and changes abruptly as the outer electrons pass from one quantum orbit to the next. Below $0\cdot885N$-chlorine-ion concentration, the outermost electrons in all the chlorine ions are in the 4th orbit, giving a radius of $2\cdot13\times10^{-8}$ cm. Between $0\cdot885N$ and $5N$, the outermost electrons in some of the chlorine ions have sunk to 3rd orbits, all being in 3rd orbits by $5N$ when the ion radius is $1\cdot2\times10^{-8}$ cm. At still higher concentrations, changes from the 3rd to the 2nd orbit take place. The theoretical discontinuities in the chlorine electrode potential calculated from these changes accord with those experimentally determined. C. C. TANNER.

Ionisation of weak electrolytes. D. A. MACINNES (J. Amer. Chem. Soc., 1926, **48**, 2068—2072).—The modified Ostwald dilution law for the acid HA, $K'=(\alpha\gamma_{H\cdot})(\alpha\gamma_{A'})c/(1-\alpha)\gamma_{HA}$ is simplified to $K=\alpha^2\gamma^2c/(1-\alpha)$, where α is the degree of dissociation, given

by Λ_c/Λ_e, Λ_c being the equivalent conductivity of a solution of HA of concentration c, and Λ_e is that of the completely dissociated acid at the ion concentration existing in the solution of concentration c, $\gamma_{H'}$, $\gamma_{A'}$, and γ_{HA} are activities, and γ is the mean activity coefficient calculated from the Debye–Hückel equation, $\log\gamma=-0{\cdot}5\sqrt{c}$. The simplified equation is shown to hold for a series of organic acids, $\alpha=\Lambda_c/\Lambda_e$ being calculated from Kendall's measurements (J.C.S., 1912, **101**, 1275). In the case of acetic acid, K tends to increase as c diminishes, probably because of personal errors in the conductivity measurements, but possibly also because of the effect of changing concentration on the dielectric constant.

S. K. TWEEDY.

Aqueous solutions of sodium silicates. IV. Hydrolysis. R. W. HARMAN (J. Physical Chem., 1926, **30**, 1100—1111; cf. Bogue, A., 1921, ii, 112; Harman, this vol., 796).—The hydroxyl-ion concentrations and percentage hydrolysis of sodium silicate solutions of ratios $Na_2O:SiO_2$, 2 : 1, 1 : 1, 1 : 1·5, 1 : 2, 1 : 3, and 1 : 4, at concentrations ranging from 2 to $0{\cdot}01N_w$ have been found by the hydrogen electrode method. The results agree, in the main, with those of Bogue (*loc. cit.*). The curves of the hydroxyl-ion concentration plotted against the ratio $Na_2O:SiO_2$ show, with concentrated solutions, a steep fall in ion concentration from that in sodium hydroxide to the ratio 2 : 1, followed by a second fall to the ratio 1 : 2, after which a constant value obtains. The first variation of hydroxyl-ion concentration with ratio is paralleled by the change of conductivity with ratio previously found (A., 1925, ii, 1065). Hydrolysis is small; thus at $0{\cdot}01N_w$ the metasilicate is 27·8% hydrolysed, and the ratios 1 : 3 and 1 : 4 at the same concentration show only 1·5% hydrolysis, whilst in concentrated solution hydrolysis is even less. The liquid–liquid *P.D.* between the silicate solutions and potassium chloride have been found by the Bjerrum extrapolation method (A., 1911, ii, 692). Much of the silica is present, probably, as simple and complex ions and ionic micelles.

L. S. THEOBALD.

Dissociation of water in potassium and sodium bromide solutions. H. S. HARNED and G. M. JAMES (J. Physical Chem., 1926, **30**, 1060—1072; cf. A., 1925, ii, 397, 398, 538; this vol., 245, 354).—Measurements have been made at 25° of the cells

$H_2|KOH(m_0),KBr(m)|K_xHg|KOH(m_0)|H_2$;

$H_2|KOH(m_0),KI(m)|K_xHg|KOH(m_0)|H_2$;

$H_2|HBr(m_0),KBr(m)|AgBr|Ag$; and

$H_2|HBr(m_0),NaBr(m)|AgBr|Ag$, where $m_0=0{\cdot}1$ and $0{\cdot}01M$, and m varied up to $3M$. The activity coefficients of potassium hydroxide in solutions of potassium bromide and iodide, and of hydrobromic acid in solutions of potassium and sodium bromides have been calculated from the results obtained. γ for hydrobromic acid is greater in sodium than in potassium bromide solutions of equal strength, resembling the behaviour of hydrochloric acid in the corresponding chloride solutions (this vol., 354). Further, the activity coefficient of hydrobromic acid in a bromide solution is greater than that of hydrochloric acid in the corresponding chloride solution. The law of linear variation of the logarithm of the activity coefficient (*loc. cit.*) does not hold exactly for hydrobromic acid in these bromide solutions.

The activity coefficient of water as an electrolyte and the ionic concentration of water in solutions of potassium and sodium bromides have been calculated. Sodium bromide produces a larger dissociation than potassium bromide and sodium chloride, and potassium bromide a larger dissociation than potassium chloride. Maximal effects occur at approximately $0{\cdot}5M$-salt concentration in every case.

L. S. THEOBALD.

Variation of the dissociation constant of boric acid with concentration. I. M. KOLTHOFF (Rec. trav. chim., 1926, **45**, 501—507).—It is shown qualitatively by means of indicators and by the variation in sensitiveness of the silver chromate reaction, and quantitatively by conductivity and hydrogen-ion measurements at 18°, 40°, and 60°, that the dissociation constant of boric acid increases with concentration. This is due to the formation of complexes according to the equations $4H_3BO_3 \rightleftharpoons H_2B_4O_7+5H_2O$ and $H_2B_4O_7 \rightleftharpoons H^+ + HB_4O_7^-$, and takes place at concentrations higher than $0{\cdot}5M$. Here the acid character of the mixture is determined principally by the tetraboric acid, which is a much stronger acid than the orthoboric acid. At concentrations less than $0{\cdot}1M$ the dissociation constant is unaltered, and corresponds with the presence of the simple ortho-acid.

J. GRANT.

Equilibrium between the ions of iodine and of tervalent iron. K. LIALIKOV and M. BELA (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 151—156).—In neutral solutions, equilibrium between ferric and iodine ions is established according to the scheme, $Fe^{\cdots}+I' = Fe^{\cdot\cdot}+I$. The equilibrium depends on the degrees of dissociation of the ferric, ferrous, and potassium chlorides, but this effect becomes less important if the reaction takes place in $0{\cdot}5N$-potassium chloride solution. The equilibrium constant is profoundly changed by the presence of an acid, the extent of the alteration varying but slightly with the concentration of the acid. The equilibrium is displaced somewhat to the right by the presence of either glycerol or methyl alcohol in 30% concentration.

T. H. POPE.

Activity coefficients of tervalent ions in very dilute solutions. J. N. BRÖNSTED and N. J. BRUMBAUGH (J. Amer. Chem. Soc., 1926, **48**, 2015—2020).—The solubility of luteocobaltic hexacyanocobaltiate, $Co(NH_3)_6,Co(CN)_6$, in sodium chloride solutions increases from $1{\cdot}375\times10^{-5}$ to $4{\cdot}56\times10^{-5}$ mol./litre as the concentration of the latter increases from 0 to $0{\cdot}02M$ (cf. Brönsted and LaMer, A., 1924, ii, 306). The activity coefficients calculated from these measurements are in agreement with those calculated by means of the Debye–Hückel interionic attraction theory.

S. K. TWEEDY.

Antagonism of ions. Ionisation of calcium. A. BELAK and E. SZEP (Biochem. Z., 1926, **171**, 22—32).—The authors have shown by the Brinkman–van Dam method that the presence of chlorides and other salts of sodium and potassium depresses the ionisation of calcium chloride. Non-electrolytes (dex-

trose, lactose, and sucrose) and magnesium salts have no effect. The antagonism of ions is therefore an effect independent of colloidal surfaces, taking place in the solution itself. E. C. SMITH.

Equilibrium of heterogeneous systems including electrolytes. I. Fundamental equations and phase rule. J. A. V. BUTLER (Proc. Roy. Soc., 1926, **A**, **112**, 129—136).—The method of Gibbs is employed to obtain the conditions of equilibrium in cases where *P.D.* may exist between one or more phases, *e.g.*, systems containing electrolytes. In addition to a consideration of the number of components, their chemical potential, temperature, and pressure, every portion of matter is characterised by an electrical potential, *i.e.*, the electrical work done in bringing unit positive charge from a standard position (or infinite distance) to a point within the matter in question. A modified form of the phase rule is given, and its application to galvanic cells is discussed. L. L. BIRCUMSHAW.

Allotropy of mercuric iodide. L. LOSANA (Gazzetta, 1926, **56**, 301—331; cf. A., 1900, ii, 141; 1903, ii, 728; 1906, ii, 757; 1914, ii, 364).—The binary systems $HgCl_2$–$HgBr_2$, HgI_2–PbI_2, and the ternary systems HgI_2–$HgCl_2$–$HgBr_2$, HgI_2–CdI_2–PbI_2 (the latter partly) were studied by thermic and dilatometric methods. The changes produced in the temperature at which red mercuric iodide is transformed into the yellow form were also determined. The bearing of the observations on the work of Smits and Bokhurst relative to the theory of allotropy is discussed. S. B. TALLANTYRE.

Binary mixtures. J. SAMESHIMA (J. Fac. Sci. Tokyo, 1925, **1**, 63—103).—In addition to an account of work previously published (cf. A., 1918, ii, 429), expressions for the partial vapour pressures of each component of a binary system are given and tested by the experimental data available for the systems benzene–carbon disulphide, acetone–ethyl ether, carbon tetrachloride–benzene, and ethyl iodide–ethyl acetate, with which they show satisfactory agreement. The expressions, which are deduced from a simplified form of Margules' equations, are $p_1=P_1xe^{(1-x)^2\alpha}$ and $p_2=P_2(1-x)e^{x^2\alpha}$, where p_1 and p_2 are the partial pressures of the first and second components, respectively, P_1 and P_2 the vapour pressures of the pure liquids, x is the molar fraction of the first component in the liquid state, and α a constant determined graphically from the experimental data. The dielectric constant of a binary mixture appears to be an additive property when both components are normal and there is no chemical interaction. A method is given for the calculation of the degree of association of one component from the dielectric constants of its mixtures with a normal liquid. Hence, from the experimental data for mixtures of ethyl alcohol and ether, a value of 1·71 for the degree of association of ethyl alcohol at 18° has been calculated. M. S. BURR.

Binary systems. III. "Thaw-melt" diagrams for systems with mixed crystals. H. RHEINBOLDT and M. KIRCHEISEN (J. pr. Chem., 1926, [ii], **113**, 199—211; cf. this vol., 25, 476).—Curves of every possible type are obtained from the following pairs. *Type* I (continuous solid solutions): naphthalene and β-naphthol; the curves agree with those of Rudolfi (cf. A., 1909, ii, 536). *Type* II (solidus and liquidus coincident at maximum): *d*- and *l*-carvoximes; the curves agree with those of Adriani (cf. A., 1900, ii, 462); a maximum is found at 92·3°. *Type* III (coincidence at minimum): naphthalene and β-naphthylamine; minimum at 32·5 wt. % of the latter, at 71·5° (cf. Rudolfi, *loc. cit.*). *Type* Ia (coincidence at point of inflexion, cf. Ruer, A., 1907, ii, 433): *p*-bromoiodo- and *p*-di-iodo-benzene; the liquidus agrees with that found by Nagornow (A., 1911, i, 27); between 0 and 18 mol. % di-iodobenzene the solidus is parallel to it and only slightly lower. *Type* IV (limited solid solubility): *p*-chloroiodobenzene and *p*-di-iodobenzene. A transition point is found at 59·5° and 13 mol. %, and a solid solution area from 18 to 71 mol. % di-iodobenzene (cf. Nagornow, *loc. cit.*). *Type* V (two limited series, with eutectic): α- and β-benzylidenenaphthylamines. The diagram obtained by Pascal and Normand (cf. A., 1913, ii, 1031) is valueless, as the m. p. of the pure components are interchanged, the points on the solidus are very irregular, and supercooling has obviously occurred. The eutectic is now found at 55·5° and 33 wt. %, whilst the solid solution area extends over 18—69 wt. % of the β-isomeride. E. W. WIGNALL.

Recurrent transition curves in anisotropic binary systems. F. WEVER [with P. GIANI and W. REINECKEN] (Z. anorg. Chem., 1926, **154**, 294—307).—The α–γ and γ–δ transition points of iron containing increasing amounts of silicon or tin were determined by plotting temperature difference curves, and, in the former case, were confirmed by microscopical observation of specimens etched over a range of temperatures with nitrogen. In both cases, the α–γ transition point is raised and the γ–δ transition point lowered, and no transition occurs in the presence of more than about 1·8% of silicon. A. GEAKE.

Melting-curves of the systems hydrogen chloride–ethyl ether and hydrogen chloride–acetone. M. HIRAI (Bull. Chem. Soc. Japan, 1926, **1**, 123—125).—The curves indicate the existence of the compounds, Et_2O,2HCl, m. p. −87·3° (cf. Maass and McIntosh, A., 1913, i, 584), and Me_2CO,HCl, m. p. −79·0°. S. K. TWEEDY.

Vapour pressure and base exchange in zeolites and permutites. V. ROTHMUND (Z. Elektrochem., 1926, **32**, 367—371).—A review of the literature.

Equilibria in systems of the type lead halide–potassium halide–water. L. J. BURRAGE (J.C.S., 1926, 1703—1709).—Equilibria in the systems PbX_2–KX–H_2O (where X=Cl, Br, or I) have been investigated at 25° by varying the concentration, from zero to saturation, of each of the component salts in turn, in presence of excess of the other. The lead was usually determined gravimetrically as chromate and the halide as silver salt. Small concentrations of lead iodide, however, were determined colorimetrically. The solid phases were analysed by the "rest" method. The following double salts exist at 25°: $KCl,2PbCl_2$; $KCl,PbCl_2,\frac{1}{3}H_2O$; $KBr,2PbBr_2$;

$KBr,PbBr_2,\frac{1}{3}H_2O$; and $KI,PbI_2,2HO$. Demassieux obtained similar results for the chlorides (A., 1924, ii, 182) and iodides (A., 1923, ii, 565). Other double salts have been described by earlier investigators, but these are, apparently, incapable of existence.

M. S. Burr.

System iron–silicon–chromium. W. Denecke (Z. anorg. Chem., 1926, **154**, 178—185).—In the two-component system iron–chromium, a continuous series of mixed crystals is formed with amounts of chromium up to 30%, and a minimum occurs in the solidification curve. No evidence was obtained for the compound Fe_2Cr, or for a eutectic containing about 15% of chromium. The reaction between mixed crystals of iron and silicon and the compound FeSi to form the compound Fe_3Si_2 is apparently accelerated by the presence of chromium. A space diagram is given for systems containing up to 30% of chromium and silicon, together with various sections and numerical data. A. Geake.

Equilibrium in the action of gaseous hydrogen chloride on potassium bromide. K. Jellinek and R. Itelsohn (Z. anorg. Chem., 1926, **155**, 130—140).—The equilibrium $KBr+HCl=KCl+KBr$ has been examined between 500° and 800°. The solid phase consists of a continuous series of mixed crystals or of a homogeneous fused mass of potassium chloride and bromide. The composition of the gas phase in its dependence on the composition of the solid phase and on the temperature is discussed. The heat of reaction is of the magnitude expected from thermochemical data. M. Carlton.

Equilibria in the reduction of chromium sesquioxide and of uranium dioxide with carbon, and in the action of nitrogen on uranium carbide. O. Heusler (Z. anorg. Chem., 1926, **154**, 353—374).—Equilibria between permanent gases and non-volatile solids can be determined in an internally heated furnace with external cooling at temperatures too high for a closed, externally heated vessel. The equilibria between carbon and manganous oxide or silica could not be determined, the solids being too volatile at the necessary high temperatures. The equilibrium between chromium sesquioxide and carbon was determined with rising and falling pressures of carbon monoxide, and using Acheson graphite or carbon obtained by adding carbon monoxide to the exhausted reaction mixture; the equilibrium between 886° and 1096° is expressed by the equation $\log p = 11{\cdot}375-11550/T$. In the reduction of uranium dioxide, care is necessary to exclude nitrogen so far as possible; the equilibrium between 1480° and 1801° is represented by the equation $\log p = 12{\cdot}09-19100/T$. The heat consumed by the evolution of 1 mol. of carbon monoxide is 52,800 cal. for chromium sesquioxide and 87,300 cal. for uranium dioxide at mean temperatures of 990° and 1670°, respectively; the carbides formed are probably Cr_3C_2 and UC_2. By the action of nitrogen on uranium carbide at 1180°, the nitride U_3N_4, insoluble in acids and alkalis, is formed. When this is heated at about 1740°, nitrogen is evolved, and the *nitride* U_5N_4 is obtained, and at about 1900° the *nitride* U_5N_2 is formed. Both these nitrides are completely soluble in acid, the nitrogen being obtained as ammonia and hydrogen evolved.

A. Geake.

Equilibrium in the action of oxygen on solid metal chlorides (cupric, nickel, and cobalt chlorides). K. Jellinek and A. Rudat (Z. anorg. Chem., 1926, **155**, 73—83).—Equilibria of the type $2MCl_2+O_2 \rightleftharpoons 2MO+2Cl_2$ were investigated by heating solid cupric, nickel, or cobalt chloride in a steady stream of oxygen between 300° and 600°. The composition of the gas mixture after passing over the chloride was determined at intervals and that of the residual solid at the end of the experiment. With cupric chloride, the reaction proceeds in two stages: $4CuCl_2+O_2 \rightleftharpoons 2CuO,CuCl_2+2Cl_2$; $2CuO,CuCl_2+O_2 \rightleftharpoons 4CuO+2Cl_2$. With nickel and cobalt chlorides, the change is directly to NiO and Co_3O_4, respectively. The heats of reaction calculated from the equilibria agree well with those observed thermochemically.

M. Carlton.

Reaction provinces. X. Fe–S–SiO_2, Fe–Mg–S, and Fe–Al–S. W. P. Jorissen and B. L. Ongkiehong (Rec. trav. chim., 1926, **45**, 540—544).—Reaction regions have been observed for mixtures of solid substances resembling those obtained with gaseous mixtures (this vol., 246). Data are given, and expressed graphically, for the limits of composition within which reaction takes place for the following mixtures: iron and sulphur; iron, sulphur, and silica; magnesium and sulphur; iron, magnesium, and sulphur; iron, aluminium, and sulphur. J. Grant.

Application of thermodynamical principles to the time rates of chemical changes and vaporisation. S. Sano (Anniversary Vol. Nagaoka, 1925, 125—135).—A formula for the rate of chemical changes, simplifying for gases to the mass action law, is derived on the assumptions that the reacting mass is a fluid, not under the influence of an electric field, that the effects of gravity and surface tension are negligible, and that the system is under an isotropic pressure. The assumption that the pressure of the vapour evaporating from a liquid may be considered equal to that of the saturated vapour in equilibrium with the liquid phase is contradictory to the laws of thermodynamics.

Chemical Abstracts.

Thermodynamic treatment of the occurrence of mixed crystal gaps and of compounds in solid solutions of binary systems. H. Bredemeier (Z. anorg. Chem., 1926, **154**, 405—412).—Theoretical. A. Geake.

Isothermal calorimetry. H. von Wartenberg and B. Lerner-Steinberg (Z. physikal. Chem., 1926, **122**, 113—120).—The troublesome and uncertain corrections for radiation necessary when using a calorimeter in the ordinary way can be dispensed with if the calorimeter liquid, while it is absorbing heat, is maintained at its initial temperature by addition of a 64% solution of ammonium nitrate. A calibrated thermometer is thus unnecessary, and the heat effect is calculated from the heat of dilution of the solution used. R. Cuthill.

Heat of dilution of ammonium nitrate. B. LERNER-STEINBERG (Z. physikal. Chem., 1926, **122**, 121—125).—Using the method of isothermal calorimetry (cf. preceding abstract), the heat of dilution of 64% solutions of ammonium nitrate to varying extents has been measured at 18·2°, 25°, and 21·6°. R. CUTHILL.

Heat of wetting of active carbon. K. ANDRESS and E. BERL (Z. physikal. Chem., 1926, **122**, 81—87).—Using a calorimeter of Schottky's pattern, the heat of wetting of active carbon by water is found to be 12·35 cal./g., and by organic liquids about 30 cal./g. R. CUTHILL.

Thermochemical studies. H. HIROBE (J. Fac. Sci. Tokyo, 1926, **1**, 155—222).—An isothermal calorimeter, specially adapted for the determination of small heats of reaction, is described. The temperature during the reaction is kept constant by the gradual addition of a compensating liquid, usually mercury (cf. J. Tokyo Chem. Soc., 1911, **32**, 551). Determinations have been made of the heat of mixing of fifty-one pairs of organic liquids. From the thermal data, the chemical equilibria have been calculated for two of the simpler cases (Ikeda, A., 1908, ii, 932), viz., the chloroform–ethyl ether and the paraldehyde–chloroform mixtures. In the first case, equilibrium corresponds with $CHCl_3+(C_2H_5)_2O \rightleftarrows CHCl_3,(C_2H_5)_2O$, the heat of formation being 3100 cal., and in the second with $2(CH_3CHO)_3+3CHCl_3 \rightleftarrows 3(CH_3CHO)_2,(CHCl_3)$. The constant a_{12}, the attraction between unlike molecules of the constituents in van der Waals' equation for a binary mixture, has been calculated from the heats of mixing. From this constant, and the molecular volume of the mixtures, the heat changes associated with the mixing of the components in varying proportions are calculated and found to agree fairly closely with the observed results. M. S. BURR.

Thermochemistry of gas reactions. I. Heat of formation and the conditions of existence of carbon tetrachloride. M. BODENSTEIN and P. GÜNTHER [with F. HOFFMEISTER] (Z. angew. Chem., 1926, **39**, 875—880).—The heat of the reaction $CCl_4+2H_2=C+4HCl$ was measured in a precision calorimeter (von Steinwehr, A., 1901, ii, 641), the reactants being mixed with hydrogen and chlorine to propagate explosion and primed with silver azide. The result, 62,570±350 cal. (evolved), when combined with Thomsen's value for the heat of formation of hydrogen chloride, gives 25,430±350 cal. as the heat of the reaction $C+2Cl_2=CCl_4$ at 20°. The equilibrium conditions for the latter reaction predicted by means of Nernst's heat theorem could not be realised experimentally, efforts to synthesise and decompose carbon tetrachloride by thermal means failing almost completely. S. K. TWEEDY.

Theory of electrolytic ions. XXXII. Determination of limiting values of the conductivity of ions of potassium, lithium, and sodium chlorides, sodium bromide, and potassium iodide. R. LORENZ and J. WESTENBERGER (Z. anorg. Chem., 1926, **155**, 144—159; cf. this vol., 360).—Theoretical. The conductivity of the ions is deduced and the values so obtained are compared with those of other investigators. M. CARLTON.

Influence of some "polyols" on the electrical conductivity of boric acid. J. BÖESEKEN (Rec. trav. chim., 1926, **45**, 552—557; cf. A., 1925, ii, 128).—The methods of preparation of β-methylbutane-βγ-diol and β-methylpentane-βδε-triol are described, and it is shown that both substances produce a slight lowering in the conductivity when added to solutions of boric acid. In the latter case, the lowering increases with the concentration of the triol. It is suggested that the hydroxyl groups are not favourably situated for the formation of complexes with the boric acid. J. GRANT.

Electrical conductivity as a basis for physico-chemical analysis. A. M. ZANKO (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 79—91).—The application of the method of conductometric titration to the determination of silver, chlorides, thiocyanates, and sulphates has been examined. In the titration of silver nitrate with sodium chloride or inversely, and of ammonium thiocyanate with silver nitrate solution, this method gives accurate results, but when it is applied to the determination of chlorine in barium chloride or ferric chloride, low results ensue. In the determination of the sulphate ion by precipitation as barium sulphate, accurate results are obtained only with sulphates of bivalent metals, low figures being given by sulphates of uni- or ter-valent metals. If the solution of the sulphate of the univalent metal is added slowly to excess of the barium chloride solution, the error may be diminished to 0·2—0·4%, but the results with salts of tervalent metals are less accurate. T. H. POPE.

Theory of electrolytic conductivity. O. REDLICH (Physikal. Z., 1926, **27**, 528).—Corrections to a previous paper (cf. A., 1925, ii, 541).

Ionisation produced by the hydration of quinine sulphate. (MLLE.) C. CHAMIÉ (J. Phys. Radium, 1926, [vi], **7**, 204—214; cf. A., 1923, ii, 113, 603).—A quantitative study of the hydration of quinine sulphate as manifested by the diminution of the ionisation current and by the increase in weight shows the parallelism between the two phenomena and confirms the various other conclusions previously recorded. Simple relations between the duration of the phenomena, the density of the layer of salt, and the initial intensity of the ionisation current are not observable unless the surface density is of the order of a few mg./cm.^{2} Under these conditions, the quantity of electricity liberated appears to be proportional to the amount of water absorbed. Continued repetition of the hydration process shows that the ionisation becomes less intense and that the current–time curves undergo progressive deformation. J. S. CARTER.

Electrolytic potential of iron amalgam. J. HEYROVSKÝ and B. SOUČEK (Compt. rend., 1926, **183**, 125—127; cf. A., 1924, ii, 598).—A difference of 0·4 volt is found between the deposition-potential of iron at the mercury dropping cathode and the electrolytic potential of pure iron. This indicates that the free energy of the metal is 0·4 volt-faraday (9220 cal.) less than that of its dilute amalgam, and

also, as experience shows, that direct amalgamation of iron is impossible. It is shown further, from the constancy of the *E.M.F.* between a mercury–iron mixture or an amalgam and a calomel electrode, that the "hyperactive" iron amalgam is metastable and is readily transformed into a mixture of the metals. The potential of the true amalgam measured 0·05 sec. after its formation by means of a rotary interrupter is found to be equal to the deposition-potential of iron on the mercury cathode. These phenomena are independent of the hydrogen-ion concentration, and are probably due to the liberation of free energy when the atoms in true solution in the amalgam rearrange themselves according to their magnetic moments into their crystalline forms and produce a suspension which is magnetic. J. GRANT.

Positions of tungsten and molybdenum in the normal potential series. A. S. RUSSELL and S. W. ROWELL (J.C.S., 1926, 1881—1892).—The chemical behaviour of tungsten and molybdenum indicates that, in some respects, they are more reactive than copper, but in others that they resemble mercury and silver, and the values given for the electrode potentials are not concordant. By the two following methods, however, it has been shown that their position in the normal potential series is approximately the same as that of mercury: (1) by finding the least reactive metal on which metallic tungsten and molybdenum can be deposited by shaking solutions of their compounds with an amalgam of the metal; (2) by finding what metals of known normal potentials lie on either side of tungsten and molybdenum in the series showing the order in which they are removed from mercury by an oxidising agent (cf. following abstract). When acid solutions of salts of these metals are shaken with different metal amalgams, small quantities of metallic tungsten or molybdenum are obtained and may be detected by the catalysis of the reaction $2H \rightarrow H_2$ which serves as a delicate means of identification. Platinum and chromium have a similar catalytic effect, and palladium and manganese somewhat less, but considerably greater than that of zinc, copper, iron, or cobalt. The solubility of chromium, manganese, iron, cobalt, copper, molybdenum, and tungsten in mercury is very small, being of the order of 10^{-5} g. per g. of mercury. There is a certain amount of experimental evidence to suggest that there may exist a more active form of both tungsten and molybdenum, of an activity comparable with that of active cobalt and nickel. M. S. BURR.

Order of removal of manganese, chromium, iron, cobalt, and nickel from amalgams. A. S. RUSSELL, D. C. EVANS, and S. W. ROWELL (J.C.S., 1926, 1872—1881).—The order zinc, cadmium, manganese, thallium, tin, lead, copper, chromium, iron, bismuth, cobalt, and nickel is the order of removal of these metals by an oxidising agent from an amalgam with mercury (cf. Russell and Evans, A., 1925, ii, 1205). This is not the order of their positions in the normal potential series, the absolute positions of chromium, manganese, iron, cobalt, and nickel being displaced towards the noble metals in mercury, but without altering their relative positions. Experimental details are given of the preparation of the amalgams and of their treatment with oxidising agents, viz., 0·1*N*-potassium permanganate, ferric sulphate, or uranyl nitrate in 2*N*-sulphuric acid. The abnormal behaviour of the elements mentioned is ascribed to a type of passivity, and an electronic theory is put forward in explanation. According to this theory, two electrons are present in the outer 4-quantum orbit of these metals in the active state. In the passive state, however, there is only one electron in the orbit, the second having passed to the incomplete 3-quantum orbit, which exists in all these metals. The difference between the electrode potentials in the active and passive states should represent the work done by the passage of this electron from one orbit to the other. There exists a certain amount of spectroscopic evidence to indicate that metallic nickel, which is ordinarily in the passive state, has only one electron in its outer orbit. The values of ${}_0E_h$ for chromium, iron, cobalt, and nickel in the passive state are of the same order as those of the higher members of group VI and of the transition groups. Observations relating to the reducing properties of manganese, thallium, tin, and iron amalgams are described. M. S. BURR.

***E.M.F.* measurements in aqueous solutions of hydrochloric acid containing sucrose.** G. SCATCHARD (J. Amer. Chem. Soc., 1926, **48**, 2026—2035).—The *E.M.F.* of the cell (I) Hg|HgCl,KCl(sat.)| 0·1012*N*-HCl, sucrose (*c*), AgCl|Ag with a flowing junction (Scatchard, A., 1925, ii, 398), and of the cell (II) Pt,H_2|0·1012*N*-HCl, sucrose (*c*), AgCl|Ag with a rocking hydrogen electrode (*ibid.*, 397), were measured at 25°, *c* varying from 0 to 700 g./litre. The potentials of both the hydrogen and silver chloride electrodes changed during inversion of the sucrose. The *E.M.F.* of (II) decreased when the hydrogen electrode was not rocked, indicating that some reaction consuming hydrogen is occurring, probably the catalytic hydrogenation of sucrose or its inversion products. The liquid-junction potential is changed considerably on addition of sucrose. The *E.M.F.* of (II) calculated from the Debye–Hückel theory agree moderately well with the experimental results provided hydrate formation is assumed in the sucrose solution (cf. A., 1922, i, 230); the effect of acid on this hydrate equilibrium is neglected by the theory, and hence the deviations in concentrated solutions increase regularly with the concentration. The results with (I) confirm the conclusion that the effect of changing dielectric constant on activity is not the same for potassium and for chloride ions (cf. A., 1925, ii, 971). The recorded values of single-ion activities in sucrose solution are considered to be of doubtful accuracy. S. K. TWEEDY.

Dissociation of lithium chloride and sodium bromide in absolute ethyl alcohol. C. DRUCKER and R. SCHINGNITZ (Z. physikal. Chem., 1926, **122**, 149—169).—*E.M.F.* measurements with solutions of the above salts in absolute ethyl alcohol have been made with the cells Ag|AgCl,LiCl|LiCl,AgCl|Ag, and Ag|AgBr,NaBr|NaBr,AgBr|Ag at 25°, and with the cells Li_xHg|LiCl,AgCl|Ag, and Na_xHg|NaBr,AgBr|Ag at the ordinary temperature. From the results, the

E.M.F. of the cell Ag|AgCl,0·1*N*-LiCl|Li in alcoholic solution at 25° is calculated to be 3·100 volts. Ebullioscopic determinations have also been made with the same solutions. In the case of the chloride, the mol. wt. rises with increasing concentration of the solution up to a concentration of about 0·5*N*, after which it slowly falls again, presumably owing to the predominating influence of solvation. From transport measurements at 25°, the following limiting values of mobility are calculated: hydrogen, 63·4; lithium, 15; chlorine, 21; sodium, 24; bromine, 20. The values of the degree of dissociation calculated from the osmotic effects, conductivities, and *E.M.F.*, respectively, vary in the same way as they do for aqueous solutions. It is pointed out that the possibility that the molecular state of the solvent may be changed by the solute prevents a satisfactory determination of the dissociation of the solute from the experimental results. It seems probable, however, that lithium chloride is more highly solvated in alcoholic than in aqueous solution, and that complex ions are present in the former solution. From measurements with the cell Ag|$AgNO_3$,$NaClO_4$|$NaClO_4$,AgCl|Ag the solubility product of silver chloride in alcoholic solution is calculated to be 4×10^{-18} at 25°. R. CUTHILL.

Oxidation–reduction potentials of 2-ketodihydroindole-3-β-propionic acid and its halogen derivatives. E. C. KENDALL and J. M. ORT (J. Biol. Chem., 1926, **68**, 611—630).—A mixture of the oxidised and reduced forms of 2-ketodihydroindole-3-β-propionic acid (cf. Kendall and others, this vol., 734) does not, in aqueous solution, attain definite oxidation–reduction potential related to the proportions in which the two forms are present. On addition of a mild oxidising agent such as 2 : 6-dibromoindophenol, the latter is partly or completely reduced, a potential being set up the magnitude of which is determined by the proportions of reduced and unchanged indophenol. The halogen derivatives of the indolepropionic acid react more rapidly with indophenol, but the final potentials attained are of the same order. It appears that the indophenol reacts stoicheiometrically with the indolepropionic acid; this reaction is inhibited by the presence of a small amount of hydrogen peroxide, which does not itself oxidise the indolepropionic acid in the same way as does the indophenol. C. R. HARINGTON.

Effect of superposed alternating current on the polarisable primary cell zinc–sulphuric acid–carbon. II. High-frequency current. A. J. ALLMAND and H. C. COCKS (Proc. Roy. Soc., 1926, **A**, **112**, 252—258; cf. Allmand and Puri, A., 1925, ii, 303).—The results obtained by Brown when using an alternating current of frequency 12,000 (A., 1914, ii, 332) have been further investigated. The effect of superposing a high-frequency current on the primary cell, amalgamated zinc–sulphuric acid–carbon, was studied from the point of view of current delivery of the cell and electrode potential. It is shown that an amalgamated zinc electrode made the anode in a solution containing free acid undergoes considerable polarisation, and that this polarisation can be more than overcome by the superposition of a sufficiently large alternating current of high frequency. It is assumed that this effect is the cause of the increased current output in the cell. The polarisation of a carbon cathode charged with hydrogen appears to be totally unaffected by alternating currents of frequency 10,000—12,000.

L. L. BIRCUMSHAW.

Polarisation of zinc electrodes in neutral and acid solutions of zinc salts by direct and alternating currents. I. A. J. ALLMAND and H. C. COCKS (Proc. Roy. Soc., 1926, **A**, **112**, 259—279; cf. preceding abstract).—A close investigation has been made of some of the factors affecting the polarisation of zinc electrodes, with a view to explain the facts previously observed (*loc. cit.*). Working at the ordinary temperature and with zinc sulphate solutions, potential measurements have been made with amalgamated zinc electrodes in absence and in presence of free sulphuric acid, and with unamalgamated electrodes in neutral solution. Alternating and compound currents have been used, and a few experiments made with direct currents. The frequencies varied from 50 to 11,000. The results are shown graphically and discussed in detail. The observed polarisation phenomena are assumed to be due to retardations in the actual electrode process, these retardations being closely connected with charges of atomic oxygen and hydrogen in the electrode surface layers. L. L. BIRCUMSHAW.

Electrochemical oxidation of organic substances. F. FICHTER (J. Chim. phys., 1926, **23**, 481—500).—A lecture delivered before the Société de Chimie-Physique on February 24th, 1926.

L. F. GILBERT.

Anode-effect in the electrolysis of fused salts. H. VON WARTENBERG [with E. MANTHEY and W. CONZELMANN] (Z. Elektrochem., 1926, **32**, 330—336; cf. Oesterheld and Brumer, *ibid.*, 1916, **22**, 38; Arndt and Probst, *ibid.*, 1923, **29**, 323).—In the electrolysis of fused salts under certain conditions, the mass withdraws from the anode and a number of small arcs are formed across the gas-space between the anode and the fused medium. A critical current density exists for each salt, above which this so-called anode-effect occurs. In presence of oxides, silicates, etc., larger current densities are necessary. Experiments with various fused halides show that the phenomenon is not a surface-tension effect, since oxides have little or no influence on the surface tensions of fused chlorides. Determinations of the solubilities of the halogens in the corresponding fused metal halides show that these solubilities are extremely small, and hence the anode gases, being practically insoluble, should escape in a continuous manner. The data lead to the conclusion that, in media free from oxides etc., the anode gas is negatively charged and therefore remains round the anode in the form of a large bubble. In presence of small amounts of oxides (*e.g.*, reaction of fused halide with air), the gas acquires a positive charge and escapes in the form of small bubbles. J. S. CARTER.

Alternating-current cell. E. S. HEDGES (J.C.S., 1926, 1892—1893).—Owing to the periodic properties

of cold-worked copper (Hedges and Myers, A., 1925, ii, 680), an alternating-current cell may be constructed by dipping two electrodes of rolled copper in a solution of 25 c.c. of nitric acid (*d* 1·42) and 10 c.c. of hydrochloric acid (*d* 1·16) in 70 c.c. of water. The positive and negative currents are usually asymmetrical, and the maximum *E.M.F.* is 0·14 volt, the frequency being about one cycle per min. A periodic unidirectional current, varying between 30 milliamp. and zero, is obtained by using annealed copper in place of one of the rolled copper electrodes. M. S. Burr.

Origin of the *E.M.F.* of a photo-electric cell containing a fluorescent electrolyte. A. Grumbach (Phil. Mag., 1926, [vii], **2**, 313; cf. A., 1925, ii, 549; Rule, this vol., 361).—Rule's interpretation of his results is criticised, in that he neglects the Becquerel effect. A. B. Manning.

Electrolysis of chromium trioxide solutions. E. Müller (Z. Elektrochem., 1926, **32**, 399—413).—From a study of the potential-current curves in 30% solutions of chromium trioxide, it is inferred that a film of chromium sesquioxide is formed at the cathode at potentials not exceeding +0·3 volt. This diaphragm hinders access of chromium ions, but is permeable to hydrogen ions. At about −0·7 volt, the diaphragm begins to be permeable, and partial continuous reduction of sexavalent to tervalent chromium ions sets in. At still more negative potentials, deposition of metallic chromium takes place, and the diaphragm disappears. Films of oxide acting as diaphragms are also formed on metallic cathodes owing to direct chemical oxidation by chromium trioxide. In presence of foreign anions such as SO_4, NO_3, ClO_4, and SiF_6, the chromium sesquioxide diaphragm is mechanically imperfect and may be swept away by the evolved gaseous hydrogen. For this reason, the presence of sulphates promotes deposition of chromium in a bright coherent form. W. A. Caspari.

Reaction velocity and thermodynamics. E. Jouguet (Ann. Physique, 1926, [x], **5**, 470—474).—Mathematical, in explanation of a previous paper on this subject (this vol., 362). C. H. D. Clark.

Reaction velocities. F. E. C. Scheffer and W. F. Brandsma (Rec. trav. chim., 1926, **45**, 522—534; cf. A., 1922, ii, 699).—From the consideration of the analogous behaviour of the velocity (v) and thermodynamic potential (μ) of a chemical reaction, the following simple relation is deduced: $v=Ce^{(\mu-\epsilon+T\eta)/RT}$, where ϵ_t and η_t are the energy and entropy magnitudes, respectively, T is the absolute temperature, and C a constant which may be considered as universal. This equation is derived from the simpler form $v=Ce^{\mu_t/RT}$ by introducing those expressions which represent energy and entropy differences, and thus render C independent of concentration, temperature, and the constants of the reacting substances. The equation involves the consideration of the existence in a chemical reaction of an intermediate state having maximum energy, the dependence of the reaction velocity on the temperature being determined by the energy difference between this and the initial state. The equation is applied to reactions in which the same reacting substances can undergo two different reactions, to catalysis, and to reactions involving association. J. Grant.

Reaction constant equation and a simple method of determining the end-point. S. E. Sheppard (Phil. Mag., 1926, [vii], **2**, 448).—The method of determining the end-point and velocity constant of a unimolecular reaction from two values obtained at times such that one time is half the other, given by Smith (this vol., 362), was previously developed by Filon in a somewhat different form (Sheppard and Mees, "Investigations on the Theory of Photographic Processes," 1907, p. 65). M. S. Burr.

Influence of pressure on the formation of the explosive wave. P. Dumanois and P. Laffitte (Compt. rend., 1926, **183**, 284—285).—The waves produced by the explosion under varying pressures of the gas mixture ($2H_2+O_2$) by means of an electric spark have been photographed. The length of the path over which the flame travels before the explosion wave is formed diminishes rapidly at first, and then more slowly with increase of pressure. J. Grant.

Rate of flame propagation in gaseous explosive reactions. F. W. Stevens (J. Amer. Chem. Soc., 1926, **48**, 1896—1906).—Flame propagation in mixtures of carbon monoxide and oxygen was examined by exploding the gases within a soap-bubble (constant-pressure bomb), the explosion being initiated at the centre, and photographing the flame on a continuous film. Under these conditions, the concentrations of the gases about to explode remain constant, so that the flame velocity is constant and is proportional to the product of the initial concentrations of the reactants. The proportionality factor depends on the moistness of the gases. S. K. Tweedy.

Autolytic decomposition of thiosulphuric acid. K. Jabłczyński and Z. Rytel (Rocz. Chem., 1926, **6**, 201—210).—Spectrophotometric measurements carried out on acidified solutions of sodium thiosulphate show that free thiosulphuric acid immediately decomposes with the formation of sulphurous acid and monatomic sulphur. This reaction is unimolecular and reversible, being retarded by liberated monatomic sulphur and by sulphur dioxide. The sulphur is at first invisible, the solutions becoming opalescent only on the formation of polyatomic aggregates, which then adsorb atomic sulphur from the solution. These aggregates may thus be considered to act as an autocatalyst, since by removing atomic sulphur they accelerate the reaction. R. Truszkowski.

Iodine and ferrous salts. K. Jabłczyński and M. Stückgold (Rocz. Chem., 1926, **6**, 211—217).—The reaction between ferrous ammonium sulphate and iodine is examined spectrophotometrically, whence it is found that combination occurs to the extent of 72% at the ordinary temperature, the velocity of reaction being 4·5 times as great as the reverse reaction of the decomposition of ferric iodide. In

view of this, the accuracy of Mohr's method for the iodometric determination of ferric iron is questioned. R. TRUSZKOWSKI.

Interferometry. III. Observation of the course of a chemical reaction by means of the Zeiss-Löwe liquid interferometer. K. SCHAUM and W. BARTH (Z. wiss. Phot., 1926, **24**, 166—171; cf. this vol., 779).—The tautomeric change of nitroethane and the hydrolysis of methyl acetate by sodium hydroxide are found to be reactions of the first and second orders, respectively. R. CUTHILL.

Reaction of the transference of electrons from iodine ions to the ions of tervalent iron. L. V. PISARSHEVSKI (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 143—150; cf. A., 1916, ii, 184).—The results previously obtained by the author and others show that, for low concentrations of the reacting substances, the reaction between ferric ions and iodine ions is always bimolecular, in accordance with the scheme: $Fe^{\cdot\cdot\cdot}+I' \rightleftharpoons Fe^{\cdot\cdot}+I$. The author's theory of catalysis indicates that the catalyst exchanges energy with the process being catalysed. Calculation shows that, both at 11° and at 25°, the magnitude of the free energy of the reaction is very considerably the greater when solid iodine separates from the solution, *i.e.*, when the reaction proceeds in sufficiently concentrated solutions. The great magnitude of the free energy is a sign of the large difference of tension between the systems of the left- and right-hand sides of the above equation. T. H. POPE.

Hydrogen ions as a factor lowering the order of a reaction. M. A. ROZENBERG (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 103—119).—Earlier investigations on the reactions $Fe(CN)_6'''+I'$, $KMnO_4+H_2C_2O_4$, $Sn^{\cdot\cdot}+2Fe^{\cdot\cdot\cdot}$, etc. showed that increase in the concentration of the hydrogen ions resulted in the conversion of these reactions from multimolecular to unimolecular (Ukraine Chem. J., 1925, **1**, 19). The experimental results now given show that the same is the case with the reaction $MnO_4'+5Br'+8H^{\cdot} \longrightarrow Mn^{\cdot\cdot}+5Br+4H_2O$. T. H. POPE.

Anomalies of certain reactions. A. ANGELI (Atti R. Accad. Lincei, 1926, [vi], **3**, 450—455).—A number of instances are cited in which the introduction of substituent groups, particularly into closed ring compounds, either favours or hinders the reactivity of substituents already present. T. H. POPE.

Kinetics of chemical reactions. IV. Velocity equation of the hydrolytic decomposition of α-bromopropionic acid. V. α-Bromobutyric acid. J. ZAWIDZKI (Rocz. Chem., 1926, **6**, 136—140, 141—144).—IV. The results obtained by Senter (J.C.S., 1909, **95**, 1827) for the velocity of hydrolysis of α-bromopropionic acid conform to the equation $dx/dt=k(a-x)/\sqrt{x}$, and not to that given by Senter, viz., $dx/dt=k(a-x)$, showing that the reaction proceeds in two stages: the production of acrylic acid with elimination of hydrogen bromide and the addition of water yielding lactic acid.

V. The values obtained by Senter (*loc. cit.*) for the velocity of hydrolysis of α-bromobutyric acid conform approximately to the equation $dx/dt=k\sqrt{(a-x)^3}/\sqrt{x}$. R. TRUSZKOWSKI.

Influence of some lyophilic colloids on the velocity of chemical reactions. E. SAUER and W. DIEM (Z. angew. Chem., 1926, **39**, 955—961).—The rate of hydrolysis of ethyl acetate by sodium hydroxide is reduced by the addition of gelatin according to the equation $K_0-K=0{\cdot}94c^{0{\cdot}873}$, where K_0 and K are the velocity constants of the reaction in the absence of gelatin and in a gelatin solution of concentration c. The decrease in the value of K caused by gelatin is due to its power of combining with the free alkali and so reducing its concentration; the increased viscosity of the solution is without influence on the results. From the value of K for different gelatin concentrations, the equivalent weight of gelatin has been calculated to be 7683. Gum arabic also reduces the velocity constant of the reaction between ethyl acetate and sodium hydroxide, but the effect in this case is due to the displacement of the calcium and magnesium in the gum by sodium and the relatively feeble dissociation of calcium and magnesium hydroxides. The decrease of the velocity constant of hydrolysis of methyl acetate in hydrochloric acid solution by the addition of gum arabic is proportional to the amount of colloid present and is therefore due to the decomposition of the gum into arabic acid, which is only very feebly dissociated, and calcium and magnesium chlorides with a consequent decrease in the hydrogen-ion concentration. The viscosity of the arabic acid solution has no effect on the hydrolysis. A. R. POWELL.

Hydrolysis of ethyl acetoacetate by acids. A. SKRABAL and A. ZAHORKA (Monatsh., 1926, **46**, 559—574).—The velocity of hydrolysis of ethyl acetoacetate in acid solutions cannot be determined by titration of the acetoacetic acid liberated, on account of the decomposition of the latter into acetone and carbon dioxide, but determinations of the diminishing concentration of the ester show that the hydrolysis is a reaction of the first order with $k=0{\cdot}000989$ at 25° with the minute as unit of time, this value being in good agreement with that found by Palomaa (A., 1914, i, 136). The theory of the acid and alkaline hydrolysis of ethyl acetoacetate is discussed in detail. The remainder of the paper is polemical against Olivier and Berger (A., 1925, ii, 802). G. M. BENNETT.

Esterification of *cyclo*hexanol and some of its homologues. I. Viscosity, surface tension, and thermochemistry. (MLLE.) G. CAUQUIL (J. Chim. phys., 1926, **23**, 586—608).—The velocity of reaction, position of equilibrium, and changes in the viscosity and surface tension have been determined for the esterification of *cyclo*hexanol and its homologues, *o*-, *m*-, and *p*-methyl*cyclo*hexanol, 1 : 3-dimethyl*cyclo*hexan-4-ol, and *o*-ethyl*cyclo*hexanol, with acetic acid at 95°. With equimolecular quantities of acid and alcohol, the values of the initial velocity (100 × mass of alcohol esterified after 1 hr./total alcohol) are, respectively, 6·20, 6·17, 6·8, 6·0, 5·38, and 4·9, values

which do not agree with those calculated from the application of the law of mass action, and no recognisable relation exists between the mean values of k_1 (constant of the esterification reaction) for the cases studied. The position of equilibrium is shifted in favour of the free alcohol and acid when hydrogen is replaced by the methyl group, the magnitude of the effects produced being in the order $o>m>p$, and in all cases being greater than that produced in the corresponding open-chain alcohols. The percentage of ester formed at equilibrium in the cases of the homologues of *cyclo*hexanol mentioned above is 55·64, 49·85, 53·10, 54·14, 47·5, and 49·21%, respectively. The percentage of ester formed at equilibrium when varying initial concentrations of acid and alcohol are used agrees with the requirements of the law of mass action. Measurements both of the viscosity and of the surface tension of the reaction mixture during esterification (equimolecular proportions of acid and alcohol) show that it is possible to follow the course of the reaction by either method, each property being represented by an equation of the type $\eta_t=\eta_0+\beta x$, where x is the percentage of acid esterified at the time t, the values of the constant β for viscosity measurements being, respectively, $-4\cdot05$, 3·95, 4·01, 3·12, 2·51, and $1\cdot80\times10^{-4}$; and for the surface tension, +3·055, 1·46, 1·40, 1·40, 1·45, and $0\cdot95\times10^{-2}$. The viscosity of the *cis*-derivatives is much less than that of the *trans*. Data concerning the thermochemistry of *cyclo*hexanol are given, the more important values being $C_6H_{11}\cdot OH_{solid}+Na_{solid}=C_6H_{11}\cdot ONa_{solid}+32\cdot49$ cal.; $C_6H_{11}\cdot ONa_{solid}+5C_6H_{11}\cdot OH_{solid}=C_6H_{11}\cdot ONa,5C_6H_{11}\cdot OH_{solid}+17\cdot75$ cal.; $C_6H_{11}\cdot OH_{liq.}+aq=C_6H_{11}\cdot OHaq+2\cdot77$ cal.; $C_6H_{11}\cdot OH_{solid}+aq=C_6H_{11}\cdot OHaq+2\cdot32$ cal., whence the heat of fusion of *cyclo*hexanol is 0·45 cal./mol. The heat of solution of *cyclo*hexanol immediately after solidification is 2·62 cal./mol., the constant value being reached only after 6 or 7 days. The heat of formation of solid $C_6H_{11}\cdot ONa$ (32·49 cal.) is 1 cal. greater than the value calculated by the method of Forcrand (A., 1900, ii, 527), and hence the acidity of the hydrogen of the hydroxyl group is increased by ring closure, and the percentage of ester formed at equilibrium for various alcohols varies inversely in accordance with the acidity calculated from thermochemical data, the values for the alcohols $-CH_2\cdot OH$, $>CH\cdot OH$ (open chain), and $>CH\cdot OH$ (ring) being: acidity, 33·05, 36·05, 37—37·5; percentage of ester at equilibrium, 66·6, 60·0, 55·5%, respectively.

J. W. Baker.

Corrosion of aluminium by water. I. L. W. Haase.—See B., 1926, 671.

Possible mechanism for the lowering of the heat of activation of a reaction by a catalytic surface. R. E. Burk (J. Physical Chem., 1926, **30**, 1134—1140).—Various catalytic phenomena are explained by a theory which involves multiple adsorption of the atoms in the reacting molecule. Both atoms in a molecule A—B must be attached to the catalysing surface in order to bring about the partial separation of the atoms A and B in the molecule and the resultant diminution in the heat of activation. Further, the adsorbing atoms must be spaced so that the distance between the points of maximum intensity in their attractive forces is not the same as the corresponding distance in the molecule A—B.

L. S. Theobald.

Transference of active states and the mechanism of catalytic action. S. Miyamoto (Sci. Papers Inst. Phys. Chem. Res., 1926, **4**, 257—261).—A theoretical paper in which the possibility of the transference of active states of molecules is considered and certain phenomena, such as induced reaction, assimilation, after-glow of fluorescence, and photochemical residual effect, are discussed from this point of view. A mechanism of catalytic processes is elaborated, according to which molecules of catalyst, activated by absorption of energy from their surroundings, transfer their active states to molecules of reactants. The theory is extended to include promoter action and catalyst poisoning. Activated molecules of the promoter transfer their active states to molecules of reactants by way of molecules of the catalyst. Poisoning occurs when molecules of the catalyst transfer their active states more easily to molecules of some foreign substance (the poison) than to molecules of reactants. J. S. Carter.

Catalytic decomposition of nitric oxide at the surface of platinum. T. E. Green and C. N. Hinshelwood (J.C.S., 1926, 1709—1713).—The decomposition reaction of nitric oxide at the surface of a heated platinum wire at temperatures from 882° to 1450° is unimolecular. Of the reaction products, nitrogen has no influence on the velocity of decomposition, but oxygen has a slightly retarding effect. The apparent heat of activation is approximately 14,000 cal. The homogeneous gas decomposition is probably bimolecular. C. H. D. Clark.

Action of nitric acid on metals in the presence of catalysts. C. C. Palit and N. R. Dhar (J. Physical Chem., 1926, **30**, 1125—1133).—The amount of mercurous nitrite formed (A., 1924, ii, 486) in the reaction between mercury and nitric acid (26%) is increased by the addition, in approximately equivalent amounts, of various nitrates in the following, descending order: mercurous, ferric, manganous, nickel, uranium, chromium, cobalt, and copper. Nitrous acid is a primary product of the reaction between nitric acid and an element (cf. A., 1925, ii, 315), and the order of 15 elements, in this connexion, is given. In the reactions between nitric acid and copper and nitric acid and mercury, tartaric, citric, and oxalic acids, glycerol, dextrose, and sucrose act as retarders, and in the latter reaction the yield of mercurous nitrite is small compared with the amount of mercury dissolved. Formic acid is a retarder with copper and nitric acid, but an accelerator with mercury. The sulphonates and other organic sulphur compounds in small concentration (1%) act in some cases as accelerators and in others as retarders, with both reactions, but in greater concentration all become retarders (cf. Moureu and Dufraisse, A., 1924, ii, 602). Alkaloids behave in a similar manner. Sunlight accelerates the reaction between nitric acid and copper or mercury. L. S. Theobald.

Formation of nitric oxide at high temperatures. E. BRINER, J. BONER, and A. ROTHEN (Helv. Chim. Acta, 1926, 9, 634—648).—No trace of nitric oxide is formed by passing air over catalysts below 1300° and only a minute amount at 1450°. At 1607°, 0·27 c.c. of nitric oxide is formed from 3·2 litres of air in 1 hr. without a catalyst, 0·8 c.c. in the presence of pure platinum, and 3·15 c.c. in the presence of pure platinum coated with an equimolecular mixture of calcium, barium, and strontium oxides. The reactivity of oxide catalysts seems to depend on their electronic emissivity. At 1607°, the equilibrium concentration of nitric oxide in air is 0·81% (±0·05), which agrees with the correct theoretical figure deduced from Nernst's theorem, but is about 100% greater than that found by Nernst and his collaborators. If x is the equilibrium concentration of nitric oxide in a mixture of oxygen and nitrogen at $T°$ Abs., then $\log x = -4726/T + 0·8 + 0·5 \log (C_{N_2} . C_{O_2})$. A. R. POWELL.

Catalytic decomposition of sodium hypochlorite solutions by finely-divided metallic oxides. E. CHIRNOAGA (J.C.S., 1926, 1693—1703).—Experiments have been made on the catalytic activities of oxide gels of cobalt, aluminium, nickel, copper, iron, manganese, mercury, and certain mixtures of these oxides in the decomposition of sodium hypochlorite solutions. In general, the reactions may be represented by $-dc/dt = k_1 c^{1/n}$, where c is the concentration of hypochlorite. The surface of catalyst is approximately proportional to k_1 over considerable ranges. The form of the equation points to adsorption phenomena, probably of hypochlorite ions. Aluminium oxide, which possesses no appreciable activity, promotes the activity of cobalt peroxide. The activity of nickel peroxide is unaffected by sodium chloride, and is decreased by sodium hydroxide, whilst aluminium oxide exerts promoter action, changing to "depressor" action as the relative amount of aluminium is increased. Mixtures of nickel and cobalt peroxides are more active than either singly, the mixture containing 30% of nickel peroxide showing maximum activity. The order of activity is Ni > Co > Cu > Fe > Mn > Hg. The apparent autodecomposition of sodium hypochlorite is unimolecular up to 317 days, after which the velocity coefficient slowly increases.
C. H. D. CLARK.

Decomposition of potassium chlorate. II. Spontaneous decomposition temperatures using various proportions of manganese dioxide, and of ferric oxide, and of a mixture of manganese dioxide and ferric oxide as catalysts. J. A. BURROWS with F. E. BROWN (J. Amer. Chem. Soc., 1926, **48**, 1790—1794; cf. Brown, Burrows, and McLaughlin, A., 1923, ii, 561).—The work previously described was repeated with carefully purified manganese dioxide and the results were confirmed. Similar results are obtained with ferric oxide, although in this case the spontaneous decomposition temperature remains constant over a wide variety of mixtures (cf. Brown and White, Proc. Iowa Acad. Sci., 1924, **31**, 291). A lowering of the spontaneous decomposition temperature occurs when half the manganese dioxide in a mixture with potassium chlorate containing more than 75 mol.-% of the latter is replaced by ferric oxide; the temperature is raised when less than 75 mol.-% of chlorate is present. The substitution of manganese dioxide for one half of the ferric oxide in mixtures of the latter with potassium chlorate lowers the spontaneous decomposition temperature for practically all proportions of catalyst. S. K. TWEEDY.

Catalytic decomposition of potassium chlorate by dust particles of manganese dioxide. S. ROGINSKI and E. SCHULZ (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 189—206).—The decomposing action of the gas generated during the catalytic decomposition of potassium chlorate (cf. Poliakov, this vol., 918) depends on the presence in the gas of very fine particles of the catalyst, these particles being more active than the ordinary catalyst. When manganese dioxide is heated alone, the gas liberated also exhibits a decomposing action towards potassium chlorate, but this is the case only when the dioxide is contaminated with volatile compounds which reduce the chlorate when heated. When pure manganese dioxide is heated, the gas formed contains no particles which pass through a filter and does not decompose potassium chlorate.
T. H. POPE.

Catalytic phenomena in the decomposition of potassium chlorate. M. BELENKI (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 171—173).—The results of experiments on the decomposition of potassium chlorate in presence of various oxides and metals show that the extent to which the temperature of the initial decomposition of the chlorate is lowered varies with the proportion of catalyst employed; thus when the ratio chlorate : manganese dioxide is 1 : 2 (20 : 1), decomposition begins at 75° (140°). The velocity of the decomposition is also influenced; with the lesser proportion of the peroxide, the reaction exhibits acceleration to a maximum and subsequently proceeds more slowly, but with the higher proportion, the decomposition is more intense and comparatively regular. The best catalysts of this change are the oxides of metals with variable valency, and peroxides and oxides are more active than suboxides. The course of the catalysis is influenced by the presence of moisture and by the temperature at which the catalyst is dried.

Most of the pure metals belong, as far as their catalytic effect is concerned, to one of two classes: good catalysts, including palladium, osmium, ruthenium, and uranium; bad catalysts, including iridium, rhodium, molybdenum, tungsten, vanadium, chromium, niobium. Excepting with molybdenum and tungsten, the poor catalytic properties of the metals of the second group are due to their increasingly rapid oxidation, evidenced by the appearance of flashes or explosions or by the formation of a layer of oxide. The possibility of oxidation is not excluded with metals of the first group, but the oxides are either volatile or capable of catalysing the reaction. The worst catalysts of the decomposition of potassium chlorate are those metals and oxides with which dissociation into ions and electrons is most strongly

marked, such metals being the most rapidly oxidised by the oxygen liberated. T. H. POPE.

Electronic character of the catalysis of potassium chlorate by oxides and metals. L. PISARSHEVSKI (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 165—169).—The catalysis of potassium chlorate by metals or their oxides is evidently due to mechanical disturbance of the equilibrium of the electrons of the chlorate molecule. It is probable, not that the electronic equilibrium is ruptured directly by the impacts of the electrons of the catalyst, but that these electrons ionise by their impacts the gases adsorbed by the catalyst. On leaving the catalyst, the gaseous ions act on the molecules of the chlorate and bring about a series of electronic transferences resulting in decomposition of the chlorate molecule. T. H. POPE.

Promoter action in homogeneous catalysis. III. Cobalt salts as promoters in the catalytic decomposition of hydrogen peroxide by potassium dichromate. A. C. ROBERTSON (J. Amer. Chem. Soc., 1926, **48**, 2072—2082).—The velocity of the above promoted reaction, which is also promoted by salts of copper, nickel, manganese, and cerium, is, in the case of cobalt chloride, an exponential function of the amount of cobalt salt added. This is explained on the assumption of a change in the path of the catalysis (cf. A., 1925, ii, 690). The unpromoted decomposition may be written: (i) $K_2Cr_2O_7+H_2O_2=2KCrO_4+H_2O$; (ii) $2KCrO_4+H_2O_2=K_2Cr_2O_7+H_2O+O_2$. In the promoted reaction, instead of (ii) the very rapid reaction (iii) proceeds, followed by (iv), the latter being more rapid than (ii) and so causing the promoter action: (iii) $2KCrO_4+CoCl_2+2H_2O=H_2CoO_3+K_2Cr_2O_7+2HCl$; (iv) $H_2CoO_3+H_2O_2+2HCl=CoCl_2+3H_2O+O_2$. This explanation agrees with the observation that a definite hydrogen-ion concentration is necessary for the promotion. Oxidation of the cobalt is indicated by a decrease in the concentration of the perchromic acid in the promoted reaction. The cobalt may be in the ter- or quadri-valent state during the promotion. S. K. TWEEDY.

Mechanism of the catalysis of hydrogen peroxide. L. PISARSHEVSKI and V. ROITER (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 93—102).—By the method of determining the order of a reaction by means of the current of the chemical reaction it is found that the catalysis of hydrogen peroxide by either platinum or manganese dioxide is, as a whole, a unimolecular process. The same is the case when the decomposition of the peroxide takes place in alkaline solution. The fact that a current traverses the wire connecting the hydrogen peroxide undergoing catalysis and the platinised platinum plate shows that the electrons of the catalyst play a direct part in the catalysis. The details of the mechanism of the decomposition are still obscure, but the nature of the mechanism seems to be the same when platinum as when manganese dioxide is used. T. H. POPE.

Catalytic activity of dust particles. F. O. RICE (J. Amer. Chem. Soc., 1926, **48**, 2099—2113).—A preliminary account of experiments dealing with the catalytic activity of dust particles. This occurs in those cases of negative catalysis in which minute traces of foreign substances cause inhibition of the reaction. The thermal decomposition of hydrogen peroxide under ordinary conditions is pseudo-unimolecular; in the absence of preservatives, however, the reaction is of zero order, *i.e.*, is a wall-reaction, the catalyst being partly the walls of the reaction vessel, but mainly dust particles. In the complete exclusion of the latter, hydrogen peroxide may be heated at 60° for several days without appreciable decomposition. The thermal oxidation of dust-free sodium sulphite is immeasurably slow. The decomposition of hydrogen peroxide by ultra-violet light is roughly proportional to the dust content; the deviation of such reactions from Einstein's photochemical law, therefore, may be due to the dust acting as a photocatalyst. In those photochemical reactions having a high quantum yield, a single light quantum is probably absorbed by one molecule in an aggregate clustered round a dust particle, and this suffices to " explode " the whole. The work described supports Taylor's idea of a catalytic surface (A., 1925, ii, 562). The possible rôle of dust in gas and other reactions is described briefly. S. K. TWEEDY.

Catalytic oxidation of carbon monoxide. III. Catalytic efficiency of mixtures of dry manganese dioxide and cupric oxide. W. C. BRAY and G. J. DOSS (J. Amer. Chem. Soc., 1926, **48**, 2060—2064).—Certain samples of dry manganese and copper oxides when ground together form a catalyst which is much more efficient in the catalytic oxidation of carbon monoxide than the constituent oxides. No change in efficiency occurs when the granules of mixed oxides are powdered, but powdered single oxides are less efficient than the granules. S. K. TWEEDY.

Reduction of carbon monoxide. O. C. ELVINS and A. W. NASH (Nature, 1926, **118**, 154).—When a mixture of 53·9% of carbon monoxide with 44·6% of hydrogen was passed at atmospheric pressure over reduced oxides of manganese, cobalt, and copper, impregnated with 0·5% of lithium carbonate, at 302°, products apparently similar to those resulting from high-pressure reactions were obtained. Thus 1·2 m.^{3} gave 1·4 g. of an oil, water-soluble acids equivalent to 0·33 g. of potassium hydroxide, 0·5 c.c. of a liquid of ketonic odour, b. p. 74—80°, and 0·5 g. of a solid which blackened on exposure to light and air. Fischer's theory of the intermediate formation of carbides does not explain the formation of oxygenated compounds. It is believed that the majority of the products obtained, in which acids, alcohols, ketones, aldehydes, and hydrocarbons are all probably present, are formed simultaneously rather than consecutively. A. A. ELDRIDGE.

Combination of carbon monoxide with a Grignard reagent in presence of chromic chloride. A. JOB and A. CASSAL (Compt. rend., 1926, **183**, 58—60; cf. A., 1924, i, 154).—The catalytic effect of a small proportion of chromic chloride causes magnesium phenyl bromide to absorb carbon monoxide (1/3 mol.) with production of benzpinacone

(33%), diphenyl (14%), and diphenylacetophenone (10%), together with benzaldehyde, benzophenone, and benzhydrol, which arise from secondary decomposition in the final distillation. Nickel chloride also induces the production of benzpinacone, nickel carbonyl being the probable intermediate in the reaction. A chromium carbonyl may perhaps be involved in the former case. G. M. BENNETT.

Catalytic preparation of sulphuric acid. M. POLIAKOV (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 207—211).—Under the influence of the silent electrical discharge, a mixture of sulphur dioxide and oxygen is converted into sulphur trioxide more or less completely according to the pressure, concentration, etc. If the oxygen alone is subjected to the action of the discharge, it will unite with the sulphur dioxide when removed from the influence of the discharge. Sulphur dioxide, however, is not thus activated by the discharge. The results similarly obtained with various catalysts, like those of the experiments on the decomposition of potassium chlorate, point to the activation by the catalyst of the gases adsorbed by the latter.
T. H. POPE.

Thermal decomposition of methane by a glowing filament. G. M. SCHWAB and E. PIETSCH (Z. physikal. Chem., 1926, **121**, 189—208).—The decomposition of methane at very low pressures to carbon and hydrogen by means of a heated platinum strip coated with alkaline-earth oxides on one side has been studied at temperatures between 1100° and 1278°. As the reaction is unimolecular, it must take place at the surface of the filament. The logarithm of the ratio of effective to total collisions on the filament is a linear function of the temperature. The heat of activation of the reaction is between 55,000 and 60,000 cal.; from this it is deduced that the primary reaction consists in the formation of solid carbon and of molecular hydrogen. The observed reaction velocities are not explicable in terms of the translational energy of methane molecules, and it appears that the translational energy of the atoms of the catalyst and the rotational energy of the methane molecules must be taken into account.
L. F. GILBERT.

Mechanism of the catalytic dehydration of methyl alcohol and some properties of the hydrous aluminium oxide catalyst. H. C. HOWARD, jun. (J. Physical Chem., 1926, **30**, 964—972).—Sabatier's hypothesis of intermediate compound formation in catalysis has been examined by the application of the phase rule to the system methyl alcohol–hydrous aluminium oxide. No compound constituting a separate phase is formed between the alcohol and oxide over the temperature range in which the alumina acts as a catalyst, but the possibility of the formation of a compound which dissolves in the catalyst is not excluded. The temperature at which water-vapour is evolved rapidly from hydrous aluminium oxide is closely related to the temperature at which catalytic dehydration of the alcohol over the oxide takes place. The relation between the marked variation of the vapour pressure of a hydrous aluminium oxide catalyst with temperature and the effect of temperature on the catalytic dehydration of methyl alcohol are pointed out.

The sensitiveness of alumina catalysts to heat treatment is probably due, not to sintering, but to the destruction of the water–aluminium oxide complex responsible for dehydration. L. S. THEOBALD.

Catalytic influence of ferric ions on the oxidation of ethyl alcohol by hydrogen peroxide. J. H. WALTON and C. J. CHRISTENSEN (J. Amer. Chem. Soc., 1926, **48**, 2083—2091).—Ethyl alcohol is quantitatively oxidised to acetic acid by hydrogen peroxide in presence of ferric (or ferrous) salts (cf. Fenton, J.C.S., 1900, **77**, 69), the acetic acid being afterwards oxidised to carbon dioxide and water; catalytic decomposition of the peroxide occurs simultaneously. Both reactions are approximately unimolecular and are retarded by acids; their velocities are proportional to the catalyst concentration. The alcohol is apparently oxidised through the intermediate formation of ferric acid. Replacement of the ferric salt in Fenton's reagent by other salts is unsatisfactory; sodium vanadate and potassium chloroplatinate were the next most efficient salts.
S. K. TWEEDY.

Catalytic action. XVII. Catalytic actions of various types of reduced copper on alcohols. T. HARA (Mem. Coll. Sci. Kyōtō, 1926, **9**, 405—425).—The products obtained on passing 11 primary and secondary alcohols over a copper catalyst at 230° and at 330° were examined. The copper was reduced from the oxide formed by precipitating copper sulphate solution with the theoretical quantity of sodium hydroxide (catalyst I) or excess of sodium hydroxide (II) or by igniting the nitrate (III). Catalyst I promotes the dehydration of the alcohols and the formation of unsaturated hydrocarbons; catalyst II promotes dehydrogenation, especially of secondary aliphatic alcohols, and catalyst III promotes both effects, although mainly the latter. The reactions are explained by the formation of one of three intermediate copper–alcohol compounds.
S. K. TWEEDY.

Formation of carbon dioxide from alcohols. W. A. LAZIER and H. ADKINS (J. Physical Chem., 1926, **30**, 895—898).—The effects of various factors on the production of carbon dioxide and of acid from alcohols by zinc oxide catalysts have been studied by methods previously described (A., 1925, i, 878). The production of carbon dioxide is independent of the depth of the catalyst bed, although the production of acid is slightly affected by this factor. The presence of water in the alcohol reduces the total activity and the proportion of ethylene produced, but increases the proportion of carbon dioxide and of hydrogen, as well as the degree of acidity produced. The proportion of carbon dioxide formed is increased by an increase in the temperature of the reaction, but decreased with an increase in mol. wt. of the alcohol used. Secondary alcohols gave a negligible amount of the gas. Heat treatment of the catalyst reduced total activity and the production of carbon dioxide to an even greater extent.

The formation of carbon dioxide is best explained by assuming the dehydrogenation of aldehydes.

L. S. THEOBALD.

Low-temperature oxidation at charcoal surfaces. II. Behaviour of charcoal in presence of promoters. E. K. RIDEAL and (MISS) W. M. WRIGHT (J.C.S., 1926, 1813—1821; cf. A., 1925, ii, 806).—A study of the effect of the presence of nitrogen and iron in the charcoal used in the catalytic oxidation of oxalic acid. Charcoals containing nitrogen show increased activity due to a large increase in specific surface rather than to an increased specific activity of the surface. In the presence of iron, carbon–iron and iron–carbon–nitrogen complexes are formed which have surfaces the specific activities of which are 50 and 800 times that of an active carbon surface, respectively. The question of the selective action of various poisons on these surfaces is discussed.

C. H. D. CLARK.

Catalysis in buffer solutions. I. M. KILPATRICK, jun. (J. Amer. Chem. Soc., 1926, **48**, 2091—2099).—The rates of catalytic decomposition of nitrosotriacetonamine in sodium hydroxide and in alkaline buffer solutions were measured between 20° and 80°. The temperature coefficient of the reaction is uninfluenced by addition of neutral salt. For the same total salt concentration, the "primary salt effect" is greater the lower the hydroxyl-ion concentration (cf. Brönsted, A., 1922, ii, 699). The results in general are in agreement with Brönsted's ideas on the "secondary kinetic salt effect" (cf. *loc. cit.*).

S. K. TWEEDY.

Influence of some radioactive elements on the catalytic activity of certain proteobismuthic precipitates. E. LABORDE, J. BRESSOLLES, and L. JALOUSTRE (Compt. rend., 1926, **183**, 354—356).—The catalytic activities of radioactive proteobismuthic precipitates formed from sodium and potassium tartarobismuthate solution and solutions of radioactive compounds have been measured by a method previously described (A., 1925, ii, 737). The radioactive substances used were compounds of radium, mesothorium, thorium, and barium. The catalytic activity depends on the nature and concentration of the radioactive element. Such precipitates are usually more active as catalysts than if non-radioactive solutions are used in their formation.

J. GRANT.

Influence of electrodes on the formation of ozone at low pressures in the electrical discharge. P. T. NEWSOME (J. Amer. Chem. Soc., 1926, **48**, 2035—2045).—The electrolysis of oxygen was investigated at 14—33 mm., as many variables as possible being eliminated. The electrodes consisted of a hollow cylinder and a wire coincident with its axis. The yield of ozone approaches a constant with decreasing pressure; for copper electrodes the limiting yield is in accordance with Faraday's law and suggests that two electrons are involved in the production of each ozone molecule. The electrode efficiency decreases in the order copper, gold, silver, aluminium; mixed electrodes were also used. When the copper cylinder is negative, the amount of ozone produced is proportional to the time; when it is positive, a temporary ageing effect becomes apparent and the efficiency increases with time, indicating that the discharge forms a protective covering (*e.g.*, a higher oxide) over the copper atoms and so preventing their decomposing the ozone. This surface-poisoning tends to attain a maximum. The results may all be interpreted on the hypothesis that a constant amount of ozone is produced, but the metallic electrodes cause catalytic decomposition; the formation may be due to electron bombardment at or near the negative electrode. No ammonia was produced when the oxygen was replaced by a mixture of nitrogen and hydrogen.

S. K. TWEEDY.

Electrochemical preparation of lead arsenates and arsenites. B. ORMONT (Ukraine Chem. J., 1926, **2**, 20—26).—Lead arsenite may be readily obtained electrochemically, the catholyte being a 15% solution of sodium hydroxide or other sodium salt or 30% potassium hydroxide solution, the cathode nickel, the anolyte a solution of an alkali arsenite neutralised towards phenolphthalein by means of acetic acid, and the anode lead. The cathode space is separated by a diaphragm of vegetable parchment. A current yield of 97% was obtained and the energy yield amounted on the average to 1 kg. per kilowatt-hour.

T. H. POPE.

Law of photochemical equivalence. P. LASAREV (J. Chim. phys., 1926, **23**, 515—520).—Einstein's law of photochemical equivalence is discussed. A number of apparent exceptions are explained on the hypothesis that the molecules in a gas, or liquid, have different internal energies, and that the internal energy of each molecule must exceed a definite value before chemical reaction can take place (cf. A., 1924, ii, 320).

L. F. GILBERT.

Transmissions of the Oldenberg chlorine filter for $\lambda = 2537$ Å. D. S. VILLARS (J. Amer. Chem. Soc., 1926, **48**, 1874—1876).—Measurements of the transmissions between 2232 and 5461 Å. of the Oldenberg (A., 1924, ii, 579) and Peskov (Z. wiss. Phot., 1919, **18**, 235) halogen filters by a photographic photometric method indicate that the latter filter is more nearly monochromatic.

S. K. TWEEDY.

Mechanism of reactions photosensitised by mercury vapour. A. L. MARSHALL (J. Physical Chem., 1926, **30**, 1078—1099; cf. this vol., 252).—The amount of energy absorbed by mercury vapour from a water-cooled quartz mercury arc has been measured, and a method of calculating the total energy radiated by such an arc evolved. The absorption by mercury in a vacuum and in the presence of hydrogen and nitrogen at 1 atm. has also been studied. Absorption with hydrogen or nitrogen present is approximately the same at a given temperature, but with oxygen absorption is much less. The effect of temperature corresponds approximately with that observed in the combination of electrolytic gas (this vol., 252). Pure nitrogen present with mercury gave the intense green fluorescence (prevented by traces of hydrogen or oxygen) previously observed by Wood (A., 1925, ii, 1015).

Hydrogen peroxide is the first product which can

be isolated from the photochemical reaction between hydrogen and oxygen when sensitised by mercury vapour, and the probable mechanism is $Hg'+H_2=2H+Hg$, followed by $H+O_2=HO_2$; $HO_2+H_2=H_2O_2+H$ and $2H_2O_2=2H_2O+O_2$. There is some evidence that the primary reaction involves the formation of mercurous hydride. The maximum yield for a mixture of 2 vols. of hydrogen and 1 vol. of oxygen was 6·6 mols. of hydrogen peroxide for each quantum of 2536·7 Å. absorbed. For the reaction $CO+H_2=H\cdot CHO$ (372 mm. CO and 346 mm. H_2), the yield was 6 mols. per quantum. Both of these quantum yields are minimal values, and further corrections would increase the length of the chains. These reactions have a "chain mechanism," and the Einstein–Stark law of photochemical equivalence does not hold.

Previous work on absorption by mercury vapour of light of wave-length 2536·7 Å. is discussed.

L. S. THEOBALD.

Decomposition of ammonia by ultra-violet radiations. W. KUHN (J. Chim. phys., 1926, **23**, 521—544; cf. Warburg, A., 1912, ii, 315; Coehn and Pringent, A., 1914, ii, 404).—Ammonia is completely decomposed to nitrogen and hydrogen when exposed to light from the zinc spark (λ=2025—2140 Å.). About 2—2·5 quanta are absorbed per mol. decomposed; this number is independent of the pressure (5—900 mm. Hg.). The divergence from Warburg's value of 4 quanta per mol. cannot be explained. The rate of decomposition is independent of the temperature (10—20°), and of the intensity of the light, and is thus proportional to the energy absorbed; it is also not affected by quartz or by metallic sodium, and is therefore apparently uninfluenced by the absence of traces of water. In light composed only of radiations of wave-lengths 2063 and 2100 Å., the number of quanta per mol. decomposed is, however, of the order of 10. This is explained on the hypothesis that the photochemical decomposition of ammonia is a consecutive photochemical reaction (cf. this vol., 584). The energies required to disrupt a molecule of ammonia to $N+H+H_2$ and to $N+3H$ are 124,000 and 208,000 cal., respectively; the energy supplied by a quantum of wave-length 2080 Å. is 120,000 cal.

L. F. GILBERT.

Alleged decomposition of ammonium nitrite solutions by light. M. HOLMES (J.C.S., 1926, 1898).—No decomposition of ammonium nitrite has been detected as a result of insolating a 2·5*N*-solution with ultra-violet light. Berthelot and Gaudechon (A., 1911, ii, 240) appear to be in error.

C. H. D. CLARK.

Action of light on concentrated aqueous ammonium thiocyanate solutions. M. HOLMES (J.C.S., 1926, 1690—1693).—An investigation of Liesegang's statement that concentrated ammonium thiocyanate solutions develop a bright red colour in sunlight after 1 min., which disappears in the dark after 2 min. Experiments conducted in glass and quartz vessels under the influence of ultra-violet light from different sources confirm the observation, but the times necessary for the changes are greater than those stated for sunlight and the colour formed is red, but never bright red. The ammonium thiocyanate solutions must be freshly prepared, and the presence of air appears to play a part. In quartz vessels, a yellowish-white substance is formed, which gives tests for sulphur; cyanide and a reducing agent are also formed in traces. It is suggested that long-wave ultra-violet light causes the irreversible reaction $NH_4CNS \rightarrow NH_4CN+S$, the pink colour being due to a sulphur sol, which slowly coagulates, especially under the influence of ultra-violet light of short wave-length.

C. H. D. CLARK.

Complex and double ferrocyanides. Photochemical reactions of the ferrocyanides of the alkali and alkaline-earth metals in the presence of mercuric chloride. T. GASPAR Y ARNAL and A. CASTRO-GIRONA Y POZURAMA (Anal. Fis. Quím., 1926, **24**, 323—335).—Potassium ferrocyanide gives a white precipitate with barium chloride in the presence of ethyl alcohol. A similar precipitate is given by sodium ferrocyanide under the same conditions. The first precipitate, treated with cobalt nitrate, changes through dirty green and violet to another shade of white, whilst the second precipitate turns green. The reactions of cobalt nitrate, nickel nitrate, ferric chloride, copper sulphate, bismuth nitrate, stannous chloride, and antimony chloride, with the ferrocyanides of sodium, ammonium, potassium, barium, and strontium, are given in tabular form. The precipitate obtained with mercuric chloride and potassium ferrocyanide changes colour slowly on exposure to light, whilst that obtained with sodium ferrocyanide changes at once and gradually becomes blue. The authors have investigated the effect of sodium chloride and ethyl alcohol on these reactions and discuss their applications in analysis.

G. W. ROBINSON.

Eder's photochemical reaction and some properties of salts taking part in it. P. BECHTEREV (J. Russ. Phys. Chem. Soc., 1925, **57**, 161—188).—Mainly a summary of the literature on the reduction of mercuric chloride by ammonium oxalate in presence of light. The displacement of the equilibrium between mercuric and potassium chlorides in aqueous solution (cf. Tichomirov, A., 1907, ii, 752) by addition of mercuric oxalate is investigated, and the results point to the formation of complex salts, but fail to indicate the composition of these.

T. H. POPE.

Photolysis of alcohols. VOLMAR (Compt. rend., 1926, **182**, 1607—1609; cf. A., 1924, ii, 244).—Alcohols exposed to radiation from a mercury vapour lamp undergo dehydrogenation according to the scheme $RCH_2\cdot OH = R\cdot CHO+H_2$; $RR'CH\cdot OH = RR'CO+H_2$; $RR'R''C\cdot OH = RR'CO+\frac{1}{2}R''\cdot R''+\frac{1}{2}H_2$. The aldehyde or ketone so formed decomposes further to carbon monoxide and a hydrocarbon. The wave-length most effective in promoting the dehydrogenation is calculated to be 0·19 μ, a value in agreement with that experimentally determined by Berthelot (Compt. rend., 1911, **153**, 383).

M. CLARK.

Photoactivity. II. Influence of adrenaline on the photographic plate. H. VOLLMER (Biochem. Z., 1926, **173**, 389—392).—0·1% Adrenaline solutions have a powerful photo-chemical effect. The effect

is not due to the formation of a peroxide. Previous exposure of the adrenaline to light slightly increases its activity. Acid increases, alkali diminishes this effect. Insulin itself is inactive, but increases the photoactivity of adrenaline if added to it.

H. D. KAY.

Relation between colour sensitiveness and the gradation given by a photographic plate. T. T. BAKER and W. A. BALMAIN.—See B., 1926, 612.

Comparative tables of spectral sensitivity of silver bromide, iodide, and chloride, and the action of the chief colour sensitisers. J. M. EDER.—See B., 1926, 611.

Action of light on silver bromide emulsions, and the rôle of the sensitising nuclei. F. C. TOY. —See B., 1926, 612.

Spectral sensitivity of silver iodide and mixtures of silver iodide and silver bromide. E. HUSE and C. E. MEULENDYKE.—See B., 1926, 611.

Chemical reactions between solids at high temperatures. G. TAMMANN (Z. angew. Chem., 1926, **39**, 869—875).—A general survey of the work carried out by the author and his collaborators, and by others, on chemical reaction at high temperatures between mixed substances in the solid state.

S. K. TWEEDY.

Displacement of platinum by hydrogen at high pressures. V. IPATIEV and A. ANDREEVSKI (Compt. rend., 1926, **183**, 51—53).—The influence of temperature, pressure, and the presence of mineral acids and of iron and nickel salts on the precipitation, by hydrogen, of platinum from solutions of platinum chloride has been studied. With platinum chloride solutions in the (initial) concentration range 3—30%, rise of temperature and increase of pressure increase the yield of platinum in a given time, and the proportion of platinum precipitated is the greater the less the (initial) concentration of the platinum chloride solution. Addition of acids and of ferric chloride inhibits the reduction, but without affecting the relative influences of the other factors. With more dilute solutions of platinum chloride (0·01—1%), in presence of iron and nickel salts, the process of reduction becomes more complicated and slow, especially if mineral acids are also present.

L. F. GILBERT.

Displacement of metals, metalloids, and their oxides from solution by hydrogen under pressure. V. IPATIEV [with N. KLJUKVIN, A. I. KISSELEV, N. V. KONDYREV, and W. I. NIKOLAJEV] (Ber., 1926, **59**, [*B*], 1412—1426).—The action of hydrogen under pressure on hot aqueous solutions of copper sulphate results in the successive production of the basic salt, $CuSO_4,2Cu(OH)_2$, cuprous oxide, and ultimately copper, the quantity of which increases with increasing amount of free sulphuric acid, which hinders the formation of hydrolytic products. Above 150°, reduction of sulphuric acid commences, whereby separation of basic salt and cuprous oxide is facilitated. At higher temperatures, production of copper sulphide is observed. Reduction of sulphuric acid is accelerated by precipitated copper. Addition of sulphuric acid retards or even inhibits the separation of copper owing to suppression of the formation of the primary basic salt. In the presence of nickel or zinc salts, pure copper is precipitated if sufficient free sulphuric acid is present to prevent the deposition of basic iron salts.

Chromic acid, alone or in the presence of sulphuric acid, is reduced to the oxide, Cr_2O_3,H_2O. Potassium dichromate in the presence of a little sulphuric acid yields the *salt*, $Cr_2(SO_4)_3,Cr_2O_3,K_2O,H_2O$. Potassium permanganate or manganese nitrate is converted into hausmannite (or manganese silicate, Mn_3O_4,SiO_2, if quartz tubes are used), whereas manganese chloride and sulphate afford hydrated manganous oxide and manganous sulphide, respectively. Iron nitrate yields ferrosoferric oxide, which, with ammonium carbonate and formic acid, is also obtained from potassium ferrocyanide or ferricyanide. Ferric chloride is reduced to ferrous chloride, ferrous sulphate transformed into ferrous sulphide and ferrosoferric oxide, whereas iron acetate is unchanged.

Nickel formate under relatively mild conditions gives nickel quantitatively, whereas in more drastic circumstances, anhydrous, crystalline *nickelous oxide* is produced owing to the oxidising action of water; the compound is also produced from nickel cyanide. Potassium manganocyanide affords manganese carbonate. Zinc nitrate in quartz tubes yields the silicate, $ZnSiO_3,3ZnO$.

Phosphoric acid is not reduced to phosphorus at 350—360°. Ferric phosphate gives a series of salts, $Fe_n'''Fe_m''PO_4,xH_2O$, closely allied to the mineral vivianite. Lead hydrogen orthophosphate is reduced to lead hydrogen phosphite, hypophosphorous acid, and colloidal lead oxide; the phosphite is further converted into lead and phosphoric acid. Lead hypophosphite affords phosphorous acid, lead oxide, and black, "metallic" phosphorus. Red phosphorus is converted into the black variety at 200° and 90 atm., whereas under milder conditions it is transformed into phosphine and phosphoric acid. Yellow phosphorus is also oxidised by water to phosphoric acid with production of black phosphorus in small amount. Ferric arsenate gives successively the mineral, skodorite, $FeAsO_4,H_2O$, ferric arsenite, arsine, ferrous arsenite, arsenic, and arsenious acid. Ferric arsenite yields colloidal iron oxide, iron arsenide, and arsenious acid. Copper arsenate affords copper, copper arsenite, domeite, Cu_3As, arsine, and arsenious acid. Arsenic yields only small amounts of arsine and arsenic acid. Antimony sulphate is reduced to antimony glance, whereas antimony oxide yields stibine and metallic antimony. Potassium hydrogen pyroantimonate gives potassium hydroxide and antimony.

H. WREN.

Potassium and sodium oxides. C. A. KRAUS and E. F. WHYTE (J. Amer. Chem. Soc., 1926, **48**, 1781—1790).—The passage of oxygen through a solution of potassium in liquid ammonia produces initially potassium dioxide, K_2O_2. If the oxygen stream is rapid, this oxide is oxidised to the tetroxide; if the current is slow, oxidation, preceded by reduction

and solvolysis, occurs: $K_2O_2+K_2=2K_2O$; $K_2O+HNH_2=KOH+KNH_2$; $KNH_2+O_2 \rightarrow KOH+KNO_2$. Similar results are obtained with sodium except that the dioxide is the final product on rapid oxidation. Evidence for the formation in liquid ammonia of the trioxides, K_2O_3, Na_2O_3, was not obtained. Reversible dissociation of potassium tetroxide occurs above 300°; the dissociation pressures depend on the oxygen content of the solid phase, which finally attains a composition corresponding with K_2O_3. Potassium tetroxide which has been exposed to moisture evolves oxygen irreversibly at 100—200° in an amount depending on the extent of the exposure. S. K. TWEEDY.

Hydrolysis of potassium cuprocyanide by sulphuric acid. A. S. CORBET and R. M. WOODMAN (Chem. News, 1926, **133**, 51).—The distillation of potassium cuprocyanide with sulphuric acid occurs in three more or less definite stages in which hydrogen cyanide, carbon monoxide, and sulphur dioxide are liberated, respectively. As the sulphuric acid concentration increases above 40%, the yield of hydrogen cyanide is gradually lessened from the maximum (55%) by progressive replacement by its hydrolysis product, carbon monoxide (cf. Bassett and Corbet, A., 1924, i, 950). S. K. TWEEDY.

Precipitation of copper from acid solutions of its salts by means of zinc. A. GALECKI (Rocz. Chem., 1926, **6**, 145—149).—The results previously published (this vol., 364) are further discussed, and again shown to support the Ericson-Palmaer theory of local currents. R. TRUSZKOWSKI.

Action of hydrobromic acid and alkali bromides, in an acetic acid medium, on cupric bromide. G. DENIGÈS (Compt. rend., 1926, **183**, 289—291).—Cupric bromide and acetic or propionic acid solutions react to give a yellow coloration which changes through green to brown and violet with successive additions of concentrated hydrobromic acid. Boiling regenerates the green colour unless more than 50% of acid is used, when the violet persists. The addition of a solution of a cupric salt to an acetic acid solution of an alkali bromide changes the colour from orange-yellow through green to red, the absorption spectrum of the green being the same as that previously obtained. This is due to the formation of the complex $MBr,CH_3{\cdot}CO_2H$ by the alkali bromide, which, on the addition of cupric bromide, yields the green $CuBr_2,CH_3{\cdot}CO_2H$, and then the violet $CuBr_2,MBr$. With hydrobromic acid, the same green compound results, followed by the violet $CuBr_2,HBr$, which is unstable on warming. These reactions may be used for the detection of cupric salts. J. GRANT.

Basic copper sulphates. G. FOWLES (J.C.S., 1926, 1845—1858).—Discrepancies relating to basic copper sulphates occurring in the literature may be attributed largely to the formation of highly stable intermediate compounds, which reach equilibrium slowly. Five basic salts are described: (1) $CuSO_4,2Cu(OH)_2$; (2) $5CuSO_4,9Cu(OH)_2,2H_2O$; (3) $2CuSO_4,Cu(OH)_2,4H_2O$; (4) $CuSO_4,3Cu(OH)_2$; (5) $2CuSO_4,3Cu(OH)_2$. The product of boiling an unsaturated solution of copper sulphate in presence of sodium nitrite is (2), which on prolonged boiling changes to (1). If an attempt is made to expedite the reaction by adding carbamide, (5) is formed, which is decomposed by water. From a saturated boiling solution of copper sulphate, a new compound (3) is deposited as green, rhombic crystals, which, decomposed by an excess of cold water, yields (4). The reaction between copper sulphate and copper hydroxide yields mixtures of (1) and (4), which change into less reactive forms, (4) changing into (1) therefore very slowly. When copper oxide is used instead of hydroxide, the salt obtained is (1), since apparently sufficient copper oxide does not dissolve to exceed the solubility of (4). The reactions between copper sulphate and bases lead to the concurrence of several reactions. The results of other authors are criticised and discussed. C. H. D. CLARK.

[**Transformation of mercury into gold.**] E. H. RIESENFELD and W. HAASE (Ber., 1926, **59**, [*B*], 1625—1629; cf. Miethe and Stammreich, Naturwiss., 1924, **12**, 597, 744; Nagaoka, A., 1925, ii, 835, 1111).—Gold and mercury cannot be efficiently separated from one another by ordinary distillation. Under otherwise similar conditions, the amount of gold distilled diminishes with decreasing rate of distillation; if the rate is constant, the amount of gold decreases with diminution in the pressure at which distillation is effected. A volatile compound of gold and mercury appears to be produced which causes the ratio gold : mercury in the vaporous phase to be less than that in the liquid, but considerably greater than that corresponding with the vapour pressure of solid gold. These gold particles are swept forward by the stream of mercury vapour when the rate of distillation is considerable, and hence cannot return to the liquid as is the case when distillation is slow. Repetition of Miethe's experiments with a Boas mercury commutator affords 10% or less of the amount of gold calculated according to Miethe's equivalent. The observed gold content is not influenced by the action or inaction of the commutator and is due solely to the materials with which the mercury comes into contact. H. WREN.

Supposed production of "artificial" gold from mercury. F. HABER, J. JAENICKE, and F. MATTHIAS (Ber., 1926, **59**, [*B*], 1641—1648; cf. this vol., 699, 930).—The arrangement of the experiments permitted study of the effect of discharge between a mercury surface covered with liquid or solid paraffin and wires of different materials, through mercury vapour between tungsten electrodes, of electronic bombardment of a frozen mercury surface and of constant and varied discharge through mercury vapour. The presence of gold and silver in quantity greater than that derivable from the electrodes could not be established. H. WREN.

Formation of gold from mercury. E. TIEDE, A. SCHLEEDE, and F. GOLDSCHMIDT (Ber., 1926, **59**, [*B*], 1629—1641; cf. preceding abstract).—Except in one case, mercury obtained from various sources yielded a residue containing gold, when once distilled according to Miethe's directions; after a second distillation, gold was detected in only two out of

twenty residues. If, however, this mercury, which appeared free from gold, was very slowly distilled in a high vacuum at about 90°, gold appeared invariably in the residues. Miethe's method of determining gold by measurement of the diameter of the gold sphere is exceedingly difficult, and the use of the ratio aggregate : sphere=2·24 : 1 for very small amounts of gold is liable to serious error. Further, the "gold" residue under certain conditions consists of a crystalline gold compound, completely stable to boiling nitric acid, from which mercury is expelled by ignition. Formation of gold could not be detected after exposure of mercury vapour to the electrodeless discharge, in the Fischer lamp, or to discharge between mercury poles in an atmosphere of hydrogen or nitrogen. Electric discharge between tungsten and mercury electrodes covered by paraffin in an atmosphere of nitrogen did not afford any evidence of transmutation, such minute amounts of gold as were detected in the sludge being due to gold from the electrodes or present originally in the mercury (if purified by Miethe's process). The yields of gold obtained in commutator experiments were only 0·1—0·001 of those calculated according to Miethe and were due to the presence of gold in the copper parts against which the stream of mercury particles played. In a modified apparatus in which the spark passed only between a mercury surface and a thin tungsten wire, the production of gold was not observed.

H. WREN.

Colloidal aurous oxide. Gold toning of photographic papers. A. STEIGMANN (Chem.-Ztg., 1926, 50, 595).—Addition of an excess of sodium carbonate to a solution obtained by boiling with aqua regia gold containing a small proportion of silver results in the formation of a deep blue solution of aurous oxide. Such a solution cannot be obtained by the use of pure gold, probably because, in this case, the gold dissolves directly to auric chloride. On evaporating the blue solution on the water-bath, a fine brown precipitate of metallic gold is obtained, but evaporation at the ordinary temperature yields a fine, bluish-green, crystalline precipitate which appears to be aurous oxide; the crystals do not redissolve in water. The blue alkaline solution becomes bluish-green, emerald-green, yellowish-green, and, finally, yellow as hydrochloric acid is added, and does not become blue again with an excess of sodium carbonate until after the lapse of several hours. The blue solution does not tone photographic paper that has been treated with sodium sulphide, thus proving the absence of gold ions and the colloidal nature of the solution.

A. R. POWELL.

Microchemical examination of gypsum. P. P. BUDNIKOV (Z. anorg. Chem., 1926, **155**, 141—143).—Gypsum heated at 400—750° loses water of crystallisation and gives a substance very similar to natural anhydrite. Hydration of both these products is extremely slow, but can be hastened by powdering very finely and also by addition of a catalyst to the finely-powdered calcium sulphate, *e.g.*, 0·1—1% of an acid salt of an alkali metal. Possibly labile complicated hydrates—salt, $m CaSO_4,nH_2O$—are first formed, and these pass into the dihydrate, formation of this being the more complete the farther the hydration has gone. The finely-powdered dihydrate can be recrystallised when mixed with water alone or containing a catalyst—an acid salt with a sulphate of a heavy metal. In all cases, structural changes have been observed microscopically.

M. CARLTON.

Decomposition of alkaline-earth sulphates. II and III. J. ZAWADZKI, J. KONARZEWSKI, W. J. LICHTENSTEIN, S. SZYMANKIEWICZ, and J. WACHSZTEJŃSKI (Rocz. Chem., 1926, 6, 120—135, 236—255; cf. this vol., 368).—II. Calcium sulphate heated at 900° with carbon yields calcium sulphide; above 900° the latter combines with undecomposed sulphate, producing calcium oxide and sulphur dioxide. The proportion of sulphate so converted into oxide increases with temperature and with diminution of percentage of carbon in the original mixture, and is also increased by the addition of oxides of silicon, aluminium, and iron. The ratio of carbon monoxide to dioxide in the reaction gases increases with greater carbon content of the initial mixture, carbon dioxide generally predominating; below 800° the proportions of these gases conform to the equation $CO_2+C \rightleftharpoons 2CO$. Mixtures of magnesium sulphate and carbon in equal quantity yield similarly magnesium sulphide and oxide, the proportion of the former increasing with greater carbon content and lower temperature; the gaseous products are sulphur, sulphur dioxide, carbon oxysulphide, monoxide, and dioxide.

Above 320° the reaction giving rise to the production of sulphur dioxide commences. With higher temperatures (600—1000°) the interaction between the latter and carbon monoxide yields greater quantities of sulphur, with carbon oxysulphide as a by-product.

III. Calcium sulphate is reduced by hydrogen between 600° and 800° with the production of calcium sulphide; above 900° a part of the latter reacts further with undecomposed sulphate, yielding calcium oxide and sulphur dioxide. Reduction by means of hydrogen sulphide is equivalent to that by hydrogen and sulphur separately, in view of its dissociation at high temperatures. The products of reaction are calcium sulphide and sulphur dioxide. Magnesium sulphate, however, under these conditions yields only oxide, the gaseous products consisting of sulphur and sulphur dioxide in various proportions, according to the reaction temperature. Carbon monoxide reduces calcium sulphate almost quantitatively to sulphide between 700° and 900°; at 900° the sulphide decomposes further, giving rise to a certain quantity of oxide in the residue.

R. TRUSZKOWSKI.

Ebullioscopic determination of double salts in solution. E. ROUYER (Compt. rend., 1926, **183**, 46—48; cf. A., 1923, ii, 534; 1924, ii, 476).—The existence of the following double *salts* in solution at 100° is claimed: $XSO_4,(NH_4)_2SO_4$, where X = Cd, Fe, Co, Mn, Zn, Mg, Cu, or Ni, and $MgCl_2,MCl$, where M = NH_4, K, Na, or Li. Similar salts to the latter, with bromine in place of chlorine, exist in aqueous solution at 100°.

L. F. GILBERT.

Influence of boric oxide on the properties of chemical and heat-resisting glasses. II. Resistance to chemical reagents. W. E. S. TURNER and F. WINKS.—See B., 1926, 584.

Action of nitric acid on aluminium. S. UCHIDA and K. SASAKI.—See B., 1926, 633.

Silicon hydrides [and derivatives]. A. STOCK (Z. Elektrochem., 1926, **32**, 341—349).—Chiefly a summary of the work of the author and co-workers on the subject (A., 1916, ii, 319; 1917, ii, 204; 1918, ii, 110, 111, 361; 1919, i, 260; ii, 218; 1920, ii, 31, 429; 1921, ii, 330, 399; 1923, ii, 67, 160, 412, 486, 633).—The similarities and dissimilarities between the physical and chemical properties of corresponding carbon and silicon compounds are discussed.

J. S. CARTER.

Silicates. III. Hydrolysis of sodium silicate. G. HÄGG (Z. anorg. Chem., 1926, **155**, 21—41; cf. Vesterberg, A., 1913, ii, 406; 1920, ii, 112; Harman, A., 1925, ii, 1065; this vol., 478, 907).—By means of electrical measurements of the hydroxyl-ion concentration as well as measurements of lowering of the f. p. of sodium silicate solutions, it has been shown that (i) the only sodium silicates existing in aqueous solution are the meta- and di-silicates, Na_2SiO_3 and $NaHSiO_3$. All other solutions contain mixtures of $xNa_2SiO_3+yNaOH$, $xNa_2SiO_3+yNaHSiO_3$ or $NaHSiO_3$ and colloidal silicic acid. (ii) When Na_2SiO_3 is hydrolysed almost entirely, $HSiO_3'$ ions are formed which do not precipitate as colloid. (iii) The hydrolysis of $NaHSiO_3$ is very small compared with that of Na_2SiO_3. Whether the H_2SiO_3 formed is colloidal or not cannot be decided. (iv) If the H_2SiO_3 is not colloidal, only solutions which are more acid than 1 : 2 contain colloid; if H_2SiO_3 is colloidal, solutions which are more alkaline than 1 : 1 contain only very small amounts of colloid; solutions between 1 : 1 and 1 : 2 contain somewhat more colloid, which increases with silicic acid content, and solutions more acid than 1 : 2 contain a large amount of colloid. (v) If H_2SiO_3 is not colloidal, the first dissociation constant of metasilicic acid is of the order 10^{-9} and the second of the order 10^{-13}. On the other hand, if H_2SiO_3 is colloidal, these are only the apparent values of the dissociation constants which, among other things, are dependent on the solubility of metasilicic acid.

M. CARLTON.

Six-membered silicon compounds. H. KAUTSKY (Z. Elektrochem., 1926, **32**, 349—354).—A discussion of the structure and of the physical and chemical properties of the siloxen compounds, chiefly based on previously published work of the author and collaborators (A., 1921, ii, 505; 1922, ii, 464; Naturwiss., 1923, **11**, 194; A., 1924, ii, 674, 852; Z. anorg Chem., 1924, **139**, 135; A., 1925, ii, 698, 941; Z. Physik, 1925, **31**, 60). Work, as yet unpublished, on the halogenation of siloxen in presence of acetic anhydride shows that halogen and anhydride form a complex which reacts as a whole with siloxen, $Ac_2O,I_2+Si_6O_3H_6 = Si_6O_3H_4I(Ac)+HI + CH_3{\cdot}CO_2H$. By reason of their peculiar lamellated structure, the siloxen derivatives have an extremely large surface and are excellent adsorbents for gases and dissolved substances.

J. S. CARTER.

Germanium. XV. Germanochloroform. L. M. DENNIS, W. R. ORNDORFF, and D. L. TABERN (J. Physical Chem., 1926, **30**, 1049—1054; cf. Winkler, J. pr. Chem., 1887, **144**, 188).—Germanochloroform, $GeHCl_3$, prepared by the action of hydrogen chloride on germanium dichloride, has m. p. −71°, b. p. 75·2°, and d^0 1·93. Decomposition of the substance begins at 140° and becomes rapid at 175°, yielding at first the dichloride and hydrogen chloride, and, finally, metallic germanium and the tetrachloride. Reaction with oxygen begins at 0°, forming the tetrachloride and a viscous, light-coloured oil which on warming decomposes, leaving a residue apparently of the dichloride. The main reaction is probably represented by the equation $4GeHCl_3+O_2=2GeCl_4+2GeCl_2+2H_2O$, and not, as suggested by Winkler (*loc. cit.*), by the equation $2GeHCl_3+O_2=2GeOCl_2+2HCl$. When mixed with 3 vols. of oxygen-free water, 1 vol. of germanochloroform yields a white solid, but with a larger proportion of water, an orange-coloured precipitate of germanous hydroxide is formed.

Measurements of vapour pressures over the temperature range −25° to 78·3° are recorded. Winkler's method of preparation (*loc. cit.*) gives a mixture of the hydrotrichloride and the tetrachloride.

L. S. THEOBALD.

Stannous phosphates. K. JABŁCZYŃSKI and W. WIECKOWSKI (Rocz. Chem., 1926, **6**, 218—227).—See this vol., 588.

Thermal decomposition of nitrous and nitric oxides. E. BRINER, C. MEINER, and A. ROTHEN (J. Chim. phys., 1926, **23**, 609—620).—Mainly an account of work previously abstracted (this vol., 685). No nitrous oxide is produced by the thermal decomposition of nitric oxide.

J. W. BAKER.

Interaction of oxides of nitrogen with arsenious acid and with sulphurous acid in presence of sulphuric acid of varied concentration. T. L. BAILEY.—See B., 1926, 628.

Bismuth compounds. I. Constitution of bismuth nitrates and tartrates. B. HEPNER and A. LIKIERNIK (Rocz. Chem., 1926, **6**, 165—176).—See this vol., 487.

Bismuth compounds. II. Constitution of bismuth subnitrates. B. HEPNER (Rocz. Chem., 1926, **6**, 190—200).—See this vol., 488.

Physico-chemical and electrochemical aspects of sulphur dioxide as an oxidising agent. S. R. CARTER.—See B., 1926, 664.

Oxidising properties of sulphur dioxide. W. WARDLAW.—See B., 1926, 664.

Decomposition of metallic sulphates by heat and the influence of certain substances on these reactions. (MLLE.) G. MARCHAL (Rev. Mét., 1926, **23**, 353—360).—A recapitulation of the principal results obtained in earlier work (cf. A., 1925, ii, 870, 1162; this vol., 27, 127, 359, 487).

A. R. POWELL.

Polyhydro-sulphates and -selenates. J. MEYER and K. GRÖHLER (Z. anorg. Chem., 1926, **155**, 91—114; cf. A., 1925, ii, 422).—The following *salts* are described: $[Co\ en_3](SO_4H)_3$; $[Co\ en_3](SO_4)(SO_4H),0{\cdot}5H_2O$; $[Co\ en_3]_2(SO_4)_3,4H_2O$; $[Co\ en_3](SeO_4H)_3$; $[Co\ en_3](SeO_4)(SeO_4H),H_2O$; $[Co\ en_3]_2(SeO_4)_3,H_2O$; $[(NH_3)_5CoCl](SO_4H)_2$; $[(NH_3)_4Co(H_2O)(NO_2)](SO_4H)_2$; $[(NH_3)_4Co(H_2O)(NO_2)](SeO_4H)_2$; $[(NH_3)_4Co(H_2O)(NO_2)]SeO_4$; $[(NH_3)_4Co(SeO_4H)_2]SeO_4,4H_2O$; $[(NH_3)_4Co(H_2O)(SeO_4)]_2SeO_4$; $[(NH_3)_4Co(H_2O)(SeO_4)]SeO_4H$; $[(NH_3)_4Co(H_2O)(SeO_4)]Cl$; $[(NH_3)_4Co(H_2O)(SeO_4)_2]SO_4,4H_2O$; $[(NH_3)_4Co(H_2O)(SO_4)]_2SO_4$; $[(NH_3)_4Co(H_2O)(SO_4)]Cl$; $[(NH_3)_4Co(H_2O)(SO_4)]_2SeO_4,4H_2O$.

The stability of these compounds is ascribed to a *trans*-arrangement of the selenate and sulphate groups. M. CARLTON.

Reaction between selenium tetrachloride and copper. W. W. TAYLOR, E. B. R. PRIDEAUX, and H. G. POOL (J. Amer. Chem. Soc., 1926, **48**, 2129—2130).—The reaction is considered to proceed according to the equations: (i) $2SeCl_4+3Cu=3CuCl_2+Se_2Cl_2$; (ii) $Se_2Cl_2+5Cu=2Cu_2Se+CuCl_2$. Selenium is produced when an excess of the chlorides is present, (iii) $2Cu_2Se+4Se_2Cl_2=4CuCl_2+10Se$. S. K. TWEEDY.

Constitution of solutions of molybdic acid. A. TRAVERS and MALAPRADE (Compt. rend., 1926, **183**, 292—294).—Aqueous solutions of the compounds $MoO_3,2H_2O$ and MoO_3,H_2O, made in the cold, differ from solutions of MoO_3 made at 100° and cooled, both in their colours and in their reactions with potassium ferrocyanide. This indicates two states of polymerisation following the ionisation of molybdic acid as follows: $4MoO_3,H_2O \rightleftharpoons [4MoO_3{\cdot}O]'' + 2H^{\cdot}$. The neutralisation curve shows inflexions at $4MoO_3,K_2O$ and MoO_3,K_2O, the first resulting from the complete neutralisation of the acid $4MoO_3,H_2O$, and the second from the decomposition of the salt formed first by the alkali. In support of this, the reactions of the tetramolybdate are found to be quite different from those of the neutral salt. From the analogy with the tungstic acids, $4MoO_3,H_2O$ is called metamolybdic acid, and assuming the existence in solution of this acid ionising as described, and of its polymerides, formulæ are assigned to the complexes it forms with boric and phosphoric acids. J. GRANT.

Compounds of uranic acid with sulphuric and selenic acids. J. MEYER and E. KASPER (Z. anorg. Chem., 1926, **155**, 49—65).—With the exception of oxygen, elements of the sixth group of the periodic system are able as oxides to combine with oxides of elements of other groups to form heteropoly-acids. Experiments on little-known compounds of selenic and uranic acids were performed, and the following were obtained as pure crystalline products and were analysed: *Selenic-uranic acid*, $H_2[UO_3(SeO_4)],2H_2O$, yellow; *diselenic-uranic acid*, $H_6[UO_4(SeO_4)_2],2H_2O$, yellowish-green, also obtained with $6H_2O$; *triselenic-diuranic acid*, $H_6[UO_2(UO_4)(SeO_4)_3],7H_2O$, yellowish-green, also with $18H_2O$. That these are complex selenic-uranic acids is confirmed by electrolysis experiments, the anode liquid always containing a complex uranic-selenic acid. The following *potassium* and *ammonium* salts are described:

$KH[UO_3(SeO_4)],H_2O$; $NH_4H[UO_3(SeO_4)],3H_2O$; $K_2H_4[UO_4(SeO_4)_2],H_2O$, also $3H_2O$; $K_2[UO_2(SeO_4)_2],H_2O$; $K_2H_4[UO_2(UO_4)(SeO_4)_3],H_2O$; $Na_4H_2[UO_3(SeO_4)_3],H_2O$; $Na_4(NH_4)_2[UO_3(SeO_4)_3],10H_2O$; $K_2H_4[UO_4(SO_4)_2],2H_2O$; $KH_5[UO_4(SO_4)_2]$; $(NH_4)_4H_2[UO_4(SO_4)_2],3H_2O$; $K_2H_2[UO_3(SO_4)_3],6H_2O$; $(NH_4)_2K_4[UO_3(SO_4)_3]$.

Attempts to replace the acid hydrogen of the complex sulphuric-uranic and selenic-uranic acids by organic bases were fruitless. M. CARLTON.

Oxidation with fluorine. IV. Qualitative and quantitative investigation of the reaction between fluorine and normal and acid sulphate solutions. F. FICHTER and K. HUMPERT (Helv. Chim. Acta, 1926, **9**, 602—611).—Treatment of ice-cold solutions of ammonium or potassium sulphate or of the corresponding hydrogen sulphate with fluorine gives a highly-oxidising solution containing permonosulphuric, perdisulphuric, and fluorosulphonic acids, ozone, and another very unstable compound of unknown composition. The proportion of the latter formed is the greater the higher is the concentration of the original solution; the lower the temperature the lower is the acidity and the shorter the period of treatment with fluorine. The amount of permonosulphuric acid formed, on the other hand, is the greater the more dilute is the solution, whilst the yield of fluorosulphonic acid is greater in concentrated solutions and the yield of perdisulphuric acid is improved by carrying out the reaction at the ordinary temperature. A. R. POWELL.

Oxidation with fluorine. V. Action of fluorine on alkali acetates and Kolbe's synthesis of hydrocarbons. F. FICHTER and K. HUMPERT (Helv. Chim. Acta, 1926, **9**, 692—697).—The current yield of ethane in the electrolysis of solutions of potassium acetate is seriously diminished by addition of fluoride, owing to the powerful oxidising action of the fluorine-ions discharged at the anode. The action of fluorine on solutions of potassium acetate cooled in a freezing mixture is entirely oxidising, experiments indicating that acetyl peroxide is the first product of the reaction. This compound immediately decomposes in two different ways, the greater part forming ethane and carbon dioxide, thus: $(CH_3{\cdot}CO_2)_2=C_2H_6+2CO_2$, and the smaller part hydrolysing as follows: $(CH_3{\cdot}CO_2)_2+H_2O=CH_3{\cdot}CO{\cdot}O{\cdot}OH+CH_3{\cdot}CO_2H$. The peracetic acid then splits up into methyl alcohol and carbon dioxide, and part of the methyl alcohol forms methyl acetate with the acetic acid previously produced. A. R. POWELL.

Autoxidation of manganous hydroxide. J. MEYER and W. GULBINS (Z. anorg. Chem., 1926, **155**, 66—72).—Although the manganous ion is not oxidisable in acid or neutral solution, the action of oxygen on solutions containing hydroxyl yields more or less hydrated manganese dioxide or manganic oxide according to the conditions (cf. Meyer and

Nerlich, A., 1921, ii, 509). Colloidal solutions of manganous hydroxide with gelatin were further examined. (i) The alkaline solution was exposed to air for several days; the total manganese was determined as pyrophosphate and the active oxygen by potassium iodide solution. Oxidation to Mn_2O_3 had taken place. (ii) The alkaline solution was oxidised with a few drops of "perhydrol"; oxidation did not go entirely to Mn_2O_3. (iii) In ammoniacal solution, Mn_2O_3 was obtained. (iv) The behaviour of bivalent manganese was studied using $K_3[Mn(CN)_6]$ and almost completely pure manganic hydroxide was obtained. Experiments on the degree of autoxidation of colloidal alkaline solutions of manganous hydroxide with time show that after 5 days oxidation to Mn_2O_3 is complete. M. CARLTON.

Oxidation of a mixed solution of two reducing agents. Y. ONO (J. Chem. Soc. Japan, 1923, 44, 726—729).—A mixture of a ferrous salt $[(NH_4)_2SO_4,FeSO_4,6H_2O, A]$ and ammonium oxalate, $[(NH_4)_2C_2O_4,H_2O, B]$ containing a small definite amount of manganous sulphate was oxidised with 0·1252N- or 0·3211N-potassium permanganate solution under agitation. The ratio of A and B was 2 : 1 mol., and their normality was less than 0·1N and 0·05N, respectively; sulphuric acid was present in 1·8N concentration. In the mixture, A was first oxidised, but when the agitation was incomplete or the addition of potassium permanganate solution was too rapid, a small amount of B was also oxidised by the local action. K. KASHIMA.

Action of solutions of salts on ferrous metals. R. GIRARD (Compt. rend., 1926, 183, 213—214; cf. A., 1925, ii, 1192).—The action on steel and cast iron of solutions of salts of concentrations approximately the same as those at which they are present in sea water has been examined. Magnesium chloride and magnesium sulphate are relatively active, and attack steel more rapidly than cast iron, but although air promotes the action considerably, in no case does rusting occur. With calcium sulphate, on the other hand, except in its action on steel in aërated solution, a protective coating of rust is formed. R. CUTHILL.

Isomeric chlororuthenates. S. H. C. BRIGGS (J. Amer. Chem. Soc., 1926, 48, 2127—2129).—A correction of some mis-statements made by Howe and Haynes (cf. this vol., 138) with regard to the author's work (A., 1925, ii, 703). A polynuclear complex exists in the chlororuthenates in which chloride ions or water molecules are shared by the ruthenium ions, various cases of isomerism occurring according to the particular components being shared. A geometrical illustration is given. Charonnat's suggestion that the "alpha" salts contain quadrivalent ruthenium is considered to be improbable (A., 1925, ii, 586). It is concluded that every constituent in a chlororuthenate must be directly determined before any formula can be assigned; water cannot be determined by merely heating the compounds. The compound K_2RuCl_5 (cf. following abstract) can be formulated so that the ruthenium has a co-ordination number of 6 or 8. The analyses of the "aquo"-salt quoted by Howe support the author's original suggestion that at least two such salts exist. S. K. TWEEDY.

Isomeric ruthenium chlorides. J. L. HOWE (J. Amer. Chem. Soc., 1926, 48, 2129; cf. preceding abstract).—A correction of a mis-statement made with respect to the work of Briggs (cf. A., 1925, ii, 703). Analyses of the aquo-salt, K_2RuCl_5,xH_2O, confirm the value $x=1$; according to Briggs $x=1·5$. The ruthenium in the anhydrous form of this salt may have a co-ordination number of 5. S. K. TWEEDY.

Production of large crystals. S. KYROPOULOS (Z. anorg. Chem., 1926, 154, 308—313).—Large crystals of alkali halides are obtained when the salt is fused in a platinum crucible heated in an electric oven at about 150° above the m. p., a platinum air cooler dipped in to a depth of 7 mm., and the oven allowed to cool to 75° above the m. p. A solid hemisphere is rapidly formed on the cooler, and this consists of a number of crystals. The cooler is then raised until the solid is only slightly in contact with the fused salt, and one or two crystals continue to grow slowly, the final dimensions being limited only by the size of the crucible. A. GEAKE.

Gold sodium thiosulphate. A. J. GELARIE and F. R. GREENBAUM (Amer. Rev. Tuberculosis, 1925, 12, 314—315).—Gold sodium thiosulphate, $Au_2S_2O_3,3Na_2S_2O_3,2H_2O$ (Møllgaard's "sanocrysin"; cf. Fordos and Gelis, Ann. Chim. Phys., 1845, 3, 394) is best prepared from concentrated solutions of sodium thiosulphate and auric chloride, the latter being added slowly with stirring. It is not reduced by ferrous chloride or sulphate, oxalic acid, or stannous chloride; in solution, it is decomposed by light. Hydrogen sulphide precipitates auric sulphide.
CHEMICAL ABSTRACTS.

Preparation of calcium salts free from barium and strontium. D. RAQUET.—See B., 1926, 629.

Preparation of strontium salts free from barium and calcium. D. RAQUET.—See B., 1926, 629.

Preparation of pure barium salts. D. RAQUET.—See B., 1926, 629.

Simple and odourless method for the preparation of chlorine water. E. RUPP and B. JOCKWIG (Pharm. Zentr., 1926, 67, 433—435).—An apparatus for the preparation of small quantities of chlorine water consists of a small generating flask fitted with a cork and glass tube, the latter passing directly through another cork into an inverted 500 c.c. round flask containing 400 c.c. of water. Chlorine is generated from potassium chlorate and hydrochloric acid in the lower flask. The apparatus is closed and set aside over-night, during which time the water in the upper flask becomes saturated with chlorine. No heating is required and there is no leakage of gas.
A. R. POWELL.

Macro-microreactions. P. N. VAN ECK (Pharm. Weekblad, 1926, 63, 913—917; cf. *ibid.*, 1925, 62, No. 14).—Methods of carrying out standard identification tests with very small quantities of material by development of colorations on strips of filter paper are described. S. I. LEVY.

Electrical conductivity as a basis for analysis. A. M. ZANKO.—See this vol., 910.

General analytical procedure: centrifugo-volumetry. R. F. Le Guyon (Compt. rend., 1926, 183, 361—363).—The method is suggested as an auxiliary to volumetric analysis, and is of general application to precipitation reactions in which there are no means of determining the end-point by coloured indicators or back-titration. Precipitation is carried out in stages in very dilute solution, and the reacting solutions are centrifuged between each stage. The point at which one drop of reagent no longer produces a precipitate when added to the clear supernatant liquid is then easily seen. J. Grant.

Systematic qualitative analysis of cations by the spot method. N. A. Tananaev (Ukraine Chem. J., 1926, 2, 27—42).—The methods previously described (A., 1924, ii, 571; 1925, ii, 324), which are far more rapid, and require far less substance and reagents, than the ordinary method, and dispense with hydrogen sulphide, are developed, so as to include all the common cations. T. H. Pope.

Use of extracts of blue cabbage as an indicator. T. Miłobędzki and S. Jajte (Rocz. Chem., 1926, 6, 177—181).—Blue cabbage leaves collected during late autumn serve as the best material for the preparation of extracts; the leaves may be extracted fresh or they may be dried and extracted with alcohol when necessary. The extract thus obtained gives a series of colours, viz., red p_H 2—3, rose p_H 4—5, rose-violet p_H 6, violet p_H 6·5, blue p_H 6·8—7·1, bluish-green p_H 7·5, green p_H 8, greenish-yellow p_H 9, yellowish-green p_H 10, and yellow p_H 11. This indicator is extremely sensitive to carbon dioxide and may be used where it is desired to titrate to true neutrality. R. Truszkowski.

Colorimetric determination of hydrogen-ion concentration. A. Janke and S. Kropacsy (Biochem. Z., 1926, 174, 120—130).—The absorption spectra of standards prepared from mixtures of ferric and cobalt chlorides differ too markedly from that of the indicator for accurate determination of p_H with methyl-red, phenyl-red, or methyl-orange. Permanent standards prepared from potassium chromate and dichromate can, however, be used for comparison with nitro- and dinitro-phenols, the correspondence in colour being very close. E. C. Smith.

Determination of p_H in natural waters. I. R. Nasini and C. Porlezza.—See B., 1926, 694.

Electrode for hydrogen-ion determination using quinhydrone. L. Smolík (Biochem. Z., 1926, 172, 171—172).—A convenient modification for routine work is described in which the fluid to be investigated is placed in a wide test-tube and the electrodes are rigidly held in a stopper. H. I. Coombs.

Accuracy of electrometric measurement of p_H. K. Wolf (Collegium, 1926, 7, 308—321).—The causes of irregularities in standard electrodes and the limits of accuracy of buffer solutions are discussed. The work of Michaelis and Kakinuma (A., 1923, ii, 824) on the calibration of standard electrodes by means of hydrochloric acid solutions has been investigated, and the p_H value of Michaelis' standard acetate solution is found to be 4·64 instead of 4·61. S. I. Levy.

Electrometric determination of hydrogen-ion concentration in colloidal solutions, particularly tan liquors. V. Kubelka and J. Wagner.—See B., 1926, 683.

Use of electrodes of *V2A*-steel in electro-analysis. A. Schleicher and L. Toussaint.—See B., 1926, 675.

New type of end-point in electrometric titration and its application to iodometry. C. W. Foulk and A. T. Bawden (J. Amer. Chem. Soc., 1926, 48, 2045—2051).—Two platinum electrodes are immersed in the well-stirred iodine solution, the *P.D.* between them being kept at 10—15 m.-volts, *i.e.*, of the same order as the polarisation *E.M.F.* Successive additions of thiosulphate or arsenite cause a sensitive galvanometer in the circuit to approach the zero position, which it reaches when all the iodine has reacted (" dead-stop " end-point). Further additions of thiosulphate do not influence the galvanometer. The method requires that at least one of the main reactants must be an efficient depolariser, whilst the products of the reaction must have no depolarising action. These conditions may also be obtained by the addition of suitable substances. The application of the method to iodometry is detailed and a modified apparatus is described which eliminates the use of a battery. S. K. Tweedy.

Apparatus for the determination of low concentrations of chlorine in chlorine–air mixtures. J. H. Yoe (J. Lab. Clin. Med., 1925, 10, 1041—1045). Chemical Abstracts.

[Colorimetric determination of] free chlorine in air. L. E. Porter (Ind. Eng. Chem., 1926, 18, 730—731).—A known volume of air is slowly aspirated through a test-tube containing 10 c.c. of a solution made by dissolving 1 g. of *o*-toluidine in 100 c.c. of concentrated hydrochloric acid and diluting to 1 litre. The yellow colour produced is compared with a series of standards made by mixing in varying proportions dilute solutions of copper sulphate and potassium dichromate (cf. Muer and Hale, J. Amer. Waterworks Assoc., 1925, 13, 50). A. R. Powell.

New method of calcination for the determination of chlorine in perchlorates. D. Dobroserdov and V. Erdmann (Ukraine Chem. J., 1926, 2, 15—18; cf. following abstract).—The following procedure obviates loss of chlorine and yields accurate results. Sufficient anhydrous sodium carbonate is introduced into a platinum crucible to cover the bottom to a depth of 0·6—1 mm. About 0·2 g. of the perchlorate is then added, and, when this is not an alkali perchlorate, one or two drops of water to induce double decomposition with the sodium carbonate. The contents of the crucible are then dried in an oven at 100—110° and are covered with a layer of anhydrous sodium carbonate 3—4 mm. in depth, which is itself covered with a tight-fitting plug of asbestos board freshly heated in the flame. Anhydrous sodium carbonate is then sprinkled between the edges of the asbestos and the walls of the crucible, which is closed

and heated, preferably over the slender flame of a vertical blowpipe, so that the crucible is heated to redness for not more than 6 mm. above the bottom; under these conditions, heating for 1 min. is sufficient. The contents of the crucible are afterwards lixiviated with hot water and the solution is neutralised with nitric acid and filtered, the whole of the filtrate and washings being titrated with silver nitrate solution.

T. H. POPE.

Comparison of various methods for the determination of perchlorates. D. DOBROSERDOV (Ukraine Chem. J., 1926, 2, 1—13).—Sjollema's method (A., 1905, ii, 21) for the determination of perchlorates does not always give complete reduction, the resulting loss of chlorine being 1·5—2%. Rothmund's method (A., 1909, ii, 434) is more rapid and more accurate, the results obtained being from 0·02 to 0·24% too low. Lamb and Marden's method (A., 1912, ii, 681) is capable of yielding accurate results rapidly, but requires practice and certain modifications. The heating must be carried out in a hard glass test-tube and must be neither too intense nor too prolonged. It may be applied also to perchlorates which give volatile or unstable chlorides, but such must be mixed with anhydrous sodium carbonate before being heated. In 10 determinations the errors varied from 0·04 to 0·25%. T. H. POPE.

Iodometric determination of the halogens. P. L. HIBBARD (Ind. Eng. Chem., 1926, **18**, 836—838).—The method previously described for the determination of small amounts of bromine (cf. this vol., 260) has been extended to the determination of iodine, bromine, and chlorine in the same sample. After destruction of organic matter by sodium peroxide, the sample is reduced by sodium hydrogen sulphite in alkaline solution, and the iodine liberated by boiling the solution with ferric sulphate in the presence of sulphuric and nitric acids, the iodine being determined as previously described for bromine. The bromine is next liberated by oxidation of the residual liquor with chromium trioxide in the cold, and finally the chlorine is freed by oxidation with potassium permanganate and sulphuric acid, a slightly modified apparatus being used in this case. Full experimental details are given, and the results are accurate to at least ±5% of the amounts present. J. W. BAKER.

Determination of iodine in natural waters. H. W. BRUBAKER, H. S. VAN BLARCOM, and N. H. WALKER.—See B., 1926, 630.

Determination of fluorine [in ores]. F. G. HAWLEY.—See B., 1926, 672.

Fatal case of poisoning with sodium fluosilicate and the detection of small quantities of sodium fluosilicate. H. LÜHRIG (Chem.-Ztg., 1926, **50**, 593—595).—The symptoms associated with a fatal case of sodium fluosilicate poisoning are briefly described, together with a method of detecting the salt in the organs, especially the liver. The organic matter is destroyed by treatment with potassium chlorate and hydrochloric acid on the water-bath, the solution rendered alkaline by the addition of calcium hydroxide and evaporated to dryness, and the residue heated gently until free from organic matter. Part of the residue is treated with concentrated sulphuric acid in a platinum crucible covered with a watch-glass to the bottom of which a drop of water adheres; after warming for 20 min. over a micro-burner, the presence of fluosilicate is indicated by a white ring of gelatinous silica around the water drop. Fluorine alone is tested for by the etching test after first moistening the ignited residue with water. If the heating has not been carried out at too high a temperature, the method will detect 0·1 mg. of fluosilicate; if the residue is heated to redness, not less than 0·3 mg. can be detected with certainty.

A. R. POWELL.

Determination of sulphate in the presence of lead. VLASTIMIL and M. MATULA (Chem.-Ztg., 1926, **50**, 486—488).—Precipitation of sulphate with benzidine hydrochloride followed by titration of the precipitate with sodium hydroxide, using phenolphthalein as indicator, gives good results provided that the precipitate is washed with 25% alcohol and precipitation effected by pouring the sulphate solution into the benzidine solution. An excess of the precipitant does not affect the results; the presence of nitrates gives high results and of acetates slightly low results. If lead is present, the precipitation must be carried out after addition of sufficient ammonium acetate to retain the lead sulphate in solution, and the filtration should be made only after 24 hrs.

A. R. POWELL.

Determination of sulphurous acid and sulphites. G. ALSTERBERG (Biochem. Z., 1926, **172**, 223—232).—Iodine cyanide is added to the solution, which is then acidified. Potassium cyanide is added and the hydrogen iodide titrated with potassium permanganate. C. RIMINGTON.

Reactions for carbonates, hydrogen carbonates, sulphites, and hydrogen sulphites. T. GASPAR Y ARNAL (Anal. Fis. Quím., 1926, **24**, 267—272).—By the use of aqueous solutions of cobalt nitrate, copper sulphate, and mercuric chloride, respectively, precipitates or colorations are obtained by means of which carbonates, hydrogen carbonates, sulphites, and hydrogen sulphites may be distinguished. The reactions are shown in tabular form.

G. W. ROBINSON.

Volumetric determination of hyposulphite. H. ROTH.—See B., 1926, 582.

Colorimetric determination of nitrates. L. W. HAASE.—See B., 1926, 582.

Mercuric bromide paper for the Gutzeit method for arsenic. G. KEMMERER and H. H. SCHRENK (Ind. Eng. Chem., 1926, **18**, 707).—To obtain highly sensitive paper for the Gutzeit test, a good quality soft filter-paper (*e.g.*, Whatman, No. 40) is dried for 1 hr. at 105° and stored in a desiccator over calcium chloride. Just before it is required for a determination, it is soaked in a 1·5% solution of mercuric bromide in 95% alcohol, allowed to drain, and dried for 10 min. in a desiccator; it should be used within 2 hrs. of preparation. Stale papers, owing to varying humidity, give uneven colouring, often accompanied by spots. A. R. POWELL.

Titration of arsenious oxide with permanganate. O. CANTONI.—See B., 1926, 663.

Analysis of the alkali group. S. ATO and I. WADA (Sci. Papers Inst. Phys. Chem. Res., 1926, **4**, 263—293).—A scheme for the qualitative analysis of the alkali metals is described, based on an initial separation of potassium, rubidium, and cæsium from sodium and lithium by evaporation of the chloride solution, obtained in the usual group analysis, with perchloric acid, followed by extraction of lithium and sodium perchlorates by means of 97% alcohol. The alcoholic solution is saturated with hydrogen chloride, which precipitates sodium completely as chloride; the precipitate is washed with alcoholic hydrogen chloride and the usual confirmatory pyroantimonate test is applied. The filtrate from the sodium chloride may contain some cæsium and rubidium if only traces are present; it is evaporated on the water-bath, and the residue, after heating to decompose perchlorates, is dissolved in 1 c.c. of hydrochloric acid. The solution is treated with 0·3 c.c. of a saturated solution of chlorostannic acid and 1 c.c. of alcohol, which effects complete precipitation of cæsium and rubidium. The filtrate is tested for lithium, after removal of tin with hydrogen sulphide, by the phosphate and flame tests. The original perchlorate precipitate is heated to convert the metals into chlorides, and the residue is extracted with 3 c.c. of strong hydrochloric acid, which leaves the greater part of the potassium chloride insoluble. The filtrate is evaporated to dryness and the residue extracted with 2 c.c. of concentrated hydrochloric acid and 2 c.c. of 97% alcohol previously mixed and saturated with hydrogen chloride. This solution may contain up to 50 mg. of cæsium chloride, up to 30 mg. of rubidium chloride, and only 1·5 mg. of potassium chloride. Repetition of the process on the residue will extract any further cæsium or rubidium present. The acid filtrates are evaporated to dryness and the cæsium and rubidium separated from the last traces of potassium by the chlorostannate method described above. The precipitate is combined with that previously obtained and dissolved in hot dilute hydrochloric acid; tin is removed from the solution by passing hydrogen sulphide, and the filtrate is evaporated twice with nitric acid to convert the chlorides into nitrates. The dried nitrates are mixed with 0·3 g. of oxalic acid and the mixture is heated gently at first, then more strongly in a platinum crucible to convert the nitrates into carbonates. The residue is dissolved in water, oxalic acid added, and the procedure repeated. The final residue of carbonates is extracted with 10 c.c. of absolute alcohol, which dissolves most of the cæsium and only a small part of the rubidium. The alcoholic solution is acidified with hydrochloric acid and evaporated to dryness, the residue is dissolved in 0·2 c.c. of strong hydrochloric acid, and a few drops of a solution of antimonious chloride in hydrochloric acid saturated with hydrogen chloride are added. A crystalline precipitate of $3CsCl,2SbCl_3$ shows the presence of cæsium; the precipitate is soluble in an excess of the precipitant. If only very small quantities of rubidium are present, the whole of this element will be in the filtrate from the antimony chloride precipitate; if large amounts are present, they will be in the insoluble residue from the alcohol extraction of the carbonates. In either case, a hydrochloric acid solution free from antimony is obtained in any suitable way, the solution is evaporated to dryness to expel acid, the residue dissolved in a few drops of water, and the solution treated with a drop of sodium hydrogen tartrate solution. A white crystalline precipitate on shaking indicates rubidium. A. R. POWELL.

Comparison of methods for the determination of sodium sulphide. P. P. BUDNIKOV.—See B., 1926, 664.

Radiometric micro-analysis. II. R. EHRENBERG (Biochem. Z., 1926, **172**, 10—16).—Micro-determinations of calcium may be carried out by the use of the radioactive properties of thorium-*B*, an isotope of lead. The calcium is precipitated as calcium oxalate by a known volume of ammonium oxalate and removed by centrifuging. The excess of oxalate is then precipitated as lead oxalate by a known excess of active lead nitrate. The residual lead in the supernatant liquid can, after evaporation, be determined radiometrically, and from this value can be calculated the amount of calcium. Barium, acids, ammonia, and other substances can be determined in a similar manner. H. I. COOMBS.

Potentiometric titration of mercury alone and in the presence of other metals. E. ZINTL and G. RIENÄCKER (Z. anorg. Chem., 1926, **155**, 84—90).—A detailed account is given of a new method for the volumetric determination of mercury alone and in presence of arsenious, antimonious, stannic, lead, cadmium, bismuth, and small quantities of iron compounds. Mercuric salts are reduced to metallic mercury by means of titanium trichloride in hot acetic acid solution containing ammonium chloride with addition of a bismuth salt as carrier, the end-point being determined potentiometrically.
M. CARLTON.

Determination of traces of mercury. II. Determination of mercury in presence of organic matter. H. S. BOOTH, (MISS) N. E. SCHREIBER, and K. G. ZWICK (J. Amer. Chem. Soc., 1926, **48**, 1815—1823; cf. this vol., 40).—Directions are given for the accurate determination of traces of mercury in presence of organic matter. The latter is oxidised by boiling with concentrated sulphuric acid and then adding pellets of potassium permanganate. Mercury in very dilute solutions is present partly in the colloidal state; by precipitating as sulphide with simultaneous precipitation of the manganese as hydroxide all the mercury is obtained in the precipitate, which is then oxidised by heating with lead chromate. The weight of the metallic mercury so obtained is computed from the length of the thread in a standardised capillary tube. S. K. TWEEDY.

Electrometric precipitation titrations. J. A. ATANASIU (J. Chim. phys., 1926, **23**, 501—514).—The electrometric titration of cerium with potassium ferrocyanide, and of barium, lead, and mercurous mercury with potassium chromate has been studied. Errors due to the solubility of the precipitates and to

the adsorption of ions on them are eliminated, and the determination of the end-point is rendered more sensitive by carrying out the titrations in the presence of 30% ethyl alcohol at about 70°. At this temperature, the reaction in the cerium determination is $Ce''' + Fe(CN)_6K''' = KCeFe(CN)_6$. L. F. GILBERT.

Reaction of "aluminon" with hydroxides of beryllium, rare earths, zirconium, and thorium. A. R. MIDDLETON (J. Amer. Chem. Soc., 1926, 48, 2125—2126).—"Aluminon" (cf. Hammett and Sottery, A., 1925, ii, 601) forms lakes with the hydroxides or the basic acetates of beryllium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium, and thorium, all of which are a deeper red than the aluminium lake, the cerium lake being much darker than the others. All are dissolved or decolorised by moderate additions of ammonium carbonate, except the beryllium lake, and, except for the zirconium lake, which is partly decolorised and flocculates as a pink precipitate, all are unaffected by ammonia in moderate concentrations. These lakes are less soluble than the corresponding hydroxides or basic acetates. After separation of the lanthanum lake, a white precipitate gradually flocculates from the colourless supernatant liquid. A small red precipitate was obtained after a few days in the case of thallium. S. K. TWEEDY.

Reduction–oxidation potentials. I. Determination of very small quantities of ferrous and ferric salt. Applicability of reduction–oxidation potentials to analytical operations. P. HIRSCH and R. RÜTER (Z. anal. Chem., 1926, 68, 328—342).—The potential of a platinum electrode against a solution containing both ferrous and ferric ions is a function of the ratio of the two ions present when the solution is sufficiently dilute and the acidity is kept constant at, say, $0{\cdot}02M$. If E_0 is the potential of the electrode against the acid solution without iron and E the potential when the mixed iron salts are added, then at 18°, $E = E_0 + 0{\cdot}0577 \log [Fe''']/[Fe'']$. By determining, therefore, the total iron or the ferrous iron in a solution and then measuring the potential under standard conditions, the proportion of each of the iron ions can be calculated or found by reference to a previously constructed graph. Alternatively, the potential of the original solution is measured (E_1), a definite amount of a ferric salt solution is added to give a concentration of a, and the potential again measured (E_2). If $\log (E_0 - E_1)/0{\cdot}058 = N_1$ and $\log (E_0 - E_2)/0{\cdot}058 = N_2$, then the concentration of ferrous ions is $(N_1 N_2 a)/(N_1 - N_2)$, and of ferric ions, $(N_2 a)/(N_1 - N_2)$. The method is extremely delicate and may be used for solutions as dilute as $M \times 10^{-6}$, as well as for neutral solutions in which the ferric salt is entirely hydrolysed to ferric hydroxide, *e.g.*, in waters in which iron has rusted. Similar results are obtained with other reversible systems, such as the quinone–quinol system. In many cases, also, addition of substances which are not electrolytically dissociated to non-reversible reduction–oxidation systems leads to a well-marked constant change of potential. Thus, addition of dextrose to sodium hypoiodite or hyposulphite solution causes very marked potential changes, the dextrose acting as the reducing agent in the first case and as the oxidising agent in the second case. Egg-albumin behaves similarly towards dilute hydrogen peroxide and sodium hyposulphite solutions. A. R. POWELL.

Colorimetric determination of nickel. A. P. ROLLET (Compt. rend., 1926, 183, 212—213; cf. Feigl, A., 1924, ii, 504).—If to a solution of a nickel salt free from copper or cobalt except as sodium cobalticyanide there is added a slight excess of bromine, followed by sufficient ammonia to absorb it and then an alcoholic solution of dimethylglyoxime, an orange coloration appears if the solution contains as little as 0·015 mg. of nickel in 100 c.c. The method is applicable to the analysis of organic substances and of steel, provided in the latter case that the dimethylglyoxime is added before the ammonia. R. CUTHILL.

Action of concentrated hydrobromic and hydriodic acids on the cobalt ion. New reaction of nickel. G. DENIGÈS (Compt. rend., 1926, 183, 55—57; cf. A., 1925, ii, 826).—Hydrobromic and hydriodic acids have characteristic influences on the colours and absorption spectra of solutions of cobalt salts. Green (not blue, as with hydrochloric acid) colours can be obtained on the addition of either acid, but under different concentration conditions. Band absorption spectra are produced. The nickel ion gives no colour change and no band absorption spectra on the addition of hydrochloric or hydrobromic acid; but hydriodic acid causes a sensitive colour change, accompanied by a banded absorption spectrum, to occur. When a drop of nickel sulphate solution (4% Ni) is added to 1—2 c.c. of concentrated hydriodic acid, an intense red colour, similar to that of ferric thiocyanate, is obtained; this colour disappears on sufficient dilution by water. Hydrofluoric acid does not markedly affect the colours or absorption spectra of solutions of cobalt or nickel salts. As sulphuric acid also has a negative influence, it is considered that such colour changes cannot be explained by a dehydration theory. L. F. GILBERT.

Determination of chromium in chromite. A. FRANKE and R. DWORZAK.—See B., 1926, 589.

Spot method for detecting titanium and uranium. N. A. TANANDEV and P. A. PANTSCHENKO (Ukraine Chem. J., 1926, 2, 43—47).—Titanium may be detected by its reaction with 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic (chromotropic) acid (cf. Hall and Smith, A., 1905, ii, 829), and uranium by its reaction with potassium ferrocyanide. The details of the procedure are described. T. H. POPE.

Determination of small amounts of bismuth in copper. C. O. JONES and E. C. FROST.—See B., 1926, 633, 671.

Gold from mercury. E. DUHME and A. LOTZ (Ber., 1926, 59, [*B*], 1649—1651; cf. this vol., 922).—Complete separation of gold from mercury can be effected by distillation from an evacuated vessel the walls of which are permeable to mercury vapour, but not to liquid mercury, or from an apparatus consisting of two vessels connected by a glass spiral. Mercury distilled in this manner does not afford any

trace of gold after subjection to the most varied electrical treatment.

Mercury which appears analytically free from gold often exhibits a gold content after being preserved, since the gold becomes non-homogeneously distributed and localised mainly at the walls of the vessel and in positions in which a film is formed. Such films are most readily produced when convection currents are most pronounced, and therefore in almost every arrangement whereby mercury is submitted to electrical discharges. H. WREN.

Separation of iridium from iron. W. R. SCHOELLER (Analyst, 1926, **51**, 392—397).—The iridium–ruthenium–iron alloy obtained after extraction of a lead button is fused as usual, the ruthenium volatilised in chlorine, and the residual suspension of hydroxides boiled with excess of sodium hydroxide and alcohol, left to settle, the iridium liquid decanted, and the bulk of the sodium salts washed out. The suspension of precipitate in hot water is evaporated to dryness after the addition of 15 c.c. of hydrochloric and 5 c.c. of nitric acids. The dry residue is taken up with hot dilute hydrochloric acid, filtered, the precipitate washed, ignited, and treated with hydrofluoric and dilute hydrochloric acids, collected, washed, and transferred to a tared porcelain crucible (precipitate A.). The iridium filtrate, after addition of 5 g. of ammonium chloride, is evaporated until the solution over the black, crystalline chloroiridate precipitate is pure green. After keeping over-night, the liquid is decanted and the precipitate (B) washed with half-saturated ammonium chloride solution and a drop of hydrochloric acid, transferred to the crucible containing (A), and gently heated. The filtrate is evaporated after addition of 1 c.c. of nitric acid until a thick crust of ammonium chloride forms, and the small quantity of soluble chloroiridate converted into insoluble chloroiridate. This precipitate (C) is collected and washed like (B), added to the other two, and the whole ignited at the lowest possible temperature until all the volatile matter is driven off. The temperature is then raised and the iridium oxide reduced as usual. The few mg. of contaminating silica are largely removed by subsequent treatment with hydrofluoric and hydrochloric acids, whilst the iron is usually negligible. The metal is then collected, washed, ignited, reduced, and weighed. If ruthenium is present, this is removed by fusion with sodium peroxide and distillation. Details are given for procedure with small amounts of iridium, for any iron corrections, and for blank fusions. D. G. HEWER.

Refractometer. H. SCHULZ (J. Sci. Instruments, 1926, **3**, 301—303).—A new refractometer on the total reflexion principle is described. It has a range from 1·330 to 1·376, and its extreme limit of accuracy is 3 or 4 units in the fifth decimal place. S. BARRATT.

Ultra-microscope. C. SPIERER (Arch. Sci. Phys. Nat., 1926, [v], **8**, 121—131).—Various methods are reviewed for obtaining an image of a brightly illuminated object on a dark background. An instrument is described in which the source of light for visual work is a 25-candle-power "half-watt" lamp placed below the object. The light passes through an iris diaphragm of special form; the direct vertical rays do not pass into the microscope, but are reflected back on the object by a small disc. A combination of convex and concave mirrors throws beams of light at an angle to the vertical, both from below upwards and from above downwards. Arrangement is made for using light of two colours; a solution of quinine is used for removing violet light. With quartz optical work, the instrument can be used for ultra-violet light, the mercury-vapour lamp being the most convenient illuminant. E. B. LUDLAM.

Electrical [thermo]regulator. V. LOMBARD (Bull. Soc. chim., 1926, [iv], **39**, 948—952).—The apparatus, designed for high temperatures (300°), consists essentially of a dilatometer tube (20 c.c.) with a tap and reservoir at the top and a side arm with a rubber membrane over the end. The whole is filled with mercury, the critical amount for a given temperature being readily obtained by heating the regulator at that temperature with the tap open, the excess entering the reservoir. When the tap is turned off, the expanding mercury causes the diaphragm to swell and to push a strip of metal against an adjustable metal contact, thereby causing a relay to insert a resistance in the heating circuit and so lower the temperature. A circuit diagram is given for those cases in which the regulator cannot be placed in the working furnace and has to be put in a small, auxiliary furnace. S. K. TWEEDY.

Device for arc-welding easily oxidisable wires. H. P. COATS (J. Amer. Chem. Soc., 1926, **48**, 2130—2131).—The wires are connected to one pole of the current supply, the other pole being attached to a graphite block in which a hole has been bored. The twisted ends of the wires are pushed into a drop of oil which has been dropped into the hole, and rapidly withdrawn a little. The resulting arc occurs in a reducing atmosphere and produces a good weld. S. K. TWEEDY.

Fractionating column. A. MÜLLER (Chem.-Ztg., 1926, **50**, 496).—A fractionating column of new pattern, consisting of concentric tubes through which water or other liquids can be circulated, and made of tinned or silver-plated copper, is described. J. W. BAKER.

Improved laboratory fractionating column. A. W. T. LOVELESS (Ind. Eng. Chem., 1926, **18**, 826).—An improved fractionating column consists of an insealed condenser, containing 0·25 in. lengths of 0·25 in. tubing, the jacket of which is silvered and highly evacuated to ensure thermal insulation. The still-head is a reflux condenser to which is sealed a stop-cock that diverts a controlled fraction of the condensate. J. W. BAKER.

Germanium. XIII. Vacuum apparatus for the purification and study of volatile compounds of germanium. A. W. LAUBENGAYER and R. B. COREY (J. Physical Chem., 1926, **30**, 1043—1046).—A modified form of the apparatus used by Dennis, Corey, and Moore (A., 1924, ii, 343) is described. L. S. THEOBALD.

Simple vacuum arc mercury still for laboratories. H. P. WARAN (Phil. Mag., 1926, [vii], **2**, 317—320).—A simple mercury still is described in which the mercury is vaporised by means of an arc passing between two mercury surfaces. The still operates continuously, the condensed mercury passing down a vertical capillary tube and maintaining a high vacuum by a Sprengel pump action.
A. B. MANNING.

Bath for observations at lower temperatures. W. H. PATTERSON (Phil. Mag., 1926, [vii], **2**, 383—384).—A bath is described which has been used at temperatures varying from −120° to 30°. It combines an electrical heating element with an internal cooling tube into which liquid air can be forced a little at a time. A steady temperature is attained within ½ min. of breaking the current or forcing over the liquid air, and the temperature can be reduced by 100° in 15—20 min. M. S. BURR.

Device for the evaporation of solutions strongly acid with hydrochloric acid. S. BIALKOWSKI (Chem.-Ztg., 1926, **50**, 595).—To prevent spraying when evaporating a concentrated hydrochloric acid solution, a filter funnel just small enough to pass inside the dish is supported immediately above the surface of the liquid. The spray condenses on the sides of the funnel and the acid vapours escape through the stem. When the concentration of the acid has been reduced to that of the constant-boiling solution, the funnel may be removed without fear of loss by spraying. A. R. POWELL.

Vacuum regulator. G. V. SCOFIELD (Ind. Eng. Chem., 1926, **18**, 717).—A regulator for maintaining any desired pressure below the normal consists of an iron pipe, 122 cm. long and 38 mm. in diameter, closed at the lower end and provided with an adjustable glass tube through the upper end, which is also connected, through a 5-litre Pyrex flask acting as a buffer, to the vacuum pump and gauge. The iron tube is filled to a height of 79 cm. with mercury, the pump is started, and the glass tube is pushed into the mercury until the gauge registers the required vacuum; then, as the pump creates a greater vacuum than that required, air passes into the system through the tube in the mercury column. The system for which the low pressure is required is connected to a third tube entering the equalising flask.
A. R. POWELL.

Simple mixing apparatus for water-bath. W. LAMPE and R. RÖSSLER (Arch. exp. Path. Pharm., 1926, **114**, 252—254).—A simple apparatus is described with a diagram whereby efficient mixing of the water in a water-bath is achieved, the external source of power being a water pump, from one of which four such units may be worked simultaneously.
W. O. KERMACK.

Filtration apparatus. ANON. (Chem.-Ztg., 1926, **50**, 496—497).—Various new types of suction filters are described, one in which the top perforated portions are separate from the bottoms, one round which a current of water can be circulated, and one adapted for electro-ultrafiltration. Gelatinous precipitates may be rapidly filtered under suction by use of a porous cone which fits into an ordinary glass funnel.
J. W. BAKER.

Silica gel as filtering agent. E. V. HOWELL (J. Amer. Pharm. Assoc., 1925, **14**, 704—706).—By the use of silica gel instead of talc in aqueous solutions, only one third as much material is required, and filtration is more rapid. Ethyl alcohol and silica gel, however, produce an effervescence and a rise in temperature. CHEMICAL ABSTRACTS.

Safeguarding laboratory motors. H. L. TRUMBULL (Ind. Eng. Chem., 1926, **18**, 675).—By covering the airholes of laboratory motors with 50-mesh copper gauze, welded on, all danger of explosion, due to ignition of inflammable vapours by sparking at the brushes, is avoided on the same principle as the Davy lamp. A. R. POWELL.

Standardisation of collodion membranes. I. C. LUNDSGAARD and S. A. HOLBØLL (J. Biol. Chem., 1926, **68**, 439—456).—The permeability of collodion membranes was measured by observing the rate of diffusion of dextrose, from a solution contained within the sac, into distilled water; the rate was found to be governed by the equation $dx/dt = e(k/2-x)$, where k is the original concentration of dextrose in the inner solution, x is the increment in concentration in the outer solution in time t, and e is the diffusion coefficient for the membrane. The permeability of the membranes could be varied by immersing them in aqueous alcohol of varying concentrations (cf. Walpole, A., 1915, ii, 549). Membranes prepared under the same conditions had always the same diffusion coefficient; the diffusion coefficient decreased in magnitude with increasing strength of the alcoholic solution with which the membrane was treated. The rate of diffusion was somewhat more than doubled by doubling the area through which it could take place. C. R. HARINGTON.

Micro-pyrometer eye-piece. A. GOETZ (Z. Physik, 1926, **38**, 119—123).—An eye-piece is described which will fit into an ordinary microscope and is very convenient for determining the temperature of small objects, incandescent filaments, etc. Inside the tube is fixed a small metal-filament lamp, the position of its filament coinciding with the image of the hot body under observation. Suitable diaphragms, screens, etc. are provided. From a preliminary calibration of the lamp, a temperature up to 3000° can be measured with an error at 1000° of ±2°, at 1500° of ±6°, and at 2000° of ±10°.
E. B. LUDLAM.

Sensitive apparatus for precision measurements of coefficients of magnetisation at various temperatures. G. FOËX and R. FORRER (J. Phys. Radium, 1926, [vi], **7**, 180—187).—An apparatus is described with which coefficients of magnetisation of less than 5×10^{-7} can be measured with an accuracy of 1 in 1000 with less than 1 g. of material. A translation method is used, the dynamometer having a very light coil, the frame of which is constructed to give the necessary damping. C. J. SMITHELLS.

Simple manometer for measuring low pressures. T. SHIRAI (Bull. Chem. Soc. Japan, 1926, **1**, 109—115).—The manometer, which measures pressures of 0·1—0·001 mm., consists of a sensitive thermometer with an elongated bulb enclosed in a tube sealed on to the exhausted apparatus. The tube is immersed in a cooling bath, and the time of cooling, under given conditions, over a small temperature range is noted. The pressure is given by $p=k(t_0-t)/(t-t_{760})$, where t is the time of cooling under pressure p, t_0 and t_{760} are the cooling times for the highest vacuum and for 760 mm., respectively, and k is an experimentally-determined constant depending on the nature of the gas and the dimensions of the apparatus. S. K. TWEEDY.

Non-spattering, continuous-stream wash-bottle. H. E. BENT and G. A. HUNT (J. Amer. Chem. Soc., 1926, **48**, 1925).—The jet and mouth-piece of a 1 litre wash-bottle are attached so that the rubber junctions act virtually as Bunsen valves. S. K. TWEEDY.

Mineralogical Chemistry.

Amounts of krypton and xenon in air. C. MOUREU and A. LEPAPE (Compt. rend., 1926, **183**, 171—175).—The krypton and xenon are separated from the crude argon by fractional absorption with coconut charcoal, and determined by the spectrophotometric method (A., 1922, ii, 394). The results of the measurements have already been published (J.C.S., 1923, **123**, 1906). R. CUTHILL.

Contents of helium and other constituents in the natural gases of Japan. Y. KANO and B. YAMAGUTI (Rep. Aeronaut. Research Inst. Tokyo Imp. Univ., 1926, **1**, 347—358).—The natural gases of Japan are roughly classified according as their chief constituents are (*a*) carbon dioxide, (*b*) methane and other hydrocarbons, (*c*) nitrogen; only the last group contain helium in reasonable, although not industrial, quantities. Mineral spring gases contain small percentages, that in hot, but not cold, spring gas depending in a measure on the content of the emanation. CHEMICAL ABSTRACTS.

Genetical interpretation of extrusive rocks. S. TSUBOI (J. Fac. Sci. Tokyo, II, 1926, **1**, 77—86).—As illustrated by an equilibrium diagram, it is shown that the bulk analysis of a volcanic rock does not represent the composition of the magma from which it separated. The compositions of the ground-mass and of the porphyritic crystals are of greater significance. L. J. SPENCER.

Dispersion method of discriminating rock-constituents. S. TSUBOI (J. Fac. Sci. Tokyo, II, 1926, **1**, 139—180).—With fragments immersed in a liquid of high dispersion, the wave-length of the light at which there is exact matching of the refractive indices is determined under the microscope with a monochromatic illuminator. The value for sodium-light is then read on a graph (Min. Mag., 1923, **20**, 108). For the discrimination of rock-forming minerals a determination of the refractive indices n_1 and n_2 in cleavage-flakes is sufficient. Formulæ are given for calculating these from the principal refractive indices. Examples are given showing the application of the method for rapidly tracing the variations in chemical composition of olivine, plagioclase, pyroxene, and hornblende in different parts of a gabbro laccolith; and its help in the solution of various petrogenic problems is suggested. L. J. SPENCER.

Colours produced by iron in minerals and sediments. G. R. MACCARTHY (Amer. J. Sci., 1926, [v], **12**, 17—36).—A series of rocks and minerals are tabulated according to their FeO/Fe_2O_3 ratio, ranging from 0·0 to 22·82, with a roughly corresponding range in colour from red, through yellow, purple, blue, and green, to black. A number of experiments were made on colour changes in various rocks, minerals, and salts of iron during oxidation, reduction (dry and wet), and dehydration. Pure ferrous compounds are colourless, whilst ferric iron gives reds and yellows. It is concluded that blues are due to hydrous ferrosoferric compounds (anhydrous ferrosoferric compounds giving only grey and black), and that greens and purples are mixtures of blue with yellow or red. There is no evidence for the existence of green or purple iron compounds. L. J. SPENCER.

[Composition of] limestones. W. MEIGEN (Chem. Erde, 1926, **2**, 396—413).—A series of shell-limestones from different horizons in the Black Forest area have been studied chemically and microscopically, with special reference to the extent of silicification. The action of solutions of alkali silicates on powdered Iceland spar gives rise to the formation of some calcium silicate. No calcium silicate is, however, found in silicified limestones in nature; hence other silica-containing solutions must have been concerned in the formation of these deposits. C. T. GIMINGHAM.

Classification of the chlorites. J. ORCEL (Compt. rend., 1926, **183**, 363—365).—A classification of the chlorites based on the results of chemical analyses is suggested, the following ratios being determined: $s=SiO_2/R_2O_3$, $r=RO/R_2O_3$, and $h=H_2O/R_2O_3$, where R represents iron, chromium, or aluminium in the R_2O_3 form, and iron, magnesium, or manganese in the RO form; $f=FeO/MgO$, $a=Fe_2O_3/Al_2O_3$, and $c=Cr_2O_3/Al_2O_3$. Seven main classes are distinguished according as s varies from 1·0 to 4·5. The variation in the optical properties between the various types of chlorites forms no trustworthy basis of classification, although it seems that for a particular group an increase in the ferric iron content produces a higher birefringence, whilst for equal iron contents the indices increase with the chromium content. J. GRANT.

Zonal growth of plagioclase and soda-orthoclase in syenitic magma. T. Itô (J. Fac. Sci. Tokyo, II, 1926, **1**, 105—109).—Crystals of felspar in syenite from Meisen, Korea, consist of a core of plagioclase, ranging from $Ab_{40}An_{60}$ inside to $Ab_{60}An_{40}$ outside, surrounded by a zone of soda-orthoclase. The growth of such zoned crystals from the magma is discussed with the aid of equilibrium diagrams. L. J. Spencer.

Fergusonite and allanite from Iyo, Japan. D. Satô (J. Fac. Sci. Tokyo, II, 1926, **1**, 49—52).—Fergusonite as acute pyramidal crystals occurs in pegmatite at Hakata-mura, prov. Iyo; d 5·30. Analysis by K. Kimura gave: $(Nb,Ta)_2O_5$ 44·97, TiO_2 1·15, SiO_2 0·79, SnO_2 0·35, UO_2 3·18, Y_2O_3 etc. 40·39, Nd_2O_3 etc. 0·89, Al_2O_3 1·35, Fe_2O_3 0·66, MgO 0·58, CaO 1·40, CO_2 0·35, H_2O 3·92, total 99·98. Spectrum analysis showed the presence of yttrium, ytterbium, scandium, lutecium, dysprosium, thulium, neodymium, erbium, europium, praseodymium, holmium, copper, lead, and germanium. Allanite is found in the same pegmatite as large irregular masses and as flat crystals up to 17 cm. in length; d 3·824. Analysis by Y. Minami gave: SiO_2 30·51, TiO_2 0·49, ThO_2 1·84, SnO_2 0·66, Al_2O_3 15·09, Fe_2O_3 3·60, Y_2O_3 etc. 3·02, La_2O_3 etc. 11·53, Ce_2O_3 8·52, FeO 11·47, MnO 2·72, MgO 0·12, CaO 8·70, Na_2O 0·06, K_2O 0·06, CO_2 0·33, H_2O 2·05, total 100·77. Spectrum analysis showed the presence also of strontium, copper, zinc, and germanium. L. J. Spencer.

Dvi-manganese in native platinum. O. Zvjaginstsev, M. Korsunski, and N. Seljakov (Nature, 1926, **118**, 262—263).—Chemical and röntgenographical examination has failed to detect the presence of element 75 in native platinum. A. A. Eldridge.

Presence of a cæsiferous variety of potassium fluoborate among the products of the present-day activity of Vesuvius. F. Zambonini (Atti R. Accad. Lincei, 1926, [vi], **3**, 644—649).—The name "avogadrite" is proposed for a crystalline potassium fluoborate (about 90·5%) containing cæsium fluoborate (about 9·5%), d 2·617, isomorphous with the potassium fluoborate examined by Brugnatelli (Rend. R. Accad. Lincei, 1894, [v], **3**, i, 339). T. H. Pope.

Age of radium-bearing rocks in Australia. L. A. Cotton (Amer. J. Sci., 1926, [v], **12**, 41—46).—Ages are calculated from the (U+Th)/Pb ratios shown by eight published analyses, the formula used being $T=[Pb/(U+0{\cdot}384Th)]\times 8\times 10^9$ years. They range from 620 million years for fergusonite to 1475 million years for mackintoshite. Less certain values are 240 for the secondary carnotite and 3840 for the altered pilbarite. The geological ages are early to late pre-Cambrian. L. J. Spencer.

Ajkaite [an organic mineral from Hungary]. L. Zechmeister and V. Vrabély (Ber., 1926, **59**, [*B*], 1426—1428).—Ajkaite, d^{20} 1·05—1·06, n_D^{18} 1·5412, $[\alpha]_D^{15}$ +2° to +3° in chloroform, acid value 0, saponification and ester value about 160, is found in amorphous, pale yellow to reddish-brown pieces in the upper limestone. It appears to be a particular variety of fossil resin with characteristic sulphur content (1·5%); it is certainly not identical with amber. H. Wren.

Organic Chemistry.

Geometrical principles of stereochemistry. I. K. Weissenberg (Ber., 1926, **59**, [B], 1526—1542).—Theoretical. The tetrahedral conception of the structure of methane derivatives in certain crystalline compounds is not compatible with the results of X-ray analysis. Since it is highly improbable that special conceptions are applicable solely to the crystalline state, an attempt is made to develop a uniform theory of stereochemical behaviour of substances applicable to all physical states. The original communication must be consulted for details. H. Wren.

Stereochemistry of molecular structure. A. Reis (Ber., 1926, **59**, [*B*], 1543—1553).—Theoretical. The following topics are considered: dependence of molecular structure on state of aggregation (maintenance of the chemical individual during crystallisation; polymorphism and isomorphism); deduction of structural formula from crystalline structure; symmetry of the molecule as basis of structure of the molecule (configuration round a C·C linking; the C·C linking in the tartaric acid group; various instances of C·C linkings; polymerisation and formation of racemates). H. Wren.

Relationship between molecular and crystal structure. A. Reis (Ber., 1926, **59**, [*B*], 1553—1558).—A theoretical discussion of molecule lattices with lower or higher symmetry and of radical lattices. H. Wren.

***n*-Δ$^\alpha$-Olefines.** M. A. Kinmann (Bull. Soc. chim., 1926, [iv], **39**, 988—991).—When allyl bromide reacts with magnesium alkyl bromides, good yields (94%) of *n*-Δ$^\alpha$-olefines are obtained. The following have been obtained pure by this method: *n*-Δ$^\alpha$-pentene, b. p. 30·5—31°/767 mm., d^{21} 0·641, n^{21} 1·3714 [dibromide, b. p. 184° (corr.), d^{18} 1·668, n^{21} 1·5088]; *n*-Δ$^\alpha$-hexene, b. p. 62°, d^{18} 0·684 (dibromide, b. p. 82—83°/11 mm., d^{19} 1·592, n^{19} 1·5012); *n*-Δ$^\alpha$-heptene, b. p. 92—93°, d^{19} 0·700, n^{19} 1·4000 (dibromide, b. p. 98—99°/12 mm., d^{19} 1·509, n^{19} 1·5020); *n*-Δ$^\alpha$-octene, b. p. 121—122°, d^{19} 0·716, n^{19} 1·4085 (dibromide, b. p. 116—118°/14 mm., d^{19} 1·453, n^{19} 1·4961). R. W. West.

Catalytic hydrogenation of conjugated double linkings. G. Vavon and Jakes (Compt. rend., 1926, **183**, 299—301).—Since catalytic hydrogenation of compounds containing a conjugated system of double linkings is less easy than that of compounds

containing unconjugated unsaturated linkings, unlike nascent hydrogen reductions, and since the products obtained by the two methods of reduction are different, it is suggested that molecular hydrogen is the reactant in the former case and atomic hydrogen in the latter. Styrene is reduced by hydrogen in the presence of platinum-black in preference to cinnamic acid and styryl methyl ketone. *cyclo*Hexene is hydrogenated before Δ^1-tetrahydrobenzoic acid. Propenylacetic acid hydrogenates as readily as allylacetic acid, dimethylacrylic acid less readily. Attempts to hydrogenate $\Delta^{1:3}$-dihydroterephthalic acid, cinnamylidenemalonic acid, and cinnamylidenecamphor in the $\alpha\delta$-position catalytically were unsuccessful.

L. F. HEWITT.

Allene hydrocarbons. M. BOUIS (Compt. rend., 1926, **183**, 133—136; cf. this vol., 495).—By reactions similar to those in the synthesis of $\Delta^{\alpha\beta}$-pentadiene its two homologues have been prepared: $\Delta^{\alpha\beta}$-*hexadiene*, b. p. 78—79°, d^{17} 0·7198, n_D^{17} 1·4298, and $\Delta^{\alpha\beta}$-*heptadiene*, b. p. 105—106°, d^{18} 0·7306, n_D^{18} 1·4322. The α-bromo-Δ^{β}-olefines and substituted allenes show optical exaltations of the order 0·8 and 0·5 unit, respectively.

G. M. BENNETT.

Isomeric bromobutylenes. II. M. LÉPINGLE (Bull. Soc. chim., 1926, [iv], **39**, 864—873).—The mixture obtained by treating Δ^{α}-buten-γ-ol with hydrogen bromide contains β-bromo-Δ^{γ}-butylene in addition to the isomeric α-bromo-Δ^{β}-butylenes (Baudrenghien, A., 1922, i, 710), since when it is heated with excess of ethyl alcohol the three corresponding ethyl ethers are formed. Other compounds, such as allyl bromide and *tert.*-butyl bromide, which contain mobile bromine atoms, also yield ethers under these conditions. β-*Ethoxy*-Δ^{γ}-*butylene*, b. p. 76·6°/760 mm., d_4^{15} 0·7760, $n_D^{17\cdot4}$ 1·3908 (*dibromide*, b. p. 95°/17 mm., d_4^{15} 1·648, $n_D^{19\cdot9}$ 1·4982); cis-α-*ethoxy*-Δ^{β}-*butylene*, b. p. 100·2—100·3°/760 mm., d_4^{15} 0·7951, $n_D^{19\cdot0}$ 1·4050 (*dibromide*, b. p. 95·3°/15·5 mm., d_4^{15} 1·6153, $n_D^{18\cdot7}$ 1·4959), and trans-α-*ethoxy*-Δ^{β}-*butylene*, b. p. 100·4—100·5°/760 mm., d_4^{15} 0·7879, $n_D^{20\cdot3}$ 1·4040, are described.

H. E. F. NOTTON.

Detection of hydroxyl groups of different types. Application to lignin. K. FREUDENBERG and H. HESS (Annalen, 1926, **448**, 121—133).—By the reaction of their toluenesulphonates with ammonia, amines, or hydrazine, a distinction may be made between primary alcohols (A), secondary alcohols (B), and phenols (C): (A) $R{\cdot}O{\cdot}SO_2Ar+NH_3 \longrightarrow R{\cdot}NH_2+Ar{\cdot}SO_3H$, (B) $\cdot CH_2{\cdot}CHR{\cdot}O{\cdot}SO_2Ar+NH_3 \longrightarrow \cdot CH{:}CHR+Ar{\cdot}SO_3H,NH_3$, (C) $Ar'{\cdot}O{\cdot}SO_2Ar+NH_3 \longrightarrow Ar'{\cdot}OH+Ar{\cdot}SO_2NH_2$. The phenol esters react with hydrazine to give phenols, nitrogen, and toluenesulphinic acid. Application of the method to lignin obtained from pine-wood by means of hydrochloric and phosphoric acids shows that of the 16 atoms of oxygen in a mol. wt. of 820, 4 are present in methoxyl groups, rather more than 4 in secondary, aliphatic hydroxyl groups (probably hydroaromatic), less than 1 in phenolic hydroxyl, one half of 1 in a ketonic group, and the remainder (6—7) are of undetermined nature, possibly oxidic or cyclic.

Glycerol di*iso*propylidene ether reacts with *p*-toluenesulphonyl chloride in the presence of pyridine at 20° to form the p-*toluenesulphonate*, m. p. 47°, converted by anhydrous hydrazine at 70—80° into $\beta\gamma$-iso*propylidenedioxypropylhydrazine*, $\begin{matrix}O\text{--}CH_2\\ |\\ CMe_2{\cdot}O\end{matrix}>CH{\cdot}CH_2{\cdot}NH{\cdot}NH_2$ (*phenylcarbimide* derivative, m. p. 163—164°), from which the acetone may be removed by concentrated hydrochloric acid at 0°, giving $\beta\gamma$-*dihydroxypropylhydrazine* (*hydrochloride*, decomp. 92°; *tetrabenzoate*, m. p. 172—173°). The *p*-toluenesulphonate of glycerol di*iso*propylidene ether reacts with alcoholic dimethylamine at 100° to form α-*dimethylamino*-$\beta\gamma$-iso*propylidenedioxypropane*, b. p. 65—66°/14 mm.; the *methiodide*, m. p. 207°, is hydrolysed by 2*N*-sulphuric acid to *trimethyl*-$\beta\gamma$-*dihydroxypropylammonium iodide*, m. p. 133—134°.

Cholesteryl p-*toluenesulphonate*, m. p. 131°, does not give a crystalline product with hydrazine.

Phenyl *p*-toluenesulphonate is unchanged by alcoholic ammonia at 180—190°, but with hydrazine at 130—135° yields phenol and hydrazine *p*-toluenesulphinate, m. p. 118°. The latter salt is also formed when *p*-toluenesulphonhydrazide (but not *p*-toluenesulphonic acid) is boiled with hydrazine. Salicylaldehyde gives a p-*toluenesulphonate*, m. p. 63—64°, which reacts similarly with hydrazine. 2 : 4-*Dinitrophenyl* p-*toluenesulphonate*, m. p. 124° (*pyridinium* compound, m. p. 255°), with hydrazine yields *p*-toluenesulphonhydrazide, m. p. 112°, and the *hydrazine* salt of dinitrophenol, m. p. 175°; with alcoholic ammonia at 100°, toluenesulphonamide and ammonium dinitrophenoxide, or at 180—190°, 2 : 4-dinitroaniline.

Lignin from pine-wood is treated with *p*-toluenesulphonyl chloride, first in the presence of sodium hydroxide, and next in the presence of pyridine. The product, $C_{83}H_{83}O_{26}NS_5$, contains a maximum of 9·4% S, and corresponds with the entry of 5 toluenesulphonyl groups and one pyridine molecule into a lignin molecule, $C_{43}H_{48}O_{16}$. Treatment with hydrazine results in the removal of all the sulphur as toluene-sulphonic and -sulphinic acids (ratio 1 : 4·6), and 1·5% N after treatment of free lignin with hydrazine. When toluenesulphonyl-lignin is heated with alcoholic ammonia at 130°, the product contains 4·7% and 3·7% N.

The methylation of lignin with diazomethane raises the methoxyl content from 15·5% to 20·5%, corresponding with the entry of 1·5 methylene groups into a lignin of mol. wt. of 820.

C. HOLLINS.

Catalytically preparing methanol or higher alcohols or other oxygenated organic compounds. L. CASALE.—See B., 1926, 692.

Manufacture of aluminium ethoxide. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1926, 691.

Preparation of acetylenic alcohols from mixed dimagnesium derivatives of acetylene. R. LESPIEAU (Bull. Soc. chim., 1926, [iv], **39**, 991—994; cf. this vol., 500).—The dimagnesium derivative, BrMgC:CMgBr, reacts with either 1 or 2 mols. of aldehyde (or ketone) to give the unsaturated alcohol, $CH{:}C{\cdot}CRR'{\cdot}OH$, or glycol. It is thought that alcohol formation is due to the reactivity of only one of the

magnesium halide groups, but alternative explanations are discussed. By this reaction α-bromoacraldehyde yields the *alcohol* $CH{:}C{\cdot}CH(OH){\cdot}CBr{:}CH_2$, b. p. 78—79°/17 mm., d^{18} 1·501, n_D^{18} 1·5135, and benzaldehyde yields the *alcohol* $CH{:}C{\cdot}CHPh{\cdot}OH$, b. p. 114—115°/18 mm., $d^{18\cdot5}$ 1·053, $n_D^{18\cdot5}$ 1·548. The yields are poor, varying from 25% using acetone to 10% in other cases. R. W. West.

New erythritol. C. Prévost (Compt. rend., 1926, **183**, 134—136).—Solid potassium hydroxide acts on the dibromide of the *trans*-penteneglycol previously described (this vol., 818), yielding *αβγδ-dioxidopentane*, b. p. 146—147°, d_4^{17} 1·08125, n_D^{17} 1·4382, which is converted by prolonged boiling with water into *αβγδ-tetrahydroxypentane*, m. p. 110°, of sweet taste. G. M. Bennett.

Synthesis and hydrolysis of a glycerolmonophosphoric diester: constitution of orthophosphoric acid. O. Bailly and J. Gaumé (Compt. rend., 1926, **183**, 67—69).—*Sodium αβ-diglycerolmonophosphate*, $CH_2(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO(ONa){\cdot}O{\cdot}CH(CH_2{\cdot}OH)_2$, is produced in poor yield from glycerol α-monochlorohydrin and sodium β-glycerolphosphate in aqueous solution, but in good yield by using epichlorohydrin, a molecule of water being added to the resulting glycido-compound. In solution, it gives no precipitate with any of the metals. On ignition, it gives sodium metaphosphate. Hydrolysis with 1 mol. of sodium hydroxide at 100° yields equal proportions of α- and β-glycerolphosphoric acids. This is held to prove the equivalence of two of the acidic hydrogen atoms of orthophosphoric acid. G. M. Bennett.

Diethylorthophosphoryl chloride. J. Walczyńska (Rocz. Chem., 1926, **6**, 110—119).—The reaction between phosphoryl chloride and 2 g.-mols. of ethyl alcohol yields as the chief product diethylorthophosphoryl chloride, b. p. 93 —94°/10 mm., d_4^{19} 1·205, together with diethyl metaphosphate, ethylorthophosphoryl dichloride, d_4^{19} 1·353, diethyl orthophosphate, and ethyl chloride as by-products. R. Truszkowski.

Formation of ethyl mercaptan from ethyl iodide in aqueous hydrogen sulphide solutions and its bearing on the mechanism of the precipitation of metals by hydrogen sulphide. F. E. Brown and J. E. Snyder (J. Amer. Chem. Soc., 1926, **48**, 1926—1928).—Contrary to the observations of Smith and Semon (A., 1924, ii, 762), ethyl mercaptan is formed by the action of ethyl iodide on hydrogen sulphide in the absence of precipitated sulphides and even in acid solution. The rate of formation, however, decreases as the acidity of the solution increases and is greatly accelerated by the presence of freshly-precipitated metallic sulphides or of adsorbing agents such as bone-black, aluminium hydroxide, gelatin, potato starch, barium sulphate. R. Brightman.

Catalytic fission and oxidation of formic acid. C. Paal and W. Poethke [with A. Pross] (Ber., 1926, **59**, [*B*], 1511—1526).—Small amounts of palladium deposited on barium sulphate cause the decomposition into hydrogen and carbon dioxide of aqueous solutions of formic acid or sodium formate or mixtures of these substances. In alkaline solution, sodium formate is stable in the presence of the catalyst in an atmosphere of nitrogen. In aqueous solution in presence of the catalyst, sodium formate is oxidised by free oxygen more rapidly than formic acid, whereas in absence of oxygen the catalytic fission of the acid is more rapid than that of the salt. The hypothesis that fission precedes oxidation appears therefore untenable. Calcium formate in aqueous solution in the presence of very small amounts of palladium is decomposed quantitatively into calcium carbonate, carbon dioxide, and water. H. Wren.

Pyrogenic decomposition of formic acid. J. A. Muller and (Mlle.) E. Peytral (Bull. Soc. chim., 1926, [iv], **39**, 995—1000).—The decomposition of formic acid at high temperatures (cf. A., 1921, i, 156) is represented by the systems: $H{\cdot}CO_2H=CO_2+H_2$ and $CO_2+H_2 \rightleftharpoons CO+H_2O$. For the second system $K=1$, and as equilibrium is reached in about 0·01 sec., the gaseous system consists of an equimolecular mixture of carbon dioxide, hydrogen, carbon monoxide, and water. R. W. West.

Organic chromium salts. E. Ageno-Valla and B. Raposio (Boll. Uff. Staz. Sperim. Ind. Pelli, 1926, **4**, 75—82).—The preparation of various chromium formates is described, those of definite compositions being: *normal chromic formate*, $Cr(CO_2H)_3$; $Cr_3(OH)_4(CO_2H)_5,15H_2O$; $Cr_3(OH)_4(CO_2H)_5,7{\cdot}5H_2O$; $Cr(OH)_2CO_2H,6H_2O$. The normal formate and, to a greater extent, the basic formates exhibit tanning properties. Treatment of chromic hydroxide with lactic acid does not yield definite salts. T. H. Pope.

Preparation of ethylidene diacetate. Soc. Chim. Usines du Rhône.—See B., 1926, 692.

Catalytic decomposition of simple glycerides. F. L. Simons (J. Amer. Chem. Soc., 1926, **48**, 1991—1994).—Triacetin on catalytic decomposition over thorium oxide at 460—525° yields acetic acid, oxides of carbon, hydrocarbons, tarry (acraldehyde) products, hydrogen, and formic acid. At 460°, about 24% of diacetin is formed, whilst at 525° its presence is doubtful, and less acraldehyde is produced. *Tripropionin*, b. p. 130—132°/3 mm., d_{18}^{20} 1·100, n_D^{15} 1·434, behaves similarly, the lower homologue of the glyceride acid being again produced, but no dipropionin was detected at either 420° or 510°. R. Brightman.

Resolution of α-iodopropionic acid into its optically active components. E. Hannerz (Ber., 1926, **59**, [*B*], 1367—1377).—*r*-α-Iodopropionic acid, m. p. 45—45·5°, is prepared by the action of potassium iodide on α-bromopropionic acid in aqueous solution and purification of the product through the *ammonium* salt. In chloroform solution, it is photochemically decomposed with separation of iodine without production of dimethylsuccinic acid. The *sodium*, *potassium*, and *α-naphthylammonium* salts, r-*α-iodopropionamide*, m. p. 156—157° after softening at 153°, and r-*α-iodopropionanilide*, m. p. 131—132°, are described. Partial resolution of the *r*-acid is effected with brucine, cinchonine, or quinine, but complete resolution is preferably accomplished with

the active α-phenylethylamines; l-α-*phenylethylammonium* d-α-*iodopropionate* and d-α-*phenylethylammonium* d-α-*iodopropionate* are described in detail. d-α-*Iodopropionic acid* has d_4^{18} 2·073, $[\alpha]_D^{17·5}$ +41·97° (±0·12°) in substance, +50·73° (±0·3°) in ether; the *ammonium* salt, $[\alpha]_D$ +13·7° (±0·13°) in water, and the *amide*, m. p. (indef.) 155·5—157° (decomp.), are described. l-α-*Iodopropionic acid* has $[\alpha]_D^{17·5}$ −41·34° (±0·12°), $[\alpha]_D^{17·5}$ −49·87° (±0·5°) in ether. The *sodium*, *potassium*, *copper*, *lead*, and *ammonium* ($[\alpha]_D$ +13·8°, ±0·14° in water) salts, and l-α-*iodopropionanilide*, m. p. (indef.) 134—136°, $[\alpha]_D$ −143° (±1°) in alcohol, are described. *l*-α-Iodopropionic acid is slowly racemised in aqueous solution owing to hydrolytically liberated hydrogen iodide; racemisation is markedly accelerated by iodine ions. The activity of the lactic acids formed by hydrolysis of the active α-iodopropionic acids in alkaline solution is of the same sign as that of the halogenated acids.

H. WREN.

Manufacture of butyric acid. D. A. LEGG and C. W. HANCOCK.—See B., 1926, 608.

Constitution of the unsaturated acid $C_{14}H_{26}O_2$ from sperm oil. M. TSUJIMOTO.—See B., 1926, 636.

Chemistry of drying oils. III. G. W. ELLIS.—See B., 1926, 678.

Acidimetric titration and composition of commercial lactic acid. R. EDER and F. KUTTER.—See B., 1926, 690.

Relationship between the optical rotatory powers and the relative configurations of optically active compounds. III. G. W. CLOUGH (J.C.S., 1926, 1674—1676).—The rational coefficients of optical rotatory dispersive power of methyl *d*-lactate, *d*-alanine, methyl *l*-malate, *l*-aspartic acid, and *l*-asparagine have been determined for the wavelengths Na 5893 and Hg 5461, and the mean value 0·844 (calculated from the rational zero −2·5°) is found. Similarly, for *d*-chlorosuccinic acid, *d*-bromosuccinic acid, and *d*-α-bromo-β-phenylpropionic acid, the mean value of the rational coefficients is 0·840. It is therefore concluded that the relative configurations of these dextrorotatory α-halogeno-acids are similar to those of the "*l*" series of α-amino- and α-hydroxy-acids.

C. J. STILL.

Configurational relationship between β-hydroxybutyric acid and propylene glycol. P. A. LEVENE and A. WALTI (J. Biol. Chem., 1926, **68**, 415—424).—The previous conclusions of Levene and Haller (A., 1925, i, 1375) and of Karrer and Klarer (*ibid.*, 1036) have been confirmed by the conversion of *l*-propylene glycol, through the bromo- and cyano-hydrin, into *l*-β-hydroxybutyric acid; the opposite conclusion of Abderhalden and Eichwald (A., 1919, i, 2) was probably due to the occurrence of Walden inversion in the conversion of propylene oxide into the bromohydrin.

l-Propylene glycol, $[\alpha]_D^{20}$ −14·57°, with hydrogen bromide gave l-α-*bromo*-β-*hydroxypropane*, $[\alpha]_D^{20}$ −2·87°; for characterisation this was oxidised, giving bromoacetone, which, in turn, was converted into the acetol (p-*nitrophenylhydrazone*, m. p. 173°; p-*nitrophenylosazone*, m. p. 291°). The bromo-compound, with potassium cyanide, gave l-α-*cyano*-β-*hydroxypropane*, b. p. 99—100°/12 mm., $[\alpha]_D^{20}$ −10·08° in water, and this, on hydrolysis, yielded l-β-*hydroxybutyric acid*, $[\alpha]_D^{20}$ −11·12° in water. *l*-α-Amino-β-hydroxypropane, prepared from *d*-propylene oxide, gave, with nitrous acid, *l*-propylene glycol, $[\alpha]_D^{20}$ −9·8° in water; with phenylcarbimide this gave d-αβ-*diphenylcarbamidopropane*, m. p. 143—144°, $[\alpha]_D^{20}$ +9·5° in alcohol.

C. R. HARINGTON.

Stereochemical studies. XIII. β-Chlorosuccinamic acids. B. HOLMBERG (Ber., 1926, **59**, [*B*], 1569—1581).—Addition of sodium nitrite to a solution of asparagine, sodium chloride, and hydrochloric acid leads to the production of d(−)-β-*chlorosuccinamic acid*, m. p. 129—130° (decomp.), $[\alpha]_D$ −56·1° and −28·9° in alcohol and water, respectively (*sodium* salt, $[\alpha]_D$ −31·9° in water; *barium* salt), which decomposes quantitatively at its m. p. into maleic anhydride and ammonium chloride. l(+)-β-*Chlorosuccinamic acid*, m. p. 126—128° (decomp.), $[\alpha]_D$ +52·1° in alcohol, is obtained in approximate optical homogeneity from *d*(−)-β-bromosuccinamic acid and sodium chloride in aqueous solution under definite conditions. dl-β-*Chlorosuccinamic acid*, prepared from its components, has m. p. 127—128° (decomp.). *d*(−)-β-Chlorosuccinamic acid is quantitatively hydrolysed in alkaline solution to fumaric acid, which is also obtained by the action of silver oxide and water on the sodium salt, but not on the silver salt. In acid solution, hydrolysis of the amido-group occurs so rapidly that isolation of the primary malamic acid is impossible, the successive products being somewhat racemised *d*(−)-chlorosuccinic acid and *l*(−)-malic acid. In originally neutral solution, the course of the reaction is β-chloro-acid → β-malamic acid → malic acid; since malic acid is little racemised, it is very probable that the primary change is accompanied by an inversion. If the elimination of halogen is facilitated by the presence of silver ions either by use of an excess of silver oxide or of the oxide in amount corresponding with the halogen or dissociable hydrogen, *l*(−)-malamic acid is obtained in almost 100% yield. The silver ion in this and analogous cases appears to facilitate the formation of an ion with positively charged carbon to such a degree that it determines the course of the change; this effect is probably due to the low halogen-ion concentration owing to the insolubility of the silver halide. The first phase of the change is therefore formulated: $\overset{-}{O}OC\cdot CHR\cdot X \rightleftharpoons \overset{-}{O}OC\cdot \overset{+}{C}HR + X'$ and $\overset{+}{Ag} + \overset{-}{X} \rightleftharpoons AgX$ (dissolved); AgX (dissolved) ⇌ AgX (solid). If the primary "intermediate ion" unites directly with the hydroxyl ion, a hydroxy-acid results which is configuratively similar to the halogen acid. In acid solution, in which the hydroxyl-ion concentration is necessarily low, the reaction, $\overset{-}{O}OC\cdot \overset{+}{C}HR + H_2O = \overset{-}{O}OC\cdot CH(OH)\cdot R + \overset{+}{H}$, occurs, and since the reaction distance of a cation is necessarily extremely small, an inversion is to be expected. A third possibility consists in the conversion without inversion

of the intermediate ion into the α-lactone followed by hydration of the latter to the hydroxy-acid with consequent inversion. These views are supported by the conversion of *d*(−)-bromosuccinamic acid by silver chloride in neutral solution into *d*(−)-chlorosuccinamic acid, whereas in neutral solution lævorotatory chlorosuccinic acid is produced.

H. WREN.

Isomerism of the dihydroxystearic acids produced by oxidation of acids of the oleic and elaidic series. T. P. HILDITCH (J.C.S., 1926, 1828—1836).—Oxidation with concentrated hydrogen peroxide in acetic acid or acetone solution converts oleic acid into ικ-dihydroxystearic acid, m. p. 95°, and elaidic acid into the corresponding acid, m. p. 132°; under the same conditions of oxidation, methyl oleate and elaidate give, respectively, esters of m. p. 71° and 105°, which are hydrolysed to the dihydroxystearic acid having m. p. 95° and 132°, respectively (cf. Albitzky, A., 1899, i, 862; 1903, i, 227, 228). That the dihydroxystearic acid of higher m. p. is produced from oleic acid only under alkaline conditions of oxidation (cf. Saytzer, A., 1885, 1049; 1886, 140) is confirmed by its formation by oxidation of oleic acid with hydrogen peroxide in alkaline solution. It is suggested that an intramolecular rearrangement of the Walden inversion type takes place in an alkaline medium at the moment of transformation of the ethylenic linking.

C. J. STILL.

Preparation by azeotropy of mono-esters of saturated, acyclic, dibasic acids. C. CONTZEN-CROWET (Bull. Soc. chim. Belg., 1926, **35**, 165—198).—Wuyts' method of esterification (A., 1924, i, 710) is applied to hydrogen esters of dibasic acids; the water formed is removed in a binary (alcohol–water) or ternary (alcohol–water–carbon tetrachloride) mixture, occasional catalysis by sulphuric acid being necessary. Rise of temperature produces marked increase in yield. The following new esters are described: *propyl* (b. p. 118·5°/3 mm.), n-*butyl* (b. p. 132°/3 mm.), n-*amyl* (decomp. on distillation) *hydrogen malonate*; *propyl* (m. p. 15°, b. p. 126°/3 mm.), n-*butyl* (m. p. 8·5°, b. p. 136·5°/3 mm.), n-*amyl* (m. p. 17·2°, b. p. 147°/3 mm.) *hydrogen succinate*; *propyl* (b. p. 146°/4 mm.) and n-*butyl* (b. p. 155·5°/4 mm.) *hydrogen adipate*. These and the ethyl hydrogen esters of the same acids have higher b. p., density, refractive index, and viscosity than the corresponding dialkyl esters, and their stability increases with rise in mol. wt. of the acid. The mechanism of the reactions is discussed. Old and new characteristic data of the dialkyl esters are listed; the present observations necessitate little revision. n-*Dibutyl* (b. p. 274·5°, 108°/4 mm.) and n-*diamyl* (m. p. −9°, b. p. 171·5°/16 mm.) *succinate*, *dipropyl* (m. p. −20°, b. p. 155°/16 mm.) and n-*dibutyl* (m. p. −37·5°, b. p. 145°/4 mm.) *adipate* are described.

J. M. GULLAND.

Active methylsuccinic acid from active β-methyladipic acid. J. VON BRAUN and F. JOSTES (Ber., 1926, **59**, [*B*], 1444—1447).—*d*(+)-β-Methyl-αδ-dibromobutane is converted by potassium acetate and glacial acetic acid into the corresponding *diacetate*, b. p. 110°/12 mm., d_4^{22} 1·027, $[\alpha]_D^{22}$ +0·96°, and thence into the *glycol*, b. p. 123°/13 mm., d_4^{22} 0·9929, $[\alpha]_D^{22}$ +11·73°. Oxidation of the latter substance by cold dilute aqueous permanganate affords *d*(+)-methylsuccinic acid, m. p. 112°, $[\alpha]_D^{17}$ +9·79° in water. Since *d*(+)-β-methyl-αδ-dibromobutane corresponds configuratively with *d*(+)-β-methyladipic acid (this vol., 825), the latter substance and *d*(+)-methylsuccinic acid must also have the same configuration.

H. WREN.

Condensation of malonic esters with acetoacetic esters. I. H. GAULT and L. KLEES (Bull. Soc. chim., 1926, [iv], **39**, 883—905).—Ethyl α-bromoacetoacetate and ethyl sodiomalonate in alcohol or ether produce ethyl ethanetetracarboxylate, ethyl succinosuccinate, and an oily product, b. p. 190—240°. When ethyl α-chloroacetoacetate reacts with ethyl sodiomalonate in alcohol, it is partly converted into ethyl chloroacetate, which then gives ethyl ethane-ααβ-tricarboxylate and ethyl propane-αββγ-tetracarboxylate. In addition, ethyl propane-ααβγγ-pentacarboxylate is formed from ethyl dichloroacetoacetate present as an impurity. It is found that ethyl acetoacetate itself is alcoholysed in a similar way by ethyl sodioacetoacetate and other sodio-derivatives. In toluene solution, however, ethyl chloroacetoacetate and ethyl sodiomalonate react normally. The fraction of the product, b. p. 160—200°/15 mm., contains *ethyl γ-hydroxy-Δ$^{\beta}$-butene-ααβ-tricarboxylate*, which is converted into the ketonic form by the action of bromine. It is hydrolysed by hydrochloric acid to lævulic acid. By this means a new synthesis of α- and αβ-alkyl derivatives of lævulic acid is afforded.

H. E. F. NOTTON.

Condensation of malonic esters with acetoacetic esters. II. H. GAULT and L. KLEES (Bull. Soc. chim., 1926, [iv], **39**, 1000—1019).—Ethyl sodioacetoacetate reacts with ethyl bromomalonate, b. p. 224—225°, 119—121°/11 mm., yielding mainly a mixture of ethyl malonate and an *ethyl diacetylpropanetetracarboxylate*, b. p. 224—229°/8 mm. Similar experiments using bromo-esters of methyl- and ethyl-malonic acids yielded no definite results. Ethyl sodioacetoacetate reacts with ethyl chloromalonate, yielding ethyl α-acetylethane-αββ-tricarboxylate, m. p. 34° (*semicarbazone*, m. p. 106°; *phenylhydrazone*, m. p. 89°). The constitutions of the ketonic and enolic forms of this ester are established by the agreement between the calculated and observed values for their molecular refractions. The enolic is completely converted into the ketonic form by the action of bromine or hydrogen bromide and partly by the action of solutions of metallic salts. The reverse change is brought about in toluene solution by the action of sodium and subsequent neutralisation with sulphuric acid. Experiments using alkyl derivatives of either ethyl sodioacetoacetate or ethyl chloromalonate yielded abnormal and indefinite results.

R. W. WEST.

Correlation of additive reactions with tautomeric change. V. Structural conditions affecting mobility and equilibrium in additive reactions. K. E. COOPER, C. K. INGOLD, and E. H. INGOLD (J.C.S., 1926, 1868—1872).—A summary

of previous work on the additive reactions related to tautomeric change. An explanation, based on the electronic theory, is suggested. C. J. STILL.

Mechanism of tautomeric interchange and effect of structure on mobility and equilibrium. I. Three-carbon system. C. K. INGOLD, C. W. SHOPPEE, and J. F. THORPE (J.C.S., 1926, 1477—1488).—The action of ethyl sodiomalonate on ethyl citraconate has been studied under various conditions (cf. Hope, *ibid.*, 1912, **101**, 894), and the following products have been isolated: ethyl malonate, itaconate, mesaconate, *n*-butane-$\alpha\alpha\beta\gamma$-tetracarboxylate, *n*-butane-$\alpha\beta\delta\delta$-tetracarboxylate, and *cyclo*pentan-3-one-1 : 2 : 4-tricarboxylate, also *ethyl* cyclo*pentanone*-2 : 4(or 2 : 3)-*dicarboxylate*, b. p. 150°/10 mm., 160°/18 mm., *ethyl* cyclo*pentanone*-3-*carboxylate*, b. p. 109—111°/10 mm. (*semicarbazone*, m. p. 153·5°), and *ethyl* 2 : 4(or 2 : 3)-*dicarboxy*-cyclo*pentenylmalonate*, b. p. 240—245°/16 mm., n_D^{21} 1·46719, *d* 1·1327. Similarly, both ethyl *n*-butane-$\alpha\alpha\beta\gamma$-tetracarboxylate and *n*-butane-$\alpha\beta\delta\delta$-tetracarboxylate may be prepared from ethyl itaconate, whence it is concluded that citraconic and itaconic esters are tautomeric in the presence of sodium ethoxide. There is no evidence that an ethoxy-ester intervenes in the conversion of citraconic ester into itaconic ester, and the ethoxy-derivative prepared from citraconic ester (Hope, *loc. cit.*), or itaconic ester, is regarded as *ethyl* ω-*ethoxymethylsuccinate*, b. p. 137—140°/23 mm. (ω-*ethoxymethylsuccinamide*, m. p. 149—150°), since the corresponding ethoxy-acid is converted by hydriodic and hydrobromic acids, respectively, into α-iodopropane-$\beta\gamma$-dicarboxylic acid and α-bromopropane-$\beta\gamma$-dicarboxylic acid, which with silver oxide yield paraconic acid. The mobile hydrogen atom in three-carbon tautomerides is assumed to be in a state of incipient ionisation, and the conditions under which the isomeric change occurs to be dependent on the extent of this. The mechanism of activation in tautomeric change is discussed, and the effect of the terminal groups on the mobility of the three-carbon system is correlated with directive action in benzene substitution. F. H. HAMER.

Oxalato-bismuthotartrates. R. PORTILLO (Anal. Fís. Quím., 1926, **24**, 244—250).—Solution of bismuthoditartaric acid, $H[Bi(C_6H_4O_6)_2,3H_2O$, in hot saturated aqueous solutions of alkali oxalates yields crystalline compounds for which the general formula $[Bi(C_6H_4O_6)\frac{1}{2}(C_2O_4)]R,xH_2O$ is suggested, where R= K ($+4H_2O$), Na ($+4H_2O$), or NH_4 ($+3H_2O$).
G. W. ROBINSON.

Polyglycuronic acids. I. E. SCHMIDT and F. VOCKE (Ber., 1926, **59**, [*B*], 1585—1588).—In confirmation of the view that union between cellulose and hemicelluloses in plants is due to polymeric anhydroglycuronic acids the extraction of the latter in quantity from *Fucus serratus* is described in detail. The mixture of polyglycuronic acids-*a* and -*b* has $[\alpha]_D$ −140·4° in 0·2*N*-potassium hydroxide solution. From this mixture, *polyglycuronic acid*-a, $[\alpha]_D$ −147·8° in 0·2*N*-potassium hydroxide solution, is isolated by treatment with sulphuric acid, which hydrolyses polyglycuronic acid-*b* to glycuronic acid, identified as the cinchonine salt, m. p. 204°. H. WREN.

Stereochemical studies. XII. Carbothionlactic acids. B. HOLMBERG (Ber., 1926, **59**, [*B*], 1558—1569).—*dl*-Ethylcarbothiolonlactic acid, $EtS{\cdot}CS{\cdot}O{\cdot}CHMe{\cdot}CO_2H$, m. p. 72—73°, is resolved into its optically active components by treatment with the active phenylethylamines in aqueous solution; d(−)-*ethylcarbothiolonlactic acid*, m. p. 36—37° or 60—62°, $[\alpha]_D$ −9·7°, −12·7°, and −8·2° in ethyl alcohol, acetone, and ethyl acetate, respectively, l-*phenylethylammonium* d(−)-*ethylcarbothiolonlactate*, m. p. 132—134° (decomp.), l(+)-*ethylcarbothiolonlactic acid*, m. p. 36—37° or 63—64°, $[\alpha]_D$ +9·80° and +12·6° in ethyl alcohol and acetone, respectively, and d-*phenylethylammonium* l(+)-*ethylcarbothiolonlactate*, m. p. 136—137·5° (decomp.), are described. dl-*Dimethylamidocarbothionlactic acid*, $NMe_2{\cdot}CS{\cdot}O{\cdot}CHMe{\cdot}CO_2H$, m. p. 136—137° (decomp.) [*barium* salt, anhydrous and $+3{\cdot}5H_2O$; *ethyl* ester, b. p. 146—147°/15 mm., d_4^{20} 1·097, n_D^{20} 1·4925], prepared from *dl*-ethylcarbothiolonlactic acid and aqueous dimethylamine, is slowly resolvable by the active phenylethylamines, but the corresponding optically active forms are most readily prepared by starting with highly-active ethylcarbothiolonlactic acids and completing the purification by the active bases. d(−)-*Dimethylamidocarbothionlactic acid*, m. p. 123—124° (decomp.), $[\alpha]_D$ −70·2°, −78·6°, −83·5°, and −10·0° in ethyl alcohol, acetone, ethyl acetate, and water, respectively, d-*phenylethylammonium* d(−)-*dimethylamidocarbothionlactate*, m. p. 158·5—159·5°, $[\alpha]_D$ −26·5° in ethyl alcohol, l(+)-*dimethylamidocarbothionlactic acid*, m. p. 123—124° (decomp.), $[\alpha]_D$ +70·1°, +83·7°, and +10·2° in ethyl alcohol, ethyl acetate, and water, respectively, and l-*phenylethylammonium* l(+)-*dimethylamidocarbothionlactate*, m. p. 158·5—159·5°, $[\alpha]_D$ +26·55° in ethyl alcohol, are described. *d*(−)-Dimethylamidocarbothionlactic acid is also prepared by the successive treatment of *d*(−)-lactic acid with carbon disulphide and ethyl bromide and dimethylamine; the resolution of *dl*-lactic acid by *d*-phenylethylamine in aqueous solution and d-*phenylethylammonium* d(−)-*lactate*, monohydrate and anhydrous, m. p. 87—90°, $[\alpha]_D$ +7·6° in water, are incidentally described. Treatment of ethyl *l*(+)-dimethylamidocarbothionlactate with bromoacetic acid in benzene affords ethyl α-bromopropionate, b. p. 52—53°/11 mm., d_4^{20} 1·390, n_D^{20} 1·446, $[\alpha]_D^{20}$ +25·2°. *d*(−)-Bromopropionic acid is therefore configuratively related to *d*(−)-lactic acid; this relationship has been deduced by Clough (J.C.S., 1918, **113**, 526) from physical measurements, but is not supported by the observations of Kenyon, Phillips, and Turley (A., 1925, i, 507). H. WREN.

Manufacture of acetaldehyde from ethyl alcohol. HOLZVERKOHLUNGS-IND. A.-G.—See B., 1926, 610.

Oxidation of ethyl alcohol to acetaldehyde. E. KRAUSE.—See B., 1926, 609.

Constitution of aldehyde and ketone hydrogen sulphites. F. RASCHIG and W. PRAHL (Annalen, 1926, **448**, 265—312).—A more extended account of work already abstracted (this vol., 598). The following compounds are described: Aminomethanesulphonic acid; *potassium iminomethanesulphonate*,

$HN(CH_2SO_3K)_2$; *potassium hydroxylaminomethanesulphonate*, $(+H_2O)$, m. p. 102° (decomp.), which decomposes into sulphur dioxide, hydroxylamine, and formaldehyde with boiling hydrochloric acid; *potassium hydroxyliminomethanesulphonate*, $HO{\cdot}N(CH_2{\cdot}SO_3K)_2$; *potassium hydrazomethanesulphonate*, $KO_3S{\cdot}CH_2{\cdot}NH{\cdot}NH{\cdot}CH_2{\cdot}SO_3K$, m. p. 220° (decomp.); *potassium hydrogen hydrazomethanesulphonate* $(+H_2O)$; *potassium dimethylhydrazomethane sulphonate*. The following *nitroso*-derivatives are described: $NO{\cdot}N(CH_2{\cdot}SO_3K)_2$,

$KO{\cdot}N(NO){\cdot}CH_2{\cdot}SO_3K,H_2O$,

$SO_3K{\cdot}CH_2{\cdot}N(NO){\cdot}NH{\cdot}CH_2{\cdot}SO_3K,H_2O$, and

$SO_3K{\cdot}CH_2{\cdot}N(NO){\cdot}N(NO){\cdot}CH_2{\cdot}SO_3K$ (unstable).

Potassium azomethanesulphonate, m. p. above 300°, is obtained in low yield by oxidising potassium hydrazomethanesulphonate with iodine in presence of potassium acetate, permanganate, or hydrogen peroxide, and readily by warming aqueous potassium dinitrosohydrazomethanesulphonate. It is decomposed by boiling hydrochloric acid into 2 mols. of sulphurous acid and 1 mol. of hydrazine, formaldehyde, and formic acid. Boiling acetic anhydride converts aminomethanesulphonic acid into the compound $CMe\langle^{N{\cdot}CH_2{\cdot}O}_{O{\cdot}CH_2{\cdot}N}\rangle CMe$, b. p. 214°/8 mm. (also *trihydrate*). Sodium formaldehydethiosulphate, $CH_2(OH){\cdot}S{\cdot}SO_3Na$, is formed together with sulphur and trithioformaldehyde by the action of cold hydrochloric acid on a mixture of formaldehyde solution and sodium thiosulphate below −5°. It is the salt of a strong acid, and is decomposed quantitatively by hydrochloric acid into sulphuric acid and trithioformaldehyde. Potassium hydroxylaminomethanesulphonate reacts with potassium hydrogen sulphite to form *potassium sulphonaminomethanesulphonate*, $KO_3S{\cdot}CH_2{\cdot}NH{\cdot}SO_3K$, which readily loses the *N*-sulphonic group as sulphuric acid with warm hydrochloric acid. Potassium nitrosohydroxylaminomethanesulphonate in a similar manner yields the *trisulphonate*, $SO_3K{\cdot}CH_2{\cdot}N(SO_3K){\cdot}NH{\cdot}CH_2{\cdot}SO_3K,H_2O$ (?), which decomposes into 2 mols. of formaldehyde, 2 mols. of sulphur dioxide, 1 mol. of sulphuric acid, and 1 mol. of hydrazine with boiling hydrochloric acid. J. S. H. Davies.

Relation between configuration and rotation direction of sugars. C. J. de Wolff (Chem. Weekblad, 1926, **23**, 353—355).—In the aldehyde and ketonic sugars, $C_nH_{2n}O_n$, when the hydroxyl group attached to the second asymmetric carbon atom falls on the left of the axis in the Fischer projection of the formula, the sugar is dextrorotatory, and conversely. Of 28 cases examined, only two, lyxose and idose, fail to conform to this rule. S. I. Levy.

Sugars. VII. H. Kiliani (Ber., 1926, **59**, [*B*], 1469—1477; cf. A., 1923, i, 1059).—*d*-Glycuronolactone is conveniently prepared by hydrolysis of mentholglycuronic acid with aqueous-alcoholic hydrochloric acid at 75—80° and removal of the mineral acid by silver carbonate. From the product of the action of hydrocyanic acid on *l*-arabinose, the bulk of the *l*-mannonic acid is separated as the lactone, after which *l*-gluconic acid is isolated as the barium salt; the process is then repeated with the mother-liquor from the latter salt. *l*-ε-Ketogluconic acid (*calcium* salt, $[\alpha]_D$ +14·6° in hydrochloric acid) is obtained in 12% yield by the oxidation of *l*-gluconic acid by 50% nitric acid at 20—25°. Purification of cadmium *d*-galactonate is effected by solution in the requisite amount of hydrochloric acid (1 : 1) and successive addition to the solution of sodium acetate and sodium hydroxide. *d*-Galactonic and gluconic acids are prepared by treatment of lactose with water and a small proportion of bromine at the atmospheric temperature until the colour of the halogen disappears, hydrolysis of the sugar by the hydrobromic acid solution thus formed, treatment of the cooled solution with bromine, and removal of hydrobromic acid by silver carbonate followed by isolation of the acids as their cadmium and calcium salts, respectively. The difference between the *l*-mannosaccharic acids obtained by the action of potassium hydroxide on the dilactone or the diamide remains unexplained; the dilactone itself appears homogeneous, and the acid obtained from the diamide does not appear to be structurally different from that of the lactone. The preparation of *d*-gluconhydrazide, m. p. 143°, can be effected at the atmospheric temperature. H. Wren.

Sugar carbonates. II. Derivatives of arabinose and xylose. W. N. Haworth and W. Maw (J.C.S., 1926, 1751—1754).—By condensation of *l*-arabinose and *l*-xylose with methyl or ethyl chloroformate in presence of aqueous sodium hydroxide or pyridine, several carbonate derivatives are obtained. *Dicarbomethoxy-l-arabinose monocarbonate*, m. p. 137°, $[\alpha]_D$ +39·5°, *tetracarbomethoxy-l-arabinose*, m. p. 123°, $[\alpha]_D$ +126·6°, *tetracarbethoxy-l-arabinose*, b. p. 230°/0·4 mm., $[\alpha]_D$ +98·8°, n_D 1·4475, *tetracarbomethoxy-l-xylose*, b. p. 215°/0·5 mm., $[\alpha]_D$ +59·5°, *tetracarbethoxy-l-xylose*, b. p. 221—222°/0·4 mm., n_D 1·4450, $[\alpha]_D$ +62·1°, and a *substance*, b. p. 219—220°/0·4 mm., $[\alpha]_D$ +89·3°, believed to contain isomeric forms of tetracarbomethoxy-*l*-arabinose, are described. When metallic sodium in anhydrous ether was used as condensing agent, there was obtained a tetracarbomethoxy-*l*-arabinose, m. p. 186°, $[\alpha]_D$ −16·4°. Provisional formulæ are suggested for these compounds. C. J. Still.

Optical enantiomeride of natural rhamnose. E. Votoček and F. Valentin (Compt. rend., 1926, **183**, 62—64; cf. A., 1911, i, 354).—*iso*Rhodeonic acid from *iso*rhodeose is inverted by heating with pyridine to give d-*rhamnonolactone*, $[\alpha]_D^{18}$ −40·9° in 10% aqueous solution (*l*-rhamnonolaetone has $[\alpha]_D$ +39·04°), which furnishes on reduction with sodium amalgam d-*rhamnose*, isolated as the *monohydrate*, $[\alpha]_D^{15\cdot5}$ −8·25° in 10% aqueous solution (p-*bromophenylhydrazone*, m. p. 167°, and p-*bromophenylosazone*, m. p. 222—223°). G. M. Bennett.

Amino-derivatives of sugars. H. von Euler and E. Brunius (Ber., 1926, **59**, [*B*], 1581—1585).—The equilibrium between dextrose, glycine, and the glucoside in solutions of differing acidity has been examined by comparison of the f. p. of mixtures in solution with the sum of those of the singly dissolved components. With increasing alkalinity of the

solution, the equilibrium is greatly displaced towards the glucoside side, until at p_H 11 it appears probable that conversion is almost quantitative. H. WREN.

Structure of fructose, γ-fructose, and sucrose. W. N. HAWORTH and E. L. HIRST (J.C.S., 1926, 1858—1868).—Oxidation of normal tetramethyl-fructose with nitric acid (*d* 1·2) yields a methyl *ester*, $C_{10}H_{18}O_7$, m. p. 119—120°, $[\alpha]_D$ −107° in water, −94° in methyl alcohol, containing one free hydroxyl group which is readily methylated to an *ester*, $C_{11}H_{20}O_7$, m. p. 102—103°, $[\alpha]$ −129° in water, −116° in methyl alcohol. When more concentrated nitric acid is employed for the oxidation, the same ester is produced, and in addition *methyl* meso*dimethoxy-succinate* m. p. 67—68° [corresponding *amide*, m. p. 245—246° (decomp.) after darkening at 220°], and methyl *d*-arabotrimethoxyglutarate; no evidence for the formation of *l*-dimethoxysuccinic acid, as recorded by Irvine and Patterson (J.C.S., 1922, **121**, 2696), could be obtained. It is reasoned that the formation of these compounds indicates an amylene oxide structure for tetramethyl-γ-fructose, and a modified formula for sucrose, embodying this structure, is suggested. C. J. STILL.

Chemical and biochemical degradations of sucrosephosphoric acid. C. NEUBERG, M. BEHRENS, O. DALMER, J. HATANO, L. ROSENFELD, and S. SABETAY (Z. Ver. deut. Zuckerind., 1926, 463—493).—A recapitulation and extension of earlier work (cf. A., 1910, i, 157; 1917, i, 680; 1925, i, 152). *d*-Fructose is now isolated in the hydrolysis of sucrosephosphoric acid (*strychnine* salt, m. p. 185°), which is converted by kidney-phosphatase (cf. Tomita, A., 1922, i, 960) into sucrose and phosphoric acid. J. M. GULLAND.

Constitution of sucrose. I. Oxidation of tetramethyl-γ-fructose. II. Oxidation of *d*-arabinose. G. MCOWAN (J.C.S., 1926, 1737—1746, 1747—1750).—I. Experiments described by Howarth and his collaborators on the methylation of sucrose, the preparation of tetramethyl-γ-fructose, and oxidation of this compound under various conditions have been repeated. No evidence for the formation of trimethoxyvalerolactone and trimethoxyglutaric acid has been obtained. By the oxidation of tetramethyl-γ-fructose (purified by Willstätter's method) with nitric acid, followed by esterification with acid methyl alcohol, a product was obtained the properties of which agree with that of a methyl ketodimethoxybutyrate, $CO_2Me{\cdot}CO{\cdot}CH(OMe){\cdot}CH_2{\cdot}OMe$ or $CO_2Me{\cdot}CH(OMe){\cdot}CO{\cdot}CH_2{\cdot}OMe$. It is argued that the amylene oxide structure for γ-fructose is no longer tenable, and a propylene oxide structure is suggested and incorporated in a new structure for sucrose.

II. The constitution assigned to sucrose by Haworth and Linnell (J.C.S., 1923, **123**, 294) is based, as regards the fructose residue, on the oxidation of tetramethyl-γ-fructose to a dextrorotatory trimethoxyglutaric ester having $[\alpha]_D$ +48·7° in water. Hirst and Robertson (*ibid.*, 1925, **127**, 358), by oxidation of trimethyl-*l*-arabinose, obtained a dextrorotatory dimethyl trimethoxyglutarate having $[\alpha]_D$ +45°. It is pointed out that these contradictory results are opposed to stereochemical considerations as *d*-fructose, corresponds with *d*-arabinose and not with *l*-arabinose.

d-Glucose has now been transformed into *d*-arabinose, and this methylated to trimethyl-α-methyl-arabinoside, which was oxidised and hydrolysed with the formation of *l-dimethyl trimethoxyglutarate*, b. p. 143°/15 mm., n_D^{18} 1·4375, $[\alpha]_D^{16}$ in water −42·5°, which is the enantiomorph of Hirst and Robertson's compound; the corresponding *diamide* has m. p. 232—233°, $[\alpha]_D^{16}$ −49·54° in water. C. J. STILL.

Relations between rotatory power and structure in the sugar group. XV. Conversion of lactose into another disaccharide, neolactose. The chlorohepta-acetate and two octa-acetates of neolactose. A. KUNZ and C. S. HUDSON (J. Amer. Chem. Soc., 1926, **48**, 1978—1984).—When lactose octa-acetate is treated with anhydrous aluminium chloride in chloroform, and the reaction is allowed to proceed until the solid phase is dark grey before treating with ice, the 30% yield of lactose α-chlorohepta-acetate is accompanied by a 20% yield of the α-chlorohepta-acetate of a new dihexose (cf. A., 1925, i, 1043) for which the name *neolactose* is proposed. If the reaction is stopped when the solid phase is cherry-red, the lactose α-chlorohepta-acetate is obtained in 60% yield and only a little neolactose derivative is formed. *Neolactose α-chlorohepta-acetate* has m. p. 182° (decomp.), $[\alpha]_D^{23}$ +71·2° in chloroform; silver acetate in glacial acetic acid, silver carbonate, or sodium acetate in acetic anhydride, or boiling with sodium acetate and acetic anhydride converts it into the *α-octa-acetate*, m. p. 178°, $[\alpha]_D^{24}$ +53·4° in chloroform, whilst silver carbonate in aqueous acetone followed by acetylation with acetic anhydride and sodium acetate affords the isomeric *β-octa-acetate*, m. p. 148°, $[\alpha]_D^{24}$ −7·1° in chloroform. On hydrolysis of the octa-acetates, neolactose is obtained as a dextrorotatory syrup, which could not be crystallised and on acetylation regenerated the acetates. Acid hydrolysis yields a lævorotatory solution, and neolactose is assigned the structure *d*-galactosido-*d*-altrose. R. BRIGHTMAN.

Relations between rotatory power and structure in the sugar group. XVI. Conversion of cellobiose into another disaccharide, celtrobiose, by the aluminium chloride reaction. Chloroacetylceltrobiose. C. S. HUDSON (J. Amer. Chem. Soc., 1926, **48**, 2002—2004).—Cellobiose when treated with aluminium chloride in chloroform (cf. preceding abstract) yields cellobiose α-chloroacetate and about 13% of an isomeric *dihexose chlorohepta-acetate*, $C_{26}H_{35}O_{17}Cl$, m. p. 137—138°, decomp. at 155—165°, $[\alpha]_D^{30}$ +59·2° in chloroform, which on hydrolysis with 0·5*N*-hydrochloric acid at 98° yields a strongly lævorotatory solution. The name *celtrobiose* is proposed for the new dihexose. R. BRIGHTMAN.

Biochemical synthesis, using almond emulsin, of α-ethyl-*l*-arabinoside. M. BRIDEL and C. BÉGUIN (Bull. Soc. Chim. biol., 1926, **8**, 469—480).—See this vol., 501.

Carbohydrates. IV. Synthesis of α-glucosides. P. BRIGL and H. KEPPLER (Ber., 1926, **59**, [*B*], 1588—1591).—α-Chloro-γεζ-triacetyl-β-trichloro-

acetylglucose (cf. Brigl, A., 1923, i, 442), which certainly belongs to the β-series, appears by reason of its greater stability to be a more suitable material than β(formerly α)-acetylchloroglucose (cf. Schlubach, this vol., 600) for the synthesis of α-glucosides. It is converted by silver carbonate in boiling methyl alcoholic solution into a mixture of α-methylglucoside (75%) and β-methylglucoside (25%); in cold solution, the yield of α-methylglucoside sinks to 54%.

H. WREN.

Violutoside, a methyl salicylate glucoside extracted from *Viola cornuta*, L. P. PICARD (Bull. Soc. Chim. biol., 1926, **8**, 568—576).—See this vol., 715.

Transformation of monomethylfructose into derivatives of γ-fructose. C. F. ALLPRESS (J.C.S., 1926, 1720—1722).—The monomethylfructose prepared from α-fructose di*iso*propylidene ether is converted into methyl-γ-methylfructoside, which on complete methylation and subsequent hydrolysis yields tetramethyl-γ-fructose. From this it is deduced that the free methyl group in α-fructose di*iso*propylidene ether occupies the 3-position, and not the 6-position assigned to it by Irvine and Hynd (J.C.S., 1909, **95**, 1220). A crystalline *monomethylmethylfructoside*, m. p. 143°, $[\alpha]_D$ −34·6° (in ethyl alcohol), has been isolated and is believed to possess the normal form.

C. J. STILL.

Hydrolysis of starch by acids. D. R. NANJI and R. G. L. BEAZELEY.—See B., 1926, 685.

Constitution of cellulose. H. PRINGSHEIM, J. LEIBOWITZ, A. SCHREIBER, and E. KASTEN (Annalen, 1926, **449**, 163—178).—By heating cellulose triacetate in naphthalene, the agglomerate molecule is gradually broken down, the mol. wt. becoming 1000—2000 by mild treatment, and finally after 1½ hrs. at 235° in 10 parts of naphthalene a mol. wt. of 288, *i.e.*, corresponding with anhydroglucose triacetate, is reached. Other solvents of high b. p. are also effective. The "de-association" is accompanied by increased solubility in acetone etc. and diminished viscosity of the solutions, but there is no change in optical properties. Hydrolysis of the final product with a small excess of 2—3*N*-alcoholic ammonia removes acetyl groups as acetamide and gives an anhydroglucose to which the name *cellosan* is assigned (cf. Karrer, A., 1922, i, 435). Cellosan is soluble in water, but the solution at temperatures above or below 73—80° is colloidal. Determination of mol. wt. at 73—80° (the temperature of minimum viscosity) by the Barger–Rast method gives 162 ($C_6H_{10}O_5$). Acetolysis by Karrer's method (A., 1923, i, 23) converts cellosan into cellobiose octaacetate, m. p. 223°, whilst fermentation with dialysed malt extract yields dextrose quantitatively. The results indicate that cellulose is an agglomerate of simple cellosan molecules and place Hess' theory of the constitution of cellulose on an experimental foundation. The term "molecular valency" is suggested in place of "subsidiary valency" to connote a type of linking which has no effect on optical activity.

C. HOLLINS.

Soluble cellulose esters of the higher fatty acids. H. GAULT and P. EHRMANN (Bull. Soc. chim., 1926, [iv], **39**, 873—883).—The esters obtained by the action of pyridine and an acid chloride on mercerised or "viscose" cellulose, like those prepared by Grün and Wittka (A., 1922, i, 114) and Karrer (A., 1923, i, 276) from unmodified cellulose, are insoluble in most organic solvents. "Cuprammonium" cellulose, however, affords 30—40% and Girard's hydrocellulose 70—90% of soluble esters. The yield of soluble product varies directly with the degree of degradation of the cellulose and inversely with the mol. wt. of the acid chloride. Prepared from Girard's hydrocellulose, the *monolaurate*, *monopalmitate*, and *monostearate* form amorphous powders, softening at 180—200°, which are gelatinised but not dissolved by solvents. The *dilaurate*, *dipalmitate*, and *distearate*, softening at 85—90°, 100°, and 85—90°, respectively, and the *trilaurate*, *tripalmitate*, and *tristearate*, softening at 90°, 80°, and 75°, are all soluble in organic liquids, especially in the benzenoid hydrocarbons, from which they are deposited as soft films. Similarly, the *laurate* and *palmitate* of cellulose dinitrate and of cellulose diacetate have been prepared. These resemble the foregoing esters in solubility and are chemically very resistant.

H. E. F. NOTTON.

Amidation of cotton. P. KARRER and W. WEHELI.—See B., 1926, 659.

Action of organo-magnesium compounds on aliphatic dialkylamides. M. MONTAGNE (Compt. rend., 1926, **183**, 216—218).—Magnesium ethyl bromide reacts with butyrdiethylamide, giving *γ-diethylamino-γ-ethylhexane*, b. p. 98°/18 mm. (*picrate*, m. p. 97°, *chloroaurate*, m. p. 82°, *chloroplatinate*, m. p. 175°), whilst magnesium methyl iodide gives *β-diethylamino-β-methylpentane*, b. p. 170°/760 mm. (*picrate*, m. p. 124°, *chloroaurate*, m. p. 82°, *chloroplatinate*, m. p. 207°); the *hydrochloride* when heated yields diethylamine hydrochloride and *β-methyl-Δ$^{\beta}$-pentene*. β-Diethylamino-β-methylpentane may be synthesised by the Hoffmann degradation of αα-dimethylvaleramide and diethylation of the base obtained. Magnesium methyl iodide reacts with butyrdimethylamide, giving *β-dimethylamino-β-methylpentane*, b. p. 140—142°/760 mm. (*picrate*, m. p. 214°, *chloroaurate*, m. p. 103°, *chloroplatinate*, decomp. above 230°).

L. F. HEWITT.

Synthesis of *N*-alkylideneamino-acids and their transformation by hydrogenation into *N*-alkylamino-acids. H. SCHEIBLER and H. NEEF (Ber., 1926, **59**, [*B*], 1500—1511).—Addition of potassium cyanide to a well-cooled aqueous solution of sodium formaldehyde-bisulphite and ethyl aminoacetate affords *ethyl cyanomethylaminoacetate*, which, with an alcoholic solution of sodium ethoxide and hydroxide, yields *sodium methyleneaminoacetate*, $CH_2{:}N{\cdot}CH_2{\cdot}CO_2Na$ (corresponding *barium*, *copper*, and *nickel* salts). It is reduced by sodium and alcohol to methylaminoacetic acid, which is also prepared by reducing methyleneaminoacetonitrile and hydrolysis of the product. Similarly, sodium formaldehyde-bisulphite, ethyl α-aminopropionate, and potassium cyanide give *ethyl α-cyanomethylaminopropionate*,

transformed into *sodium α-methyleneaminopropionate* (corresponding *barium* and *copper* salts), which is reduced to α-methylaminopropionic acid (*copper* salt). *Ethyl α-cyanoethylaminoacetate, sodium ethylideneaminoacetate*, and *ethylaminoacetic acid hydrochloride*, m. p. 179·5°, are described. *Ethyl α-cyanomethylamino-β-p-hydroxyphenylpropionate*, from tyrosine ester, sodium formaldehyde-bisulphite, and potassium cyanide, yields *sodium α-methyleneamino-β-p-hydroxyphenylpropionate*, which could only be hydrogenated incompletely. Sodium benzaldehyde-bisulphite and ethyl β-aminobutyrate afford *ethyl βα′-cyanobenzylamino-n-butyrate*, $CHPh(CN)\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2Et$ [*hydrochloride*, m. p. 132—134° (corr.)], which is converted into *sodium β-benzylideneamino-n-butyrate*, which suffers hydrolysis when reduced in alkaline solution. Sodium formaldehyde-bisulphite, ethyl αα′-iminodipropionate, and potassium cyanide yield *ethyl cyanomethyl-αα′-iminodipropionate* (*hydrochloride*, m. p. 256—258° after softening), which is reduced to *αα′-carboxymethyliminodipropionic acid*, m. p. 232° (corr.) (*copper* salt). The product of the action of acetic anhydride on sodium benzylideneaminoacetate [regarded by Scheibler and Baumgarten (A., 1922, i, 655) as *N*-acetyl-*N*-benzylidenebetaine and by Bergmann, Ensslin, and Zervas (A., 1925, i, 890) as 3-acetyl-2-phenyloxazolid-5-one] is converted by anhydrous ammonia into ammonium acetate, aminoacetamide, and benzaldehyde, and by aniline into benzylideneaniline and aceturanilide; it is therefore the mixed *anhydride*, $CHPh{:}N\cdot CH_2\cdot CO\cdot OAc$, of benzylideneaminoacetic and acetic acids. H. Wren.

Activation of hydrogen by iron. S. Toda (Biochem. Z., 1926, **172**, 34—35).—When all the reagents in the reaction of cysteine (by neutralising cysteine hydrochloride with ammonia to about p_H 8) with methylene-blue are carefully freed from iron, the time for decolorisation is very much longer than when ordinary reagents are used. Addition of very small quantities of iron greatly accelerates the reaction. H. I. Coombs.

Transposition of groups. E. E. Blaise and J. Miliotis (Compt. rend., 1926, **183**, 218—220).—Ethoxyurethanes are obtained from ethoxyacetamide by the action of bromine in the presence of sodium derivatives of alcohols by means of a Hoffmann rearrangement. *Methylethoxymethylurethane*, b. p. 97°/16 mm., and *ethylethoxymethylurethane*, b. p. 105°/16 mm., are obtained in 100% and 80% yield, respectively, and when treated with dilute hydrochloric acid give formaldehyde, ethyl alcohol, and methyl or ethyl carbamate. The carbamate formed reacts with formaldehyde, giving methylenediurethanes. L. F. Hewitt.

Methylguanidine picrate. R. Kapeller (Ber., 1926, **59**, [*B*], 1652).—The compound, decomp. 285°, obtained from dicyanodiamide, methylamine hydrochloride, and picric acid (cf. Werner and Bell, J.C.S., 1922, **121**, 1790) is not methylguanidine picrate. H. Wren.

Preparation of aqueous thiocyanic acid. W. Gluud, K. Keller, and W. Klempt (Ber., 1926, **59**, [*B*], 1384—1386).—Water (10 c.c.), ammonium sulphate (40 g.), and concentrated sulphuric acid (30 c.c.) are heated at 60° and 20—30 mm. pressure in a Claisen flask. As soon as distillation commences, dilute sulphuric acid (100 g. of 96% acid diluted to 120 c.c. with water) and ammonium thiocyanate solution (25%; 300 c.c.) are added at equivalent rates in such a manner that the volume of liquid in the flask remains approximately constant. Aqueous thiocyanic acid (18—20%) collects in a well-cooled receiver in 96—100% yield. Solutions containing up to 5% of thiocyanic acid may be regarded as stable, whereas stronger solutions decompose appreciably in a few days when preserved in closed containers. H. Wren.

Supposed isomeride of methyleneaminoacetonitrile. Methylenebisiminodiacetonitrile. M. Delépine (Compt. rend., 1926, **183**, 60—62; cf. A., 1924, i, 625).—The substance of m. p. 86° described as an isomeride of methyleneaminoacetonitrile (m. p. 129°) is *methylenebisiminodiacetonitrile*, $CH_2[N(CH_2\cdot CN)_2]_2$, losing two thirds of its nitrogen on hydrolysis with alkali and yielding with hydrogen chloride in ethyl alcohol iminodiacetonitrile hydrochloride and diethylformal. The structure is also confirmed by synthesis from iminodiacetonitrile and formaldehyde in presence of hydrochloric acid. G. M. Bennett.

Action of ethylcarbylamine on heavy-metal catalysis. S. Toda (Biochem. Z., 1926, **172**, 17—30).—Ethylcarbylamine inhibits the oxidation of cysteine, but this is restored by the addition of iron or in a less degree by copper. Valeronitrile has no such action. Ethylcarbylamine also inhibits the oxidation of lævulose in phosphate solution and of leucine on hæmin-charcoal. This latter action is not merely due to adsorption on the surface of the charcoal, because, whereas it is adsorbed more strongly than propionitrile and less strongly than valeronitrile, its activity as an inhibitor of oxidation is many times greater than that of either. Ethylcarbylamine does not affect the action of the catalase of the liver of rats and is about one tenth as toxic as prussic acid. H. I. Coombs.

Electron displacement in carbon compounds. IV. Derivatives of benzene. H. J. Lucas (J. Amer. Chem. Soc., 1926, **48**, 1827—1838; cf. A., 1925, i, 769).—On the basis of four assumptions, theoretically reasonable, it is shown that the screening effect of electrons offers a mechanism for electron displacement. These assumptions do not harmonise with the view that the atoms in a molecule are alternately polarised. As a consequence of the postulates, the displacement of an orbit in one part of a molecule (*e.g.*, by a substituent) must cause displacement of the other orbits in the molecule. Application of this idea to Pauling's model of the benzene molecule leads to the deduction of seven rules of substitution which conform, in general, with the known facts. The ionisation constants of *p*-substituted benzoic acids are a measure of the electron attractions of the substituent radicals. S. K. Tweedy.

Effect of unsaturation of the activity of alcoholic hydroxyl. I. Action of allyl alcohol on benzene in the presence of aluminium chloride. R. C. HUSTON and D. D. SAGER (J. Amer. Chem. Soc., 1926, **48**, 1955—1959; cf. A., 1925, i, 249).—Only those aromatic alcohols in which the hydroxyl group is attached to the carbon atom adjacent to the ring condense with benzene in the presence of aluminium chloride. The saturated aliphatic alcohols, up to and including *iso*amyl alcohol, under similar conditions give no alkylbenzenes, whereas allyl alcohol gives a 16% yield of allylbenzene, together with β-chloropropylbenzene (probably from the action of hydrogen chloride on allylbenzene) and a little αβ-diphenylpropane, b. p. 277—280°/745 mm. The latter is also obtained directly from allylbenzene, aluminium chloride, and benzene. *βγ-Dibromopropylbenzene* has b. p. 114—115°/5 mm., 242—244°/760 mm. (decomp.), d_4^{20} 1·62. An unsaturated carbon atom adjacent to the alcoholic group thus increases the reactivity of the hydroxyl group with aluminium chloride. R. BRIGHTMAN.

Additive compounds of sulphur dioxide and benzene. C. MAZZETTI and F. DE CARLI (Gazzetta, 1926, **56**, 34—36).—A study of the solvent action of sulphur dioxide on benzene and of the system sulphur dioxide–benzene. The diagram shows four marked eutectics and three maximum points, from which the formation of the following compounds, stable at low temperatures, is deduced: C_6H_6,SO_2, crystallising point, −15°; $C_6H_6,2SO_2$, −40°, and $C_6H_6,3SO_2$, − 52°. S. B. TALLANTYRE.

Hydrolysis of substituted benzyl chlorides and the theory of induced alternate polarities. S. C. J. OLIVIER and G. BERGER.—See this vol., 805.

Structure of dialkylmethyl and benzyl groups. A. STEOPOE (Bul. Chim., Soc. Româna Stiinte, 1925, **28**, 87—89).—The apparent exceptions to the theory of variable affinity observed by von Auwers and Pfuhl (A., 1925, i, 1100) may be explained by assuming that, in favourable cases, C·C or C·N linkings tend to strengthen themselves at the expense of C·H linkings, the hydrogen atoms becoming more or less mobile. H. E. F. NOTTON.

Methyldiphenyls. M. GOMBERG and J. C. PERNERT (J. Amer. Chem. Soc., 1926, **48**, 1372—1384; cf. A., 1924, i, 1295).—In the preparation of diaryl compounds by the action of aromatic hydrocarbons on diazonium compounds, it is generally advantageous to add the diazo-solution to a mixture of the hydrocarbon with sufficient aqueous alkali to form the diazotate, together with an excess of alkali, the amount of which, for optimum results, varies with the individual preparation. In addition to the coupling reaction, reactions also take place whereby the diazo-group is replaced by hydrogen, or, by less complete reduction, is converted into an azo-compound.

Condensation of toluene-*p*-diazonium chloride with benzene affords 4-methyldiphenyl, m. p. 47·7° (cf. Kliegl and Huber, A., 1920, i, 835), b. p. 267—268° (22%), and a *hydrocarbon*, m. p. 249—250°, probably p-*di*-p-*tolylbenzene*. Diazotised *o*-toluidine yields similarly 2-*methyldiphenyl* (8%) as well as indazole (cf. Bamberger, A., 1899, i, 543), whilst diazotised aniline and toluene yielded mixtures of 2- and 4-methyldiphenyl. Bromination of 4-methyldiphenyl in carbon tetrachloride affords 4-bromo-4′-methyldiphenyl, m. p. 133°, b. p. 314—315° (cf. Carnelley and Thomson, J.C.S., 1885, **47**, 588; 1887, **51**, 87). This is obtained, together with 4-*bromo*-2′-*methyldiphenyl*, b. p. 303—305°, by coupling *p*-bromodiazobenzene with toluene, or, together with 2-*bromo*-4′-*methyldiphenyl*, b. p. 301—303°, by coupling diazotised *p*-toluidine with bromobenzene. 4-*Bromodiphenyl*-4′-*carboxylic acid*, m. p. 304°, 2-*bromodiphenyl*-4′-*carboxylic acid*, m. p. 242°, and 4-*bromodiphenyl*-2′-*carboxylic acid*, obtained by the oxidation of the above corresponding methyl derivatives, are described. The last-named acid was converted, by the action of aluminium chloride on the acid chloride (cf. Scholl and Seer, A., 1913, i, 56), into 2-bromofluorenone, m. p. 149° (cf. Schmidt and Bauer, A., 1906, i, 25). 4-*Chloro*-4′-*methyldiphenyl*, m. p. 122°, and 2-*chloro*-4′-*methyldiphenyl*, b. p. 288—290°, were obtained as above from *p*-toluidine and chlorobenzene. When diazotised *p*-toluidine is condensed with nitrobenzene, 4-nitro-4′-methyldiphenyl, m. p. 141°, is obtained (cf. Carnelley, J.C.S., 1876, **29**, 20), the structure of which was established by conversion, through the amine and Sandmeyer reaction, into the above 4-bromo-4′-methyldiphenyl. The following diphenyl derivatives were prepared by the above general reaction: 3-*methyldiphenyl*, b. p. 267—269°; 4 : 4′-ditolyl, m. p. 121° (cf. Ullmann and Meyer, A., 1904, i, 725); 2 : 4′-*ditolyl*, b. p. 273—276°; 2-*bromo*-4-*methyldiphenyl*, b. p. 301—303°; and 4-*bromo*-2-*methyldiphenyl*, b. p. 303—304°. 2-Bromodiphenyl-4-carboxylic acid, m. p. 215—216°, and 4-*bromodiphenyl*-2-*carboxylic acid*, m. p. 161—162°, are described. The latter is converted into 2-bromofluorenone on distillation.

4-p-*Tolylbenzophenone*, m. p. 129—130°, obtained from benzoyl chloride and 4-methyldiphenyl, affords, on reduction, 4-p-*tolylbenzhydrol*, m. p. 96·5—97°, and, when treated with magnesium phenyl bromide, 4-p-*tolyltriphenylcarbinol*, m. p. 95—96° (*chloride*, m. p. 122°; *methyl ether*, m. p. 110°; *ethyl ether*, m. p. 130—131°), converted into 4-p-*tolyltriphenylmethane*, m. p. 131°, 4-p-*tolyltriphenylmethyl*, and 4-p-*tolyltriphenylmethyl peroxide*, m. p. 169—170° (decomp.). Treatment of 4-*p*-tolylbenzophenone with magnesium α-naphthyl bromide affords 4-p-*tolyldiphenyl*-α-*naphthylcarbinol*, m. p. 130—135° with loss of benzene of crystallisation, or m. p. 186°, solvent-free. The corresponding *chloride*, m. p. 192°, *methane*, m. p. 171°, and *methyl peroxide*, m. p. 128—129° (decomp.), are described. F. G. WILLSON.

Reaction between magnesium benzhydryl chloride and methyl sulphate. H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1926, **48**, 1733—1736).—When benzhydryl chloride is added to magnesium in ethereal suspension in presence of a trace of iodine, an immediate precipitate of tetraphenylethane is produced, and this product is eventually obtained in a yield of 95·5%. Subsequent addition of methyl sulphate, however, affords, in

addition, a trace of αα′-diphenylethane, indicating the presence of magnesium benzhydryl chloride. Diphenylacetic acid can be obtained in 32·5% yield by adding benzhydryl chloride to magnesium in ethereal suspension in presence of carbon dioxide.

F. G. WILLSON.

Coloured hydrocarbon—rubrene. C. MOUREU, C. DUFRAISSE, and P. M. DEAN (Compt. rend., 1926, **182**, 1440—1443).—Diphenylphenylacetylenylmethyl chloride, $CPh{:}C{\cdot}CPh_2Cl$ (A., 1923, i, 921), when heated in a vacuum, loses hydrogen chloride to give an orange-red hydrocarbon, *rubrene*, $C_{42}H_{28}$, m. p. 331°. Rubrene quickly takes up bromine in chloroform solution, forming several compounds with very high m. p.; in daylight it takes up oxygen from the air, becoming colourless, and presumably forming a peroxide. A benzene solution of rubrene has an intense yellow fluorescence.

B. W. ANDERSON.

Dissociable peroxide of rubrene. C. MOUREU, C. DUFRAISSE, and P. M. DEAN (Compt. rend., 1926, **182**, 1584—1587; cf. preceding abstract).—The presumed molecular compound, *rubrene peroxide*, crystallised from benzene, m. p. about 190°, decomposes when heated with almost quantitative regeneration of rubrene, free oxygen, and solvent. M. CLARK.

Rubrene peroxide. C. MOUREU, C. DUFRAISSE, and C. L. BUTLER (Compt. rend., 1926, **183**, 101—105; cf. preceding abstracts).—Rubrene is oxidised under the influence of visible radiation from an arc or incandescence lamp when the hydrocarbon is completely or only partly dissolved in a solvent. The failure of the reaction in water or acetic acid is due to the insolubility of rubrene in these liquids, and not to any specific inhibiting influence. When benzaldehyde or propaldehyde is used as solvent, the reaction proceeds in preference to the oxidation of the solvent. The yellowish-green fluorescence of rubrene vanishes when the oxidation is complete, but with impure rubrene an intense violet fluorescence remains, due to a *substance*, m. p. 477° (corr.).

The reaction is retarded by quinol, pyrocatechol, and their monomethyl ethers and by iodine, the effect being chemical, and not due to absorption of light. When rubrene peroxide is suddenly heated at 180—190°, either in the dry solid state or in solution in vaseline, benzaldehyde, or pentachloroethane, it emits a greenish-yellow light for several minutes, during which the peroxide is dissociated and red rubrene is regenerated. The reaction is thus reversible with respect to the photochemical effect. G. M. BENNETT.

Diphenyl series. I. Isomeric 4 : 4′-dichloro-3 : 3′(2 : 3′?)- and 3 : 5′-dinitrodiphenyls. H. H. HODGSON and F. C. GOROWARA (J.C.S., 1926, 1754—1759).—By decomposition, with cuprous chloride in the cold, of the diazo-compound prepared from 3 : 3′(2 : 5′?)-dinitrobenzidine, there is produced 4 : 4′-dichloro-3 : 3′(2 : 5′?)-dinitrodiphenyl, m. p. 129° [Cain, Coulthard, and Micklethwait (J.C.S., 1912, **101**, 2298; 1913, **103**, 2074) give m. p. 111—112°]. The direct nitration of 4 : 4′-dichlorodiphenyl gives a product having a considerably higher m. p. (completely molten at 140°, after sintering at 133·5°) and regarded as 4 : 4′-dichloro-3 : 3′(2 : 5′?)-dinitrodiphenyl. Both products yield the same 4-chloro-4′-aminodinitrodiphenyl when heated at a high temperature with excess of alcoholic ammonia.

4 : 4′-*Dichloro*-3 : 5′-*dinitrodiphenyl*, m. p. 237°, is obtained by the addition of cuprous chloride solution to a solution of diazotised 4-chloro-3-nitroaniline. 3 : 5′-*Dinitro*-4′-*amino*-4-*hydroxydiphenyl*, decomp. 240—260°, is formed by hydrolysis of 3 : 5′-dinitrodiacetylbenzidine. C. J. STILL.

Breakdown of substituted guanidines at a high temperature. R. KLINGNER (Z. physiol. Chem., 1926, **155**, 206—239).—*as*-Triphenylguanidine, m. p. 134° (corr.) [lit. 131°], reacts with an excess of boiling aniline, giving diphenylamine, triphenyldicarbimide, *s*-triphenylguanidine, and ammonia. The reaction is explained by the annexed scheme: $NHPh{\cdot}C(NPh)_2{:}NH \longrightarrow NHPh_2+NHPh{\cdot}CN$; $NHPh{\cdot}CN+NH_2Ph \longrightarrow (NHPh)_2C{:}NH \longrightarrow C(NPh)_2+NH_3$; $C(NPh)_2+NH_2Ph \longrightarrow (NHPh)_2C{:}NPh$; $C(NPh)_2+NHPh{\cdot}CN \longrightarrow NPh{:}C\langle^{NPh}_{NPh}\rangle C{:}NH$.

The initial breakdown into diphenylamine and phenylcyanamide is conditioned by heat only; in the presence of aniline an almost quantitative yield of diphenylamine is obtained, the phenylcyanamide being removed from the sphere of action by polymerisation. A crystalline *product*, $C_{26}H_{22}N_6$, m. p. 204—214°, is described. In presence of excess of diphenylamine, *as*-triphenylguanidine is not decomposed at the temperature of boiling aniline. The alternative breakdown to diphenylcyanamide and aniline requires a much higher temperature. When *s*-diphenylguanidine is heated with an excess of boiling aniline, *s*-triphenylguanidine is obtained through intermediate formation of diphenylcarbodi-imide (cf. Rathke, Ber., 1887, **20**, 1067). Decomposition of the diphenylguanidine into aniline and phenylcyanamide is prevented by the presence of excess of aniline. Alternative reaction of diphenylcarbodi-imide with phenylcyanamide from the initial breakdown explains the formation of triphenyldicarbimide.

When NN′-α-*naphthylbenzylguanidine*, m. p. 121° (*hydrochloride*, m. p. 197—198°), is heated with a sixfold excess of benzylamine in a sealed tube at 220—230°, *di*-α-*naphthylbenzyldicarbimide* (III) (*hydrochloride*, unmelted at 290°; *sulphate*, m. p. 210°) and s-α-*naphthyldibenzylguanidine* (IV), sinters 50—51°, m. p. 54—55° (*hydrochloride*, sinters 194—195°, m. p. 197—198°), are obtained. The reaction scheme is analogous to that for *as*-triphenylguanidine: $NH(C_7H_7){\cdot}C(NH{\cdot}C_{10}H_7){:}NH \longrightarrow N(C_{10}H_7){:}C{:}N{\cdot}C_7H_7+NH_3$ (I) or $NH(C_{10}H_7){\cdot}CN+NH_2{\cdot}C_7H_7$ (II); $N(C_{10}H_7){:}C{:}N{\cdot}C_7H_7+NH(C_{10}H_7){\cdot}CN \longrightarrow NR{:}C\langle^{NR}_{NR}\rangle C{:}NH$ (III); $N(C_{10}H_7){:}C{:}N{\cdot}C_7H_7+NH_2{\cdot}C_7H_7 \longrightarrow NH(C_{10}H_7){\cdot}C(NH{\cdot}C_7H_7){:}N{\cdot}C_7H_7$ (IV). The initial breakdown according to reaction (II) proceeds less readily in presence of a tenfold excess of amine, with consequent increase in the yield of the substituted guanidine and decrease in the yield of dicarbimide. When *NN′*-α-naphthylbenzyl-

guanidine is heated alone at 240° in a stream of nitrogen, a greatly increased yield of the dicarbimide, together with ammonia, benzylamine, and a little α-naphthylcyanamide, is obtained. It is clear from these experiments that amine-replacement in substituted guanidines does not take place through intermediate formation of a tetra-aminomethane derivative, which is subsequently decomposed. The following are described: Triphenyldicarbimide +EtOH, m. p. 60—69°, anhyd., m. p. 155° (cf. Rathke, *loc. cit.*, m. p. 70—74°); *α-naphthylcyanamide*, m. p. 135°; benzylcyanamide, m. p. 43°; *α-naphthylguanidine*, m. p. 129—130° (*nitrate*, m. p. 196—197°); as-*diethylguanidine* (*hydrobromide*, $+2H_2O$, m. p. 50°, anhyd., sinters 46°, m. p. 75—80°; *sulphate*, sinters 280°, decomp. 287°; *picrate*, m. p. 224—225°); NN′-*phenyl*-p-*anisylguanidine*, m. p. 132—133°; s-*phenyl*-o-*anisyl*-*α-naphthylguanidine* (*sulphate*, m. p. 184—185°); s-*methylethylallylguanidine* (*sulphate*, m. p. 190°). M. Clark.

Action of nitrous acid on *p*-iododimethylaniline. M. F. Aitkin and T. H. Reade (J.C.S., 1926, 1896—1897).—*p*-Iododimethylaniline, which suffers no displacement of iodine with boiling alcoholic potassium hydroxide, sodium ethoxide, potassium phthalimide, or cold 4*N*-sulphuric acid, is decomposed by sodium nitrite and 4*N*-sulphuric acid into iodine (none with silver nitrite), *p*-nitrodimethylaniline, m. p. 163°, and 4-*iodo*-2-*nitrodimethylaniline*, m. p. 60·5°, which is also obtained as the hydrochloride from iodine monochloride and *o*-nitrodimethylanilime (sulphate, m. p. 168°, and not 126—127°, as given by Weissenberger, A., 1912, i, 690). Koch's compound, m. p. 67·5° (Ber., 1887, **20**, 2460), is also produced by brominating *o*-nitrodimethylaniline and is probably 4-bromo-2-nitrodimethylaniline. The iododimethylaniline, m. p. 79·5°, of Weber (Ber., 1877, **10**, 765; Reade and Sim, J.C.S., 1924, **125**, 158) is the 4-iodo-compound. J. S. H. Davies.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. I. Nitration of some derivatives of benzylamine. H. R. Ing and R. Robinson (J.C.S., 1926, 1655—1668).—Benzylamine forms a mixture of *m*- and *p*-nitro-derivatives, whilst crystallisation of the crude nitration product of benzylammonium nitrate furnishes the *p*-nitro-isomeride, and not the *m*-nitro-isomeride (cf. Holmes and Ingold, A., 1925, i, 1142). Further, contrary to the statement of these authors, a mixture of *m*- and *p*-nitro-derivatives is formed by nitrating benzylamine at 100°, and diacetylbenzylamine is largely nitrated in the *p*-position, to some extent in the *o*-position, and possibly to some extent in the *m*-position, although none of the last isomeride was isolated. Similarly, phthalbenzylimide nitrates in the *o*- and *p*-positions in the benzyl group. On the other hand, benzylpiperidinium nitrate, dibenzylmethylammonium nitrate, and benzyltrimethylammonium nitrate are largely nitrated in the *m*-position, showing that, contrary to the conclusions of Holmes and Ingold, it is the benzylammonium salts that are nitrated in the *m*-position. It appears that the tendency to *m*-substitution rises in the series benzylamine, dibenzylamine (the yield of *mm′*-dinitro-derivative claimed by Holmes and Ingold is much too high), benzylpiperidine. The results obtained are considered in terms of the influence of an ionic charge on a conjugated system (cf. Allan, Oxford, Robinson, and Smith, this vol., 397). *Benzyltrimethylammonium nitrate*, m. p. 151—160°, o-*nitrobenzyltrimethylammonium perchlorate*, m. p. 166°, m-*nitrobenzyltrimethylammonium nitrate*, m. p. 251° (decomp.), and p-*nitrobenzyltrimethylammonium nitrate*, m. p. 211° (decomp.), derived from the condensation products of alcoholic trimethylamine with benzyl chloride, *o*- and *m*-nitrobenzyl chloride, and *p*-nitrobenzyl bromide, respectively, are described. The *m*-nitro-compound is identical with that obtained by nitrating benzyltrimethylammonium nitrate.

J. S. H. Davies.

Separation of the constituents of commercial xylidine. G. T. Morgan and W. J. Hickinbottom. —See B., 1926, 656.

Preparation of tertiary amines derived from tertiary alcohols. M. Sommelet (Compt. rend., 1926, **183**, 302—304).—Methyl iodide reacts with the methylimide of benzophenone yielding the solid *methiodide*, which reacts with magnesium methyl iodide in ethereal solution, giving β-*dimethylamino*-ββ-*diphenylethane*, b. p. 167—168°/17 mm., m. p. 44—44·5°, decomposed by boiling acetic anhydride, giving αα-diphenylethylene and dimethylacetamide, and reacting with methyl iodide, giving αα-diphenylethylene, tetramethylammonium iodide, and the hydriodide of the base. L. F. Hewitt.

Radicals and *meri*-quinonoid compounds. J. Piccard (Ber., 1926, **59**, [*B*], 1438—1444).—So far as can be at present ascertained, certain *meri*-quinonoid salts derived from *p*-phenylenediamine and the majority or all those obtained from benzidine belong to the quinhydrone type (β-form), whereas certain prepared from *p*-phenylenediamine are unimolecular, partly oxidised derivatives of the parent base (α-form). Since the latter contain an odd number of valencies, they must be regarded as radicals in the sense of Hantzsch's theory. Weitz's dictum (this vol., 527) that " all *meri*-quinonoid salts are to be regarded as unimolecular and hence as radicals " is not universally applicable.

H. Wren.

Orientation effects in the diphenyl series. II. Constitution of Bandrowski's dinitrobenzidine. R. J. W. Le Fèvre and E. E. Turner (J.C.S., 1926, 1759—1764).—Whereas the compound described by Strakosch (Ber., 1872, **5**, 236) is 3 : 5′(or preferably 3 : 3′)-dinitrobenzidine, the dinitrobenzidine in question, which was described as 3 : 3′-dinitrobenzidine by Bandrowski (cf. A., 1888, 286; Cain and others, J.C.S., 1912, **101**, 2298; 1914, **105**, 1444), is now found to be the 2 : 3′-isomeride. Further, if there is isomerism of the 3 : 3′–3 : 5′ type in the benzidine series (Cain, *loc. cit.*), the second isomeride has yet to be discovered. 2-*Nitrodiacetylbenzidine*, m. p. above 300°, on nitration yields 2 : 3′-*dinitrodiacetylbenzidine*, m. p. 220—222°, which furnishes 2 : 3′-*dinitrobenzidine*, m. p. 236° (Bandrowski, m. p. 233°), with sulphuric

acid, whereas with concentrated alcoholic potassium hydroxide a different product is obtained by possible loss of ammonia. The derived 4 : 4′-*dibromo*-2 : 3′-*dinitrodiphenyl*, m. p. 148° (Cain, m. p. 137—138°), which is identical with the nitration product of 4 : 4′-dibromodiphenyl, yields 4-*bromo*-4′-*piperidino*-2 : 3′-*dinitrodiphenyl*, m. p. 137°. 4 : 4′-Dipiperidino-3 : 5′-dinitrodiphenyl has m. p. 159—160°.

J. S. H. Davies.

Relations between azoxy-compounds and diazo-hydrates. A. Angeli (Ber., 1926, **59**, [*B*], 1400—1403).—Although the existence of stereoisomeric diazo-compounds in general is not called into question, the differences in behaviour of the diazo-hydrates is satisfactorily explained by the assumption that the normal and *iso*diazotates are structurally and not configuratively different.

H. Wren.

Mechanism of the reduction of azobenzene by magnesium organohalides. H. Gilman and C. E. Adams (J. Amer. Chem. Soc., 1926, **48**, 2004—2005).—Under conditions in which azobenzene is converted into hydrazobenzene, excess of magnesium phenyl or ethyl bromide is without action on triphenylhydrazine. The reaction suggested by Busch and Hobein (A., 1907, i, 552) does not therefore precede that proposed by Franzen and Deibel (A., 1905, i, 843) for the reduction of azobenzene (cf. A., 1925, i, 1336). R. Brightman.

Hydrolysis of *o*-benzylideneaminophenyl acetate. F. Bell and J. Kenyon (J.C.S., 1926, 1893).—Aqueous hydrolysis of *o-benzylideneaminophenyl acetate*, m. p. 93—96° (prepared by acetylating *o*-benzylideneaminophenol), into benzaldehyde and *o*-acetamidophenol, m. p. 202°, illustrates the ease with which an acyl group migrates from oxygen to nitrogen. Acid hydrolysis involves the loss of both acetic acid and benzaldehyde. J. S. H. Davies.

Preparation of phenacetin from *p*-chloronitrobenzene. D. H. Richardson.—See B., 1926, 689.

Alternating effect in carbon chains. VII. Relative directive efficiencies of oxygen and sulphur in aromatic substitution. E. L. Holmes, C. K. Ingold, and E. H. Ingold (J.C.S., 1926, 1684—1690).—It is established that sulphur has a greater *op*-directive efficiency than oxygen when these atoms are in the neutral state and directly attached to the benzene ring, and the results are discussed in terms of the theory previously proposed (Ingold and Ingold, this vol., 833; Holmes and Ingold, *ibid.*, 831). *S*-Methylthioguaiacol nitrates to form more than 80% of the 3-*nitro*-derivative (OMe = 1) b. p. 144—146°/2 mm., which yields 6-*nitro*-2-*methoxyphenylmethylsulphone*, m. p. 144—145°, with fuming nitric acid. 2-Methoxyphenylmethylsulphone yields on nitration 3-*nitro*-2-*methoxyphenylmethylsulphone*, m. p. 109°, together with the 5-*nitro*-isomeride, m. p. 149°, which is also obtained by methylating 4-*nitroanisole*-2-*sulphinic acid*, m. p. 134—136°, prepared from 4-nitro-*o*-anisidine by the Gattermann reaction. 4-*Nitro*-2-*methoxyphenylmethylsulphone*, m. p. 163—164°, is obtained from 5-nitro-*o*-anisidine either by conversion as above into 5-*nitroanisole*-2-*sulphinic acid*, m. p. 127—129°, followed by methylation, or by successive conversion into 5-*nitrothioguaiacol*, m. p. 80—81°, 5-*nitro*-*S*-*methylthioguaiacol*, m. p. about 95°, by methylation, 4-*nitro*-2-*methoxyphenylmethylsulphoxide*, m. p. 129—130°, by oxidation, followed by further oxidation to the sulphone. The monobromination of *S*-methylthioguaiacol furnishes considerable quantities of a dibromo-compound, probably the 3 : 5-*dibromo*-derivative, m. p. 88—90°. J. S. H. Davies.

Method of inserting the thioaryl group. L. G. S. Brooker and S. Smiles (J.C.S., 1926, 1723—1729).—The decomposition of aromatic disulphoxides according to the equation: $R'\cdot SO_2\cdot SR''+Na[CHX_2]=R'\cdot SO_2Na+R''\cdot S\cdot CHX_2$, (I), where X represents an acetyl, a carbethoxyl, or cyano-group, affords further confirmation of their thiolsulphonate structure (A., 1924, i, 275; 1925, i, 391, 1137). There is no evidence of an intramolecular change of the type: $R'\cdot SO_2\cdot SR'' \rightleftharpoons R'\cdot SO\cdot SOR'' \rightleftharpoons R'\cdot S\cdot SO_2R''$, since only one sulphinic acid and one thioaryl derivative is obtained from disulphoxides containing different aromatic groups, the sulphinic acid obtained being the one from which the disulphoxide was synthesised. The reaction (I) is extended to other substances containing a labile ketonic or enolic structure. The degree of substitution by the thioaryl group depends on the nature of the substance. Thus, ethyl phenylacetate, phenylacetonitrile, deoxybenzoin, α-naphthol, and 8-hydroxyquinoline yield dithioaryl derivatives, whilst phloroglucinol, resorcinol, and orcinol yield trithioaryl compounds, whereas β-naphthol and 6-hydroxyquinoline form monothioaryl derivatives. Phenol, *m*- and *p*-cresol, resorcinol monomethyl ether, dibenzoylmethane, and anthrone, on the other hand, do not undergo the reaction. The behaviour of sodium enolates appears to depend on the mobility of their tautomeric systems. The preparation of the following compounds is described: *p*-tolylthiolacetic acid, m. p. 92·5°, and *p*-tolylsulphinic acid from *p*-tolyl disulphoxide and ethyl malonate, cyanoacetate, or acetoacetate; *p*-chlorophenylthiolacetic acid, m. p. 104°, and the corresponding sulphinic acid from *p*-chlorophenyl disulphoxide and ethyl malonate; α-p-*tolylthiolpropionic acid*, m. p. 75°, from *p*-tolyl disulphoxide and ethyl malonate; *o*-nitrophenylthiolacetic acid and 2 : 5-dichlorophenylsulphinic acid from *o*-nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate and ethyl malonate; *ethyl bis*-2 : 5-*dichlorophenylthiolphenylacetate*, m. p. 118°, from 2 : 5-dichlorophenyl disulphoxide and ethyl phenylacetate; *di*-p-*tolylthiolphenylacetonitrile*, m. p. 89°, and *p*-tolylsulphinic acid from *p*-tolyl disulphoxide and phenylacetonitrile; *bis*-2 : 5-*dichlorophenylthiolphenylacetonitrile*, m. p. 129°, similarly from 2 : 5-dichlorophenyl disulphoxide; p-*tolyl acetylacetonyl sulphide*, m. p. 53°, from acetylacetone and *p*-tolyl disulphoxide; 2 : 5-*dichlorophenyl acetoacetonyl sulphide*, m. p. 97·5°, from 2 : 5-dichlorophenyl disulphoxide; 4-*chlorophenyl acetylacetonyl sulphide*, m. p. 70°, from *p*-chlorophenyl disulphoxide; *o-nitrophenyl acetylacetonyl sulphide*, m. p. 136—137° similarly from *o*-nitrophenyl disulphoxide, *o*-nitrophenyl 2 : 5-dichlorobenzenethiolsulphonate, *o*-nitro-

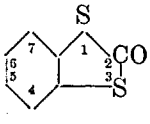
phenyl *p*-chlorobenzenethiolsulphonate, and *o*-nitrophenyl sulphur chloride; *phenyl αα-bis*-2 : 5-*dichlorophenylthiolbenzyl ketone*, m. p. 138°, from deoxybenzoin and 2 : 5-dichlorophenyl disulphoxide, and from benzil and 2 : 5-dichlorophenylmercaptan; *phenyl α-5-chloro-2-methoxyphenylthiol-α*-2 : 5-*dichlorophenylthiolbenzyl ketone*, m. p. 170°, from 2 : 5-dichlorophenyl disulphoxide and 5-chloro-2-methoxyphenyl desyl sulphide, is not identical with the symmetrical mercaptol formed from benzil and 5-chloro-2-methoxyphenylmercaptan; 2 : 4 : 6-*tri*-p-*chlorophenylthiolphloroglucinol*, m. p. 174°, from phloroglucinol and *p*-chlorophenyl disulphoxide; 2 : 4 : 6-*tri*-p-*tolylthiolphloroglucinol*, m. p. 175°, similarly from *p*-tolyl disulphoxide; 2 : 4 : 6-*tri*-2′ : 5′-*dichlorophenylthiolphloroglucinol*, m. p. 223—224°, similarly from 2 : 5-dichlorophenyl disulphoxide (*triacetyl* derivative, m. p. 163°); 2 : 4-*di*-4′-*chlorophenylthiol*-1-*naphthol*, m. p. 135°, from sodium α-naphthoxide and *p*-chlorophenyl disulphoxide (*acetyl* derivative, m. p. 135°); 2 : 4-*bis*-2′ : 5′-*dichlorophenylthiol*-1-*naphthol*, m. p. 172°, similarly from 2 : 5-dichlorophenyl disulphoxide; 1-*o*-nitrophenylthiol-2-naphthol, m. p. 179—180°, from sodium β-naphthoxide and *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate, also from β-naphthol and *o*-nitrophenyl sulphur chloride (Zincke, A., 1912, i, 763); 1-p-*tolylthiol*-2-*naphthol*, m. p. 84°, from sodium β-naphthoxide and *p*-tolyl disulphoxide; 1-β-*naphthylthiol*-2-*naphthol*, m. p. 92°, similarly from β-naphthyl disulphoxide; 2 : 4 : 6-*tri*-p-*tolylthiolorcinol*, m. p. 143°, from orcinol and *p*-tolyl disulphoxide; 2 : 4 : 6-*tri*-p-*chlorophenylthiolresorcinol*, m. p. 158°, from resorcinol and *p*-chlorophenyl disulphoxide; 2 : 4 : 6-*tri*-2′ : 5′-*dichlorophenylthiolresorcinol*, m. p. 187°, similarly from 2 : 5-dichlorophenyl disulphoxide; 5-p-*tolylthiol*-6-*hydroxyquinoline*, m. p. 138°, from 6-hydroxyquinoline and *p*-tolyl disulphoxide; 5 : 7-*di*-p-*tolylthiol*-8-*hydroxyquinoline*, m. p. 126°, similarly from 8-hydroxyquinoline; 5 : 7-*bis*-2′ : 5′-*dichlorophenylthiol*-8-*hydroxyquinoline*, m. p. 196°, similarly from 2 : 5-dichlorophenyl disulphoxide.

J. S. H. Davies.

Nitro-derivatives of thioresorcinol ethers. C. Finzi and E. Pagliari (Gazzetta, 1926, **56**, 331—337; cf. this vol., 309).—The condensation of thioresorcinol with *p*-chloronitrobenzene and chloro-2 : 4-dinitrobenzene has been studied, and the following compounds have been obtained: *di*-p-*nitrophenyl* m-*phenylene sulphide*, $C_6H_4(S{\cdot}C_6H_4{\cdot}NO_2)_2$, m. p. 138°; *di*-2 : 4-*dinitrophenyl* m-*phenylene sulphide*, m. p. 168°; *di*-p-*aminophenyl* m-*phenylene sulphide dihydrochloride*, losing hydrochloric acid in the air, forming the free base, which gives a *dibenzoyl* derivative, m. p. 214°; *di*-2 : 4-*diaminophenyl* m-*phenylene sulphide*, *dibenzoyl* derivative, m. p. 234—235°. m-2 : 4-*Dinitrophenylthiolphenylthioglycollic acid*, $C_6H_3(NO_2)_2{\cdot}S{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m. p. 146°, was obtained from thioresorcinol, chloro-2 : 4-dinitrobenzene and chloroacetic acid.

S. B. Tallantyre.

***o*-Dithiolbenzene.** W. R. H. Hurtley and S. Smiles (J.C.S., 1926, 1821—1828).—*o*-Ethylsulphonylbenzenesulphonic acid, isolated as the *sulphonamide*, m. p. 190°, is formed during the preparation of potassium benzene-*o*-disulphonate, for which an improved method of preparation from aniline-*o*-sulphonic acid is given. *o*-Dithiolbenzene is best obtained by reducing the disulphonyl chloride with zinc dust and hydrochloric acid in presence of alcohol. *o*-Phenylene dithiolbenzoate has m. p. 94—95°. Potassium benzene-*o*-disulphonate yields *benzene-o-disulphonic anhydride*, m. p. 180°, with chlorosulphonic acid, whilst the *o*-disulphinic acid (see below) with nitrous acid forms *benzene-o-disulphonhydroxyimide*, $C_6H_5O_5NS_2,H_2O$, m. p. 90—91° (decomp.), which is reduced by sulphurous acid to benzene-*o*-disulphonimide, m. p. 186° (Holleman, Rec. trav. chim., 1910, **29**, 416; A., 1921, i, 552, gives m. p. 192°), the *silver* salt of which is described. The N-*phenylimide*, m. p. 195°, is formed by the action of aniline on the disulphonyl chloride, and readily by oxidation of *o*-sulphinylbenzenesulphonanilide with sodium hypochlorite. The unstable benzene-*o*-disulphinic acid, which is obtained by reducing the disulphonyl chloride with sulphite, but purer by applying the method of Suzuki (A., 1908, i, 870) to the hydroxylimide, is characterised by conversion into *benzene-o-dimethylsulphone*, m. p. 225°. Carbonyl chloride and carbon disulphide react with *o*-dithiolbenzene in excess of alkali hydroxide to form 1 : 3-*benzdithiol*-2-*one* (*o-phenylene dithiolcarbonate*),



m. p. 78—79° (annexed formula) and 2-*thio*-1 : 3-*benzdithiole* (*o-phenylene trithiocarbonate*), m. p. 165°, respectively. Similar treatment of ethylene dimercaptan gives ethylene trithiocarbonate. The thion sulphur in thiobenzdithiole is not readily removed by copper, but reacts with hydroxylamine to form 2-*oximino*-1 : 3-*benzdithiole*, m. p. 129—130°. 1 : 3-Benzdithiol-2-one forms a *nitro*-derivative, m. p. 157°, whilst with benzaldehyde and acetophenone it yields 2-*phenyl*-1 : 3-*benzdithiole*, m. p. 72°, and 2-*phenyl*-2-*methyl*-1 : 3-*benzdithiole*, m. p. 83°, respectively. With nitric acid, phenylbenzdithiole is converted into a complex *nitrate*, m. p. 96° (decomp.), which on hydrolysis yields the corresponding *base*, convertible by warm solvents into 2-*phenyl*-1 : 3-*benzdithiole*-2-*oxide*, $\left[C_6H_4\langle{}^{S}_{S}\rangle C\langle{}^{Ph}\right]_2O$, m. p. 134°. The latter behaves as the oxide of a ψ-base, $C_6H_4S_2{:}CPh{\cdot}OH$, in being converted by acid into yellow or orange salts of 2-*phenyl*-1 : 3-*benzdithiole*-1-*sulphonium*, of which the *nitrate*, *sulphate*, *perchlorate*, *chloride*, m. p. 110°, *chloroplatinate*, darkening at 240°, and *perbromide*, m. p. 212°, are described.

J. S. H. Davies.

Dependence of rotatory power on chemical constitution. XXX. Resolution of methylcyclohexylcarbinol. A. Domleo and J. Kenyon (J.C.S., 1926, 1841—1845).—dl-*Methylcyclohexylcarbinyl hydrogen phthalate*, m. p. 140°, obtained by the interaction of phthalic anhydride and the potassium salt of the alcohol in benzene, is resolved by fractional crystallisation, with the aid of brucine and cinchonine. The *dAlB* (brucine) *salt* has m. p. 179°, and is decomposed with hydrochloric acid, forming d-*methylcyclohexylcarbinyl hydrogen phthalate*, m. p. 75°, $[\alpha]_D^{20}$

+55·4°. The *l*A*d*B (cinchonine) *salt*, m. p. 160—165°, $[\alpha]_D^{20}$ +77·3°, similarly furnishes l-*methyl*cyclo*hexylcarbinyl hydrogen phthalate*, m. p. 75°, $[\alpha]_D^{20}$ —55·0°. The d- and l-*methyl*cyclo*hexylcarbinols* are readily obtained by passing steam through sodium hydroxide solutions of the corresponding hydrogen phthalic esters. The *d*-alcohol has b. p. 82—83°/12 mm., $[\alpha]_D^{20}$ +5·68°, n_D^{20} 1·4635, d_4^{20} 0·9254; the *l*-alcohol has α_D^{21} —2·57°; the d-*acetate* has b. p. 98°/30 mm., $[\alpha]_D^{17}$ —3·12°, d_4^{17} 0·9500, n_{6708}^{25} 1·4404. Densities at various temperatures, refractive indices for various frequencies, and rotatory powers at various temperatures and frequencies are tabulated, and a comparison is made of the data obtained with those derived from optically active phenylmethylcarbinol and methyl-*n*-hexylcarbinol. J. S. H. Davies.

Esters of dinitrobenzyl alcohol. K. Krassovski and A. Plissov (Ukraine Chem. J., 1925, **1**, 638—642).—2 : 4-*Dinitrobenzyl benzoate*, m. p. 141°, is prepared from 2 : 4-dinitrobenzyl chloride and potassium benzoate in alcohol. In the same way, 2 : 4-*dinitrobenzyl salicylate*, m. p. 168°, and p-*nitrophenyl* 2 : 4-*dinitrobenzyl ether*, m. p. 202—204°, were obtained. The esters give characteristic quinonic colours with strong alkalis in alcoholic or acetone solution. S. Botcharsky.

Stereochemistry of the styrene series : β-ethoxystyrenes. C. Dufraisse and R. Chaux (Bull. Soc. chim., 1926, [iv], **39**, 905—922).—The divergences in the physical constants of samples of β-ethoxystyrene from different sources (cf. Moureu, A., 1904, i, 285; Auwers, A., 1912, ii, 3) are due to the presence of varying quantities of the *cis*- and *trans*-isomerides. The product obtained from ββ-diethoxy-α-phenylethane (Bodroux, A., 1904, i, 421) or from phenyl β-ethoxystyryl ketone (this vol., 617) yields, after fractionation and recrystallisation, a pure isomeride of m. p. —1° to 0°, b. p. 102—103°/11 mm., $d_4^{19\cdot5}$ 0·976, n_D^{23} 1·550. The second isomeride forms the greater part of the substance, b. p. 109—109·5°, n_D^{20} 1·5545, d_4^{20} 0·967, obtained by a modification of Moureu's method from phenylacetylene and alcohol. This cannot be further purified by distillation and has not been obtained crystalline. Both forms readily undergo autoxidation, which is retarded by antioxygens (cf. A., 1922, i, 250). H. E. F. Notton.

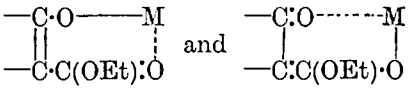
Sterol from *Ulmus campestris*. L. Schmid and R. Stöhr (Ber., 1926, **59**, [*B*], 1407—1408).—Stigmasterol is the main component of the sterol from *Ulmus campestris* (cf. Zellner, this vol., 646). H. Wren.

Sterol from *Parthenium argentatum*. L. Schmid and R. Stöhr (Ber., 1926, **59**, [*B*], 1408—1410).—The *sterol*, $C_{27}H_{46}O$, m. p. 137° (corr.), from *Parthenium argentatum* gives an *acetate*, m. p. 196° after softening, and a *tetrahydro*-derivative, m. p. 149·5° (*acetate*, m. p. 222° after softening). It is not identical with sitosterol. H. Wren.

Hydrogenation of triphenylcarbinol and 9-phenylfluorenyl alcohol under pressure. V. Ipatiev and B. Dolgof (Compt. rend., 1926, **183**, 304—306).—Triphenylcarbinol is hydrogenated at 275°, yielding *tricyclohexylmethane*, d_0^{50} 0·9413, n^{50} 1·4919, together with di*cyclo*hexylmethane, a small amount of di*cyclo*hexyl, and methane. 9-Phenylfluorenyl alcohol on hydrogenation yields *perhydro*-9-*phenylfluorene*. This is stated to be different from tri*cyclo*hexylmethane, but the same *d* and *n* are quoted for both. L. F. Hewitt.

Solvatochromism. E. Fischer (J. pr. Chem., 1926, [ii], **113**, 192—198; cf. Hantzsch, A., 1922, i, 556).—Contrary to the contention of Madelung (A., 1925, i, 1459), the phenomenon of solvatochromism is held to be distinct from that of halochromism. The colour of an ethereal solution of Homolka's "tetramethylfuchsine" dried over potassium hydroxide, and thus free from any acid, is found to be deepened by added nitrobenzene, more so by dinitrobenzene, and still more by trinitrobenzene. Similar solvatochromic effects on the fuchsine are obtained with tetrachloro- or pentachloro-ethane. As the formation of a colouring matter on adding acid to the imine is held to be due to a complex of 1 mol. of the compound $C(C_6H_2Me_2\cdot NH_2)_2{:}C_6H_4{:}NH$ with 1 mol. of acid, so in solvatochromism a similar complex is assumed, in which a molecule of solvent replaces that of the acid. Imine bases have a greater solvatochromism the greater their ease of salt formation, and rise of temperature decreases the effect, presumably owing to dissociation of the complex solvate. E. W. Wignall.

Conjugation- and complex-formulæ. A. Hantzsch (J. pr. Chem., 1926, [ii], **113**, 185—191).—A theoretical paper in which misrepresentations by Madelung (A., 1925, i, 1459) are discussed. It is considered that isomerism of the type



is possible, the difference between whole and partial valencies disappearing only in a symmetrical structure. E. W. Wignall.

Cæsium eosinate. R. Delaplace (Compt. rend., 1926, **183**, 69—70).—The preparation of cæsium metal from the chloride is described and its conversion into the hydroxide. *Cæsium eosinate* is obtained crystalline by evaporation of a solution of the hydroxide to which an excess of eosin (as free acid) has been added and the excess removed by filtration. G. M. Bennett.

Pyrogallolsulphonephthalein, sulphonegallein, 2 : 3 : 4-trihydroxybenzoylbenzene-*o*-sulphonic acid (the intermediate acid), and some of their derivatives. W. R. Orndorff and N. Fuchs (J. Amer. Chem. Soc., 1926, **48**, 1939—1951).—Ammonium hydrogen *o*-sulphobenzoate when heated with pyrogallol at 190—195° affords *ammonium* 2 : 3 : 4-*trihydroxybenzoylbenzene-o-sulphonate* (+0·25H_2O), m. p. 298° (darkens at 296°), from which the free *acid* (+3H_2O), m. p. 108—109° (*tribenzoate*, m. p. 62—64°), is obtained on treatment with hydrogen chloride in alcohol. When heated alone or with pyrogallol at 135—145°, trihydroxybenzoylbenzene-*o*-sulphonic acid is converted into *pyrogallolsulphonephthalein*, $O{:}C_6H_2(OH)_2{:}C(C_6H_4\cdot SO_3H)\cdot C_6H_2(OH)_3$,+3$H_2O$, green crystals, m. p. above 315°. The latter

is also obtained by heating the chlorides of *o*-sulphobenzoic acid with pyrogallol (a little *dipyrogallyl* o-*sulphobenzoate*, m. p. 109—111°, b. p. 230°, is also formed) or "saccharin" with sulphuric acid and pyrogallol, but is best obtained (yield 51%) from *o*-sulphobenzoic anhydride and pyrogallol in the presence of zinc chloride. The *ammonium*, $C_{19}H_{13}O_9S{\cdot}NH_4,2H_2O$, *monosodium* ($+5H_2O$), *zinc*, $C_{19}H_{10}O_9SZn_2,5H_2O$, *lead*, $(C_{19}H_{11}O_9S)_2Pb_3$ (blue), and *barium*, $(C_{19}H_{13}O_9S)_2Ba,6H_2O$, salts of pyrogallolsulphonephthalein are described. With the exception of the lead and barium salts, the above salts, like the parent substance, when heated at 200° are converted into the corresponding derivative of *sulphonegallein*, $(OH)_2C_6H_2\langle\begin{matrix}C{\cdot}C_6H_4{\cdot}SO_3H\\ \| \\ O\end{matrix}\rangle C_6H_2\langle\begin{matrix}OH\\ =O\end{matrix}$ ($+3H_2O$), bright red, m. p. above 315°, which in the presence of moisture reverts to pyrogallolsulphonephthalein. Both compounds absorb 4—5 mols. of ammonia, and retain only 1 mol. in a desiccator over sulphuric acid. Aniline converts pyrogallolsulphonephthalein quantitatively into the red *aniline* salt of sulphonegallein, $C_{19}H_{11}O_8S(C_6H_5NH_3)$, m. p. above 315°, whilst acetic anhydride similarly affords *sulphonegallein tetra-acetate*, $SO_2\langle\begin{matrix}C_6H_4\\ O\end{matrix}\rangle C\langle\begin{matrix}C_6H_2(OAc)_2\\ C_6H_2(OAc)_2\end{matrix}\rangle O$, m. p. 218° (decomp.), a colourless compound containing a pyrone ring, since on hydrolysis with dilute sodium hydroxide it shows a green fluorescence, rapidly changing to a blue colour. The corresponding *tetrabenzoate*, m. p. 235°, behaves similarly. *o*-Sulphobenzoic anhydride and pyrogallol 1-methyl ether yield *pyrogallolsulphonephthalein monomethyl ether*, red needles, decomp. 270°. The *trimethyl ether*, red, m. p. above 315°, is obtained, together with a little *sulphonegallein dimethyl ether* (red and orange forms, both with m. p. above 315°), by treating pyrogallolsulphonephthalein with methyl iodide and sodium methoxide, a small amount of the *sodium* salt of the trimethyl ether being obtained on extracting the product with acetone. Both the trimethyl ether and the sulphonegallein dimethyl ether absorb about 3 mols. of dry ammonia and over sulphuric acid lose 2 mols. to yield a monoammonium salt. Bromine in alcohol converts pyrogallolsulphonephthalein into *dibromopyrogallolsulphonephthalein*, green crystals, m. p. above 315° (*ammonium* salt, red), affording *dibromosulphonegallein* (*tetrabenzoate*, colourless, m. p. 269—270°) at 200°. Both compounds absorb 5—6 mols. of dry ammonia and retain 3 mols. over sulphuric acid. On reduction with zinc dust and water, pyrogallolsulphonephthalein yields *pyrogallolsulphonephthalin*, $[(OH)_3C_6H_2]_2CH{\cdot}C_6H_4{\cdot}SO_3H$, softens at 146—147°, m. p. 170°, decomp. at 226° (*zinc* salt, $[C_{19}H_{15}O_9S]_2Zn+2H_2O$, which at 200° affords the *zinc* salt of the *sulphonegallin*), readily oxidised by air to the phthalein. R. BRIGHTMAN.

Action of α-oxides on esters of aromatic amino-acids. A. KIPRIJANOV (Ukraine Chem. J., 1925, **1**, 644—654).—When equimolecular quantities of ethylene oxide and methyl anthranilate are heated for 8 hrs. at 125° in a sealed tube, *methyl* β-*hydroxyethylanthranilate*, m. p. 70·5—71·5°, is obtained; it forms a *hydrochloride*, m. p. 100° (decomp.), *picrate*, m. p. 97—98°, *chloroplatinate*, m. p. 180° (decomp.), and *dibenzoyl* derivative, m. p. 145—146°. The free *acid* has m. p. 145° (decomp.). *Methyl di*-β-*hydroxyethylanthranilate hydrochloride* has m. p. 160° (decomp.).

Methyl p-β-*hydroxyethylaminobenzoate*, m. p. 120°, obtained in the same way, forms a *picrate*, m. p. 79°, *nitroso*-compound, m. p. 89°, and *dibenzoyl* derivative, m. p. 104—105°; the free *acid* has m. p. 197° (decomp.). Ethylene oxide and methyl *N*-methylanthranilate give o-*methyl*-β-*hydroxyethylaminobenzoic lactone*, $C_6H_4\langle\begin{matrix}CO\text{——}O\\ NMe{\cdot}CH_2\end{matrix}\rangle CH_2$, m. p. 81—82° (*hydrochloride*; *chloroplatinate*, m. p. 160°; *picrate*, m. p. 120°). The compounds described have anæsthetic properties. S. BOTCHARSKY.

Carbolthionic acids and esters. Y. SAKURADA (Mem. Coll. Sci. Kyōtō, 1926, **9**, 237—241; cf. Matsui, A., 1909, i, 463; 1912, i, 261),—The following thionic esters were obtained by treating the ethereal solution of the requisite imino-ether with dry hydrogen sulphide: ethyl thionbenzoate, b. p. 124—127°/3—5 mm. or 240°/atm. (partial decomp.), d_4^{20} 1·0452, r_α (D line) 0·5570, η^{17} 1·8169; ethyl thionacetate, b. p. 105—107°/atm., d_4^{17} 0·8980, r_G 0·5002, η^{17} 0·7167; *amyl thionacetate*, b. p. 72—74°/55 mm., d_4^{23} 0·8639, r_G 0·4977, η^{23} 0·8592; *phenyl thionacetate*, b. p. 90—94°/38 mm., d_4^{20} 0·9914, r_G 0·5008; *ethyl phenylthionacetate*, b. p. 170°/99 mm., d_4^{12} 1·0142, r_G 0·5317, η^{12} 1·9276; ethyl thionpropionate, b. p. 125—129°/atm., d_4^{20} 0·8912, r_G 0·4844, η^{20} 0·6519; *amyl thionpropionate*, b. p. 84—86°/30 mm., d_4^{22} 0·8595, r_G 0·5050, η^{22} 0·8784; ethyl thion-*p*-toluate, b. p. 140—145°/70 mm., d_4^{20} 0·9992, r_G 0·5527, η^{20} 2·1141; *ethyl thion*-β-*naphthoate*, solid, b. p. 188—194°/30 mm. Thionbenzoic and thionacetic acids, obtained from the esters with alcoholic potassium hydroxide, decompose rapidly into the carboxylic acid and hydrogen sulphide. The *silver*, *lead*, and *barium* salts of thionbenzoic acid are described, but copper and iron salts could not be isolated. J. S. H. DAVIES.

Dibenzylacetic [β-phenyl-α-benzylpropionic] acid and its substituted amides. N. MAXIM (Bull. Soc. chim., 1926, [iv], **39**, 1024—1029).—Convenient methods are described for the preparation of β-phenyl-α-benzylpropionic acid and its chloride and amide. The following substituted amides are obtained in 95% yield by the action of dibenzylacetyl chloride on solutions of the amines: *monomethylamide*, m. p. 89—90°; *dimethylamide*, b. p. 229°/16 mm., m. p. 45°; *diethylamide*, b. p. 225°/13 mm., m. p. 56°; o-*toluidide*, m. p. 134°; p-*toluidide*, m. p. 175°; α-*naphthalide*, m. p. 155°; β-*naphthalide*, m. p. 145°. R. W. WEST.

Action of organo-magnesium derivatives on glycidic esters. (MLLE.) BARDON and (MME.) RAMART (Compt. rend., 1926, **183**, 214—216).—When excess of magnesium methyl iodide reacts with diphenylglycidic ester in the cold or when warmed, *ethyl* α-*hydroxy*-ββ-*diphenylbutyrate*, b. p. 210°/23 mm., m. p. 73°, giving, on hydrolysis, the corresponding *acid*, m. p. 167°, is formed. Magnesium phenyl bromide reacts with diphenylglycidic ester giving the *ethyl*

ester of a *hydroxy-acid*, m. p. 130°, and a *product*, m. p. 203—205°. L. F. HEWITT.

Iminolactones and salts of unsaturated nitriles. J. HOUBEN and E. PFANKUCH (Ber., 1926, **59**, [*B*], 1594—1605).—Substances containing the hydroxyl and cyano-groups in the δ-position to one another undergo intramolecular transformation in the presence of hydrochloric acid with production of imino-δ-lactones containing the group ·O·C(:NH)-.

o-Acetoxycinnamic acid is converted successively into the corresponding *chloride*, m. p. 54° after softening, *amide*, m. p. 123—125°, *nitrile*, m. p. 68—69°, and *o-hydroxycinnamonitrile*, m. p. 125—126°. Similarly, β-*o*-hydroxyphenylpropionamide yields β-*o-acetoxyphenylpropionamide*, m. p. 68—70°, β-*o-acetoxyphenylpropionitrile*, b. p. 144°/1·3 mm., m. p. 60—61°, and β-*o-hydroxyphenylpropionitrile*, b. p. 147—149°/1 mm. (*m-nitrobenzoyl* derivative, m. p. 164—165°). α-Phenyl-*o*-hydroxycinnamonitrile is converted by hydrogen chloride in anhydrous ether into 2-*imino*-3-*phenylcoumarin hydrochloride*, m. p. 140—141°, which is relatively stable towards water, but is converted by pyridine into 2-*imino*-3-*phenylcoumarin*, m. p. 105—106°, by excess of alkali hydroxide into α-phenyl-*o*-hydroxycinnamonitrile. The hydrochloride is converted by hydroxylamine hydrochloride in pyridine into 2-*oximino*-3-*phenylcoumarin*, decomp. 195—200°, by phenylhydrazine hydrochloride into the *compound*, $C_{21}H_{16}ON_2$, m. p. 146—147°, by hydrazine hydrate (1¼ mols.) into the corresponding *hydrazone*, m. p. 108—110°, by the same reagent (3½ mols.) into *phenylcoumaric acid hydrazidine*, m. p. 105—107°, and by semicarbazide hydrochloride into the *semicarbazone*, decomp. 210—213° when rapidly heated; with anthranilic acid, it yields a *compound*, m. p. 180—185° after softening. *o*-Hydroxycinnamonitrile with ethereal hydrogen chloride affords an unstable *dihydrochloride* which slowly passes into 2-*iminocoumarin dihydrochloride*, convertible by solution in glacial acetic acid and precipitation with ether into the *monohydrochloride*; the latter compound is completely stable towards water, but when treated with sodium carbonate gives the unstable 2-iminocoumarin characterised by conversion into the corresponding oxime, phenylhydrazone (a pale yellow *modification*, m. p. 143—144°, in addition to the known golden-yellow form is described), and *semicarbazone*, decomp. 218—220°. β-*o*-Hydroxyphenylpropionitrile and ethereal hydrogen chloride give unstable 2-*iminodihydrocoumarin hydrochloride*, which could not be caused to react with ketonic reagents; alkali hydroxide transforms it into a *substance*, $(C_9H_{11}O_2N)_x$, m. p. 164°. *o-Methoxycinnamonitrile*, b. p. 133—135°/0·7 mm., gives readily-dissociable *o-methoxycinnamonitrile dihydrochloride*; *p-methoxycinnamonitrile dihydrochloride* is described. *Cinnamonitrile monohydrochloride* is slowly converted by ethereal hydrogen chloride containing alcohol into *ethyl α-iminocinnamyl ether hydrochloride*, which is remarkably stable towards water, but is transformed by alkali hydroxide into the free *ether*, very readily polymerised to the *compound*, $\begin{matrix}CHPh\cdot N\text{———}C(OEt)\cdot CH_2\\ |\quad\quad\quad

m. p. 159—162°), from 6-bromopiperonal and malonic acid in presence of pyridine and piperidine, yields a product, probably 6-ω-*dibromo*-3 : 4-*methylenedioxystyrene*, m. p. 73—75°, with bromine and alkali, and furnishes on reduction β-6-bromopiperonylpropionic acid, m. p. 138—140° (*methyl* ester, m. p. 44—45°; *anhydride*, m. p. 140°; amide, m. p. 151—152°). This is identical with the product obtained by brominating β-piperonylpropionic acid, and yields 4-*bromo*-6 : 7-*methylenedioxy*-1-*hydrindone*, m. p. 197—199° (*piperonylidene* derivative, m. p. 278—281°), on treatment with phosphorus pentoxide. The derived 4-*bromo*-6 : 7-*methylenedioxy*-2-*oximino*-1-*hydrindone*, m. p. about 240° (decomp.), undergoes the Beckmann change with phosphorus pentachloride, forming the corresponding *o*-carboxyphenylacetonitrile, which is readily hydrolysed to 4-*bromo*-6 : 7-*methylenedioxyhomophthalic acid*, m. p. 215° (decomp.). This product on dehalogenation with sodium amalgam in hot alkaline solution furnishes 3 : 4-methylenedioxyhomophthalic acid, m. p. 203—204° (decomp.), the *anhydride* of which has m. p. 195°.

J. S. H. Davies.

Constitution of carbonyl-hydrogen sulphite compounds. W. Fuchs (Ber., 1926, **59**, [*B*], 1411).—Raschig's proof that the additive compounds of aldehydes or ketones with hydrogen sulphites are hydroxysulphonic acids strengthens the author's conception of the nature of the additive compounds of phenols with hydrogen sulphites. H. Wren.

Action of sulphur on organic compounds. VII. Aromatic aldehydes. L. Szperl and S. Wydrzycki (Rocz. Chem., 1926, **6**, 155—164).—Benzaldehyde when heated with sulphur in a sealed tube yields benzoic acid, stilbene, tetraphenylthiophen, γ-thiobenzaldehyde, and a hydrocarbon, m. p. 238°. Similarly treated, anisaldehyde gives anisic acid, tetramethoxytetraphenylthiophen, a sulphur-containing substance, m. p. above 360°, together with unchanged anisaldehyde. Methylenedioxybenzaldehyde yields methylenedioxybenzoic acid, probably tetra-(3 : 4-methylenedioxyphenyl)thiophen, and a stilbene derivative, m. p. 206—207°. The above reactions indicate that substitution of sulphur in the benzene nucleus does not take place under these conditions. R. Truszkowski.

Decomposition of complex aldehydes. A. Mailhe (Bull. Soc. chim., 1926, [iv], **39**, 922—924).—When complex aromatic aldehydes are heated with finely-divided nickel at 370—390° they undergo normal decomposition (cf. Sabatier and Senderens, A., 1905, i, 401) into a hydrocarbon and carbon monoxide. The product consists of this hydrocarbon and the substances formed from it by secondary reactions. Thus vanillin is converted into guaiacol and pyrocatechol, piperonal into pyrocatechol and phenol, and cinnamaldehyde into styrene, together with benzene, toluene, and ethylbenzene.

H. E. F. Notton.

Carbylamines. XIV. Reaction of phenylcarbylamine with 2-hydroxy-1-naphthaldehyde. M. Passerini (Gazzetta, 1926, **56**, 365—368; cf. A., 1924, i, 1319, 1320).—By boiling phenylcarbylamine and 2-hydroxy-1-naphthaldehyde with alcohol for 5 hrs., 2-*hydroxy*-1-*naphthylglyoxalmonoanil*, m. p. 189—191°, is obtained. By treatment with boiling 20% alcoholic sodium hydroxide, this is converted into 3 : 4-benzocoumaran-1 : 2-dione, and by excess of phenylhydrazine into 2-hydroxy-1-naphthylglyoxaldiphenylhydrazone. S. B. Tallantyre.

Catalytic action of reduced copper on oximes. (Beckmann's rearrangement. XV.) S. Yamaguchi (Mem. Coll. Sci. Kyōtō, 1926, **9**, 427—437).—See this vol., 520.

Three-carbon system. V. Alkylation of unsaturated ketones. G. A. R. Kon and (in part) L. F. Smith (J.C.S., 1926, 1792—1801).—The ready alkylation of unsaturated ketones by the action of alkyl iodide and sodium alkoxide is confined to ketones possessing a mobile three-carbon system, and can be used as a test for mobility, since static αβ- or βγ-unsaturated ketones do not react under these conditions. *cyclo*Hexenylacetone, although readily ethylated, resists methylation under similar conditions. This behaviour, which is shared by *cyclo*pentenylacetone and α-Δ^1-*cyclo*hexenylmethyl ethyl ketone, is ascribed to the dissociating action of methyl alcohol on the sodio-derivative of the ketone; it proceeded smoothly in a neutral solvent. α-*Methyl*-Δ^1-cyclo*hexenylacetone*, b. p. 101°/20 mm., 209—210°/762 mm., $d_4^{19\cdot9}$ 0·92766, $n_D^{19\cdot9}$ 1·47153, $[R_L]_D$ 45·88 (*semicarbazone*, m. p. 169°), is obtained in poor yield by using sodium methoxide in benzene, sodium ethoxide in ethyl alcohol, or sodium butoxide in butyl alcohol, the product consisting chiefly of oils of higher b. p., and in better yield by preparing the sodio-derivative with "molecular" sodium in dry ether or benzene; ethyl, *n*-propyl, *n*-butyl, and allyl derivatives were prepared in a similar manner; the *semicarbazones* of the last three melted at 152°, 125°, and 163°, respectively. α-Δ^1-cyclo*Hexenylmethyl ethyl ketone*, b. p. 90°/9 mm., $d_4^{15\cdot7}$ 0·93303, $n_D^{15\cdot7}$ 1·47697, $[R_L]_D$ 46·07 (*semicarbazone*, m. p. 153°), could not be methylated in presence of sodium methoxide, but ethylation was successful in benzene solution or in presence of sodium ethoxide. The *semicarbazone* of the ethylated ketone had m. p. 115°. Hexahydrobenzaldehyde when condensed with acetone forms α-*hydroxy*-α-cyclo*hexylbutan*-γ-*one*, b. p. 140—146°/15 mm., d_4^{20} 0·99795, n_D^{20} 1·47604, $[R_L]_D$ 47·98 (*semicarbazone*, m. p. 171—172°), *hexahydrobenzylideneacetone*, b. p. 230—232°/765 mm., 103°/9 mm., $d_4^{19\cdot6}$ 0·92228, $n_D^{19\cdot6}$ 1·48424, $[R_L]_D$ 47·21 [*semicarbazone*, m. p. 168°, *semicarbazide-semicarbazone*, m. p. about 235° (decomp.)], together with a small quantity of β-cyclo*hexylidene-ethyl methyl ketone* (α-cyclo*hexylidenebutan*-γ-*one*), b. p. 101°/9 mm., $d_4^{18\cdot6}$ 0·93706, $n_D^{18\cdot6}$ 1·47683, $[R_L]_D$ 45·86 (*semicarbazone*, m. p. 162—162·5°), which is best prepared by distilling α-hydroxy-α-*cyclo*hexylbutan-γ-one with a trace of iodine. Hexahydrobenzylideneacetone, which is readily formed from the hydroxy*cyclo*hexylbutanone by potassium hydrogen sulphate, or hydrated oxalic acid, or by oxalic acid on its semicarbazone, forms viscous polymerisation or internal condensation products when alkylated in presence of alcohol or indifferent solvents. It is oxidised to hexahydrobenzaldehyde and hexahydrobenzoic acid with per-

manganate, and condenses with ethyl malonate to form *ethyl* 1-cyclo*hexyl*-3 : 5-*diketo*cyclo*hexane*-6-*carboxylate*, m. p. 140°, which is hydrolysed by barium hydroxide to 1-cyclo*hexyl*-3 : 5-*diketo*cyclo*hexane*, m. p. 162°. α-*cyclo*Hexylidenebutan-γ-one resists oxidation with ozone, condensation with ethyl sodiomalonate, and ethylation with ethyl iodide and sodium ethoxide. Oxidation with permanganate yields adipic acid, whilst "molecular" sodium and ethyl iodide in ether furnished, apparently, a reduction product. The αβ- and βγ-ketones are converted one into the other by addition and elimination of hydrogen bromide, and show purely static relations to each other. Alkyl derivatives of allylacetone, methylheptenone (γδ-unsaturated), mesityl oxide, piperitone, *iso*phorone, and Δ^1-tetrahydroacetophenone, b. p. 81°/13 mm., d_4^{20} 0·9685, n_4^{20} 1·49042, $[R_L]_D$ 37·09 (semicarbazone, m. p. 216—217°), could not be obtained. *iso*Phorone with "molecular" sodium and ethyl iodide gave dihydro*iso*phorone (semicarbazone, m. p. 205°) and a compound, m. p. 162°, identical with the product of Hess and Munderloh (A, 1918, i, 291). J. S. H. DAVIES.

Action of benzaldehyde on cyclic ketones. R. CORNUBERT and C. BORREL (Compt. rend., 1926, **183**, 294—296; cf. A., 1924, i, 1203; 1925, i, 1070, 1071).—When treated with benzaldehyde in presence of hydrochloric acid, 6-benzyl-2-methyl*cyclo*hexanone yields a *compound*, $C_{28}H_{28}O_2$, m. p. 196° (corr.), 2-methyl*cyclo*pentanone yields a *compound*, $C_{20}H_{20}O_2$, m. p. 105° and 125°, thujone yields a *compound*, $C_{24}H_{26}O_2$, m. p. 115° and 147, all of which are considered to be of the tetrahydropyrone type (cf. A., 1925, i, 1071). 3 : 5-Dimethyl-, 3 : 5 : 5-trimethyl-, and 3-methyl-5-*iso*propyl-Δ^2-*cyclo*hexenones yield *benzylidene* compounds, m. p. 99—100°, 78—78·5°, and 91—92°, respectively, whilst 2 : 2-methyl*iso*propyl*cyclo*pentanone, 2 : 2-dibenzyl*cyclo*hexanone, and menthone do not give such compounds. The formation of a tetrahydropyrone derivative from a cyclic ketone is thus evidence of existence in the molecule of the group –CHMe·CO·CHR– or –CHMe·CO·CH_2–, and the latter group may be distinguished by the fact that it forms a benzylidene compound, whereas the former does not. L. F. HEWITT.

Organic compounds of sulphur. IV. Action of triethylphosphine and triethylphosphine peroxide on thioketones. A. SCHÖNBERG and H. KRÜLL (Ber., 1926, **59**, [*B*], 1403—1407).—Thioketones do not react with triethylphosphine at 128° in the absence of air. In boiling toluene in free presence of air, ketones, triethylphosphine oxide, and triethylphosphine sulphide are produced. The active agent is triethylphosphine peroxide; triethylphosphine oxide does not react with thioketones in the presence of air or of triethylphosphine. Di-*p*-anisyl ketone, 4 : 4′-diethoxybenzophenone, 4 : 4′-dimethoxy-3 : 3′-dimethylbenzophenone, 4 : 4′-diethoxy-3 : 3′-dimethylbenzophenone, and xanthone are obtained from the respective thio-compounds, whereas 4 : 4′-tetramethyldiaminothiobenzophenone could not be desulphurised in this manner. H. WREN.

Reactivity of *meso*-substituted anthracenes. II. J. W. COOK (J.C.S., 1926, 1677—1684; cf. this vol., 838).—Anthraphenone (9-benzoylanthracene) behaves like an αβ-unsaturated ketone in forming 9 : 10-dihydroanthraphenone, m. p. 103° (m. p. 101°, Lippmann and Keppich, A., 1901, i, 37), and/or 10 : 10-*dibenzoyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthryl*, m. p. 269°, on reduction under a variety of conditions. They are produced by the ketonic rearrangement of the primarily formed enols, which could not be isolated, although in one case evidence of the *diacetate*, m. p. 315°, of the dienol, which is also formed by the direct acetylation of the latter, was obtained during reduction with zinc and acetic anhydride. Dihydroanthraphenone readily loses its benzoyl group with alkali, forming dihydroanthracene, m. p. 108—110°. This instability, which is also shared by the tetrahydrodianthryl, appears to depend on the presence of a potentially mobile hydrogen. When reduced with sodium and alcohol, or with zinc dust and potassium hydroxide, dihydroanthraphenone forms dihydroanthracene, whilst with hydriodic acid and phosphorus it forms 9-benzyl-9 : 10-dihydroanthracene, m. p. 119—120° (m. p. 110—111°, Bach, Ber., 1890, **23**, 2530). Although it forms an *acetate*, m. p. 202°, which regenerates the dihydroanthraphenone with alcohol and sulphuric acid and forms the dihydroanthracene with alcoholic potassium hydroxide, the keto–enol equilibrium is in favour of the ketonic form [stercoisomeric(?) oximes, m. p. 162—163° and 187—190°, *ketimine*, m. p. 185—186°]. With bromine, dihydroanthraphenone forms 10-bromoanthraphenone, a reaction which probably involves the primary addition of halogen to the ethylenic linking of the enol. The dibenzoyltetrahydrodianthryl is converted by sodium amyloxide into 9 : 9′ : 10 : 10′-tetrahydrodianthryl, m. p. 256—257°, which is also obtained by reducing dihydrodianthryl.

9 : 10-*Dibenzoyl*-9 : 10-*dihydroanthracene*, m. p. 194—195°, which is obtained by reducing 9 : 10-dibenzoylanthracene, and is converted into 9 : 10-dihydroanthracene by sodium amyloxide, also displays tautomerism, its formation being probably due to the addition of hydrogen to the extreme ends of the conjugated system with subsequent rearrangement to the ketone. The diacetate of the dienol could not be prepared, although a *compound*, m. p. 145—150°, contaminated with dibenzoylanthracene, was obtained by acetylation, which gave ethyl acetate on hydrolysis. Dibenzoyldihydroanthracene is oxidised by bromine to dibenzoylanthracene, and reduced by hydriodic acid and phosphorus to 9-benzyl-9 : 10-dihydroanthracene. The "tribenzoylanthracene" and the tetrahydro-compound, m. p. 187—188°, of Lippmann and Keppich (*loc. cit.*) are probably impure specimens of 9 : 10-dibenzoylanthracene and 9 : 10-dibenzoyl-9 : 10-dihydroanthracene, respectively. J. S. H. DAVIES.

Polycyclic structures in relation to their homocyclic unsaturated isomerides. VII. Tautomerism corresponding with that of nitrosophenol and quinoneoxime in the *dicyclo*pentane series. A. HASSELL and C. K. INGOLD (J.C.S., 1926, 1836—1840).—The behaviour of 5-*cyclo*hexane-*spirocyclo*penten-3-ol-1 : 4-dione in forming 4-*oximino*-5-cyclo*hexane*spirocyclo*penten*-3-*ol*-1-*one*, m. p. 205°, which shows evidence of existing as 4-*nitroso*-5-cyclo*hexane*spiro-0 : 1 : 2-dicyclo*pentene*-1 : 3-*diol* in being

readily oxidised by potassium ferricyanide to 4-*nitro*-5-cyclo*hexane*spiro-0 : 1 : 2-dicyclo*pentene*-1 : 3-*diol*, m. p. 137—139°, which gives the same 4-*nitro*-1 : 3-*dimethoxy*-5-cyclo*hexane*-0 : 1 : 2-spirodicyclo*pentene*, m. p. 70—73°, on methylation, as that obtained by the oxidation and subsequent methylation of 3-*methoxy*-4-*oximino*-5-cyclo*hexane*spirocyclo*pentene*-1 : 4-*dione*, m. p. 150—160° (impure), derived from 3-*methoxy*-5-cyclo*hexane*spirocyclo*pentene*-1 : 4-*dione*, m. p. 117°, which is obtained by methylating 5-*cyclo*hexane*spirocyclo*penten-3-ol-1 : 4-dione, shows that the reactions of these oximes are closely parallel to those of benzoquinonemonoxime. 4-Oximino-5-*cyclo*hexane*spirocyclo*penten-3-ol-1-one on further oximation yields the 1 : 4-*dioximino*-derivative, m. p. 250° (decomp.). J. S. H. DAVIES.

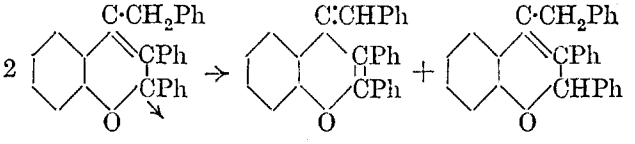
Acid constituents of the resin of *Pinus pinea*. G. DUPONT and J. DUBOURG (Bull. Soc. chim., 1926, [iv], **39**, 1029—1036; cf. A., 1924, i, 866, 1068).—If the solid constituent of the gum of *Pinus pinea* is fractionally precipitated by water from its solution first in ethyl and then in methyl alcohol, pineic acid, m. p. 119—120°, $[\alpha]_D$ −113·3°, is obtained; as it is readily isomerised to abictic acid by the action of hydrochloric acid or heat, it must have the formula $C_{20}H_{30}O_2$. During the isomerisation to abietic acid, a minimum value for the rotatory power $[\alpha]_D$ −25·3° is reached. If the solution is then neutralised and the intermediate product isolated, an acid is obtained which cannot be purified, as it readily changes to abietic acid, with which it is isomorphous. This acid is termed pinabietic acid, and is very similar to, if not identical with alepabietic acid. Experiments show that it is unlikely that this intermediate product is either a mixture of pineic and abietic acids or a compound of pineic acid with hydrochloric acid or the solvent. R. W. WEST.

Sesquiterpene family in camphor blue oil. I. Reaction with sulphur and the resulting compounds. T. KOIKE (J. Soc. Chem. Ind. Japan, 1926, **29**, 214—221).—A sesquiterpene, b. p. 122—125°/12 mm., d_4^{21} 0·91242, n_D^{21} 1·5035, $[\alpha]_D^{24}$ −28·55°, and two sesquiterpene alcohols, b. p. 156—159°/18 mm., 165—169°/18 mm., d_4^{21} 0·95902, 0·96353, n_D^{21} 1·5017, 1·5017, $[\alpha]_D^{24}$ +40·98°, +61·67°, were isolated from a commercial Japanese camphor blue oil. By heating the sesquiterpene or alcohols (20 g.) with sulphur (12 g.) at 215—225° until hydrogen sulphide was no longer evolved, a black, semi-solid substance was obtained, which was divided into two fractions, soluble and insoluble in ether, respectively. From the insoluble part, a compound corresponding with $C_{20}H_{16}O_4$ was obtained. The soluble part was distilled under 20—25 mm. pressure and cadalene was isolated from the distillate. From the residue, compounds, $C_{20}H_{18}O_5$ and $C_{30}H_{26}O_2S_5$, were isolated. When the latter is heated at 250—260°/70 mm. in a current of moist air, hydrogen sulphide, methyl and *iso*propyl alcohols, and compounds closely corresponding with $C_{20}H_{20}O_6$ and $C_{20}H_{22}O_7$ are obtained. K. KASHIMA.

Constitution of catechin. IX. Disintegration products of acacatechin. M. NIERENSTEIN (J. Amer. Chem. Soc., 1926, **48**, 1959—1975).—In view of the uncertainty of the structure of cyanidin chloride (cf. A., 1925, i, 422), its conversion into epicatechin (Freudenberg, A., 1925, i, 1165) is as consistent with the author's diphenylpropane structure for acacatechin as with Freudenberg's formula. On oxidation with neutral permanganate in acetone, 4 : 6 : 3′ : 4′-tetramethylacacatechin (4 : 6 : 3′ : 4′-tetramethoxy-2-hydroxy-3-phenylchroman) affords the 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one (p-*bromophenylhydrazone*, m. p. 257—259° [decomp.]) previously described (J.C.S., 1921, **119**, 167), together with some 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-1 : 2-dione, 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylcoumarin, 6-hydroxy-2 : 4 : 3′ : 4′-tetramethoxy-αα-diphenylacetic acid, and resinous by-products. Amyl nitrite in alcohol with hydrochloric acid converts the ketone into 1-iso*nitroso*-4 : 6 : 3′ : 4′-*tetramethoxy*-3-*phenylchroman*-2-*one*, m. p. 116° (yield 88%), which with acetic acid and 10% sulphuric acid gives in 91% yield 2-*hydroxy*-4 : 6 : 3′ : 4′-*tetramethoxy*-3-*phenylcoumarin*, m. p. 181° (*acetyl* derivative, m. p. 153°). The formation of this substance instead of the 4 : 6 : 3′ : 4′-tetramethylquercetin required by the Freudenberg formula for catechin affords confirmation of the author's formula. 2 : 4 : 6 : 3′ : 4′-*Pentamethoxy*-3-*phenylcoumarin*, obtained with diazomethane or methyl iodide and silver oxide in ethereal solution, has m. p. 146°. On treatment with sodium hydroxide, 2-hydroxy-4 : 6 : 3′ : 4′-tetramethoxy-3-phenylcoumarin yields veratric acid and trimethylphloroglucinol, whilst with hydriodic acid (*d* 1·7) and acetic anhydride it affords a substance $(C_{15}H_{11}O_6)_x$, m. p. 162—163°, apparently identical with the product obtained by Ciamician and Silber by the action of hydriodic acid on 4 : 6 : 3′ : 4′-tetra-acetoxy-3-phenylcoumarin (A., 1894, i, 471). Dissolved in acetone, it is converted into the yellow α-diketone, 4 : 6 : 3′ : 4′-*tetramethoxy*-3-*phenylchroman*-1 : 2-*dione*, m. p. 134°. The latter, which is best obtained by the oxidation of 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one, is converted into the colourless enol by solution in alcohol; both forms appear to be stable in carbon tetrachloride. With 3 : 4-tolylenediamine, the diketone affords no definite condensation product, but diazomethane in ether yields 1 : 2-*methylenedioxy*-4 : 6 : 3′ : 4′-*tetramethoxy*-3-*phenylchroman*, m. p. 122°, and oxidation with neutral permanganate gives formic acid and 6-hydroxy-2 : 4 : 3′ : 4′-tetramethoxy-αα-diphenylacetic acid (yield 93%). Since on oxidation in alkaline solution with potassium permanganate tetramethylacacatechin also affords the latter acid, together with dimethylphloroglucinol and veratic acid and 4 : 6 : 3′ : 4′ tetramethoxy-3-phenylchroman-2-one, it is concluded that fission of the chroman nucleus precedes oxidation and that the veratric acid and phloroglucinol ether are secondary products. This view is supported (1) by the oxidation of 2 : 4 : 6 : 3′ : 4′-pentamethoxy-αα-diphenylacetic acid and of pentamethylmaclurin with alkaline potassium permanganate to trimethylphloroglucinol and veratric acid, and (2) by the conversion of pentamethylacacatechin with alcoholic potassium hydroxide and methyl iodide or methyl sulphate into βγ-2 : 4 : 6 : 3′ : 4′-*heptamethoxy*-αα-*diphenylpropane*, m. p. 122°, which itself affords

2 : 4 : 6 : 3′ : 4′-pentamethoxy-αα-diphenylacetic acid on oxidation. The structure of the heptamethoxy-compound is further confirmed by its synthesis from 2 : 4 : 6 : 3′ : 4′-pentamethoxydiphenylmethyl chloromethyl ketone (J.C.S., 1920, **117**, 1154). The latter with alcoholic potassium acetate affords *γ-acetoxy-2 : 4 : 6 : 3′ : 4′-pentamethoxy-αα-diphenylpropan-β-one*, m. p. 162°, converted by acetic anhydride in the presence of zinc dust into *βγ-diacetoxy-2 : 4 : 6 : 3′ : 4′-pentamethoxy-αα-diphenylpropane*, m. p. 173°, from which the βγ-2 : 4 : 6 : 3′ : 4′-heptamethoxy-derivative is obtained by treatment with alcoholic potassium hydroxide and methyl sulphate. Recent work by Ryan (A., 1925, i, 1268) is discussed and the different results obtained by different workers on Kostanecki's methylated reduction products of catechin are attributed to mobility of the nucleus B. The author concludes that 2 : 4 : 6 : 3′ : 4′-pentamethoxy-αα-diphenylpropane is the normal disintegration product. In reply to Freudenberg and Purrmann (A., 1924, i, 868), the different results obtained by ethyl acetate and by ether extraction in the preparation of catechin are emphasised. The low m. p. recorded by these workers for tetramethylacacatechin is attributed to the presence of traces of the heptamethyl derivative, and in view of their criticisms, the synthesis of 4 : 6 : 3′ : 4′-tetramethoxy-3-phenylchroman-2-one and its reduction to tetramethylacacatechin have been repeated and confirmed. R. BRIGHTMAN.

2 : 3 : 4-Trisubstituted chromenyl radicals. A. LÖWENBEIN and B. ROSENBAUM (Annalen, 1926, **448**, 223—248).—*2 : 3 : 4-Triphenylchroman-2-ol*, m. p. 159°, from 3-phenylcoumarin and magnesium phenyl bromide, loses the elements of water when boiled with acetic acid, forming *2 : 3 : 4-triphenyl-γ-chromene*, m. p. 131°, which partly regenerates the chromanol when boiled with aqueous-alcoholic potassium hydroxide, and is oxidised by ferric chloride to *2 : 3 : 4-triphenylbenzopyrylium ferrichloride*, m. p. 189°; this is hydrolysed with aqueous acetone to the *ψ*-base, *2 : 3 : 4-triphenylchromen-2-ol*, m. p. 158° (*methyl ether*, m. p. 139°, *ethyl ether*, m. p. 126°), which with perchloric acid yields the corresponding *benzopyrylium perchlorate*, m. p. 268°. The latter reacts with magnesium phenyl bromide to form *bis-2 : 3 : 4-triphenylchromenyl*, m. p. 150—165°, and 2 : 2 : 3 : 4-tetraphenyl-α-chromene, m. p. 195°. The former on air oxidation yields the corresponding *peroxide*, m. p. 152°, which regenerates the above pyrylium salts with ferric chloride and perchloric acid, respectively, and with sodium–potassium alloy in absence of air it forms *potassium 2 : 3 : 4-triphenylchromenyl*, whilst with ethereal hydrogen chloride it furnishes the *triphenylbenzopyrylium chloride hydrochloride*, m. p. 167°, together with an oil. The following compounds were prepared by the same general methods: *2 : 3-diphenylbenzopyrylium perchlorate*, m. p. 248°; 2 : 3-diphenyl-4-(α-naphthyl)-γ-chromene, m. p. 166° (*benzopyrylium ferrichloride*, m. p. 220°; *pyrylium perchlorate*, m. p. 247°), *bis-2 : 3-diphenyl-4-(α-naphthyl)chromenyl*, m. p. 185° (*peroxide*, m. p. 171°); *2 : 3-diphenyl-4-benzyl-γ-chromene*, m. p. 118° (*pyrylium ferrichloride*, m. p. 181°; *pyrylium perchlorate*, m. p. 186°), *bis-2 : 3-diphenyl-4-benzylchromenyl*, m. p. 160°; *2 : 4-di-α-naphthyl-3-phenyl-γ-chromene*, m. p. 204° (*pyrylium ferrichloride*, m. p. 233°; *pyrylium perchlorate*, m. p. 223°), *bis-2 : 4-di-α-naphthyl-3-phenylchromenyl peroxide*, m. p. 252—253°. 2 : 4-Di-α-naphthyl-3-phenylchroman-2-ol could not be isolated owing to the ease with which it loses the elements of water to form the chromene. The corresponding bischromenyls are the sole products of the action of magnesium α-naphthyl bromide on the triphenylbenzopyrylium perchlorate, and of magnesium phenyl bromide on 2 : 3-diphenyl-4-α-naphthyl-, 2 : 3-diphenyl-4-benzyl-, 2 : 4-di-α-naphthyl-3-phenyl-benzopyrylium perchlorates. In the case of the last compound, it was not isolated, but its presence was shown by conversion into the peroxide. The colourless bischromenyls, which are also readily formed by treating acetone solutions of the pyrylium perchlorates with zinc, develop a green colour on dissolution or fusion, owing to dissociation into free radicals, which probably contain a tervalent carbon atom in the 2-position. The green solutions are decolorised by air oxidation, forming colourless peroxides. The dissociation was followed by mol. wt. determinations in naphthalene solution. The behaviour of bis-2 : 3-diphenyl-4-benzylchromenyl is exceptional here, in that the green solutions of the free radicals are decolorised on boiling, forming *2 : 3-diphenyl-4-benzylidene-γ-chromene*, m. p. 154° (also formed from 2 : 3-diphenyl-4-benzylbenzopyrylium perchlorate and pyridine), and probably 2 : 3-diphenyl-4-benzyl-α-chromene, which was not obtained pure:



J. S. H. DAVIES.

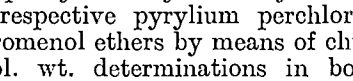
Tervalent carbon. V. Dissociation of bischromenyls and the use of chromous chloride for the preparation of free methyl radicals. K. ZIEGLER, F. A. FRIES, and F. SALZER (Annalen, 1926, **448**, 249—264; cf. preceding abstract).—The following benzopyrylium perchlorates were prepared by the action of magnesium phenyl bromide on the requisite flavone, followed by treatment of the chromenols with perchloric acid: *2 : 4-diphenyl-6-methylbenzopyrylium perchlorate*; *2 : 4-diphenyl-6-methyl-3-ethylbenzopyrylium perchlorate*, m. p. 205°; *2 : 4-diphenyl-6-methyl-3-propylbenzopyrylium perchlorate*, m. p. 194°; *2 : 3 : 4-triphenyl-6-methylbenzopyrylium perchlorate*, m. p. 282°; the corresponding 3 : 6-*dimethyl* and 3-iso*propyl* compounds were not obtained pure. The *methyl ethers* of 2 : 4-diphenyl-3 : 6-dimethylchromen-2-ol and 2 : 4-diphenyl-6-methyl-3-*iso*propylchromen-2-ol melt at 123° and 117—118°, respectively. Labile *2 : 3 : 4-triphenyl-6-methylchromen-4-ol*, m. p. 139—140°, is obtained from the corresponding flavone and magnesium phenyl bromide, whereas on fusing the labile isomeride or heating its benzene solution, stable *2 : 3 : 4-triphenyl-6-methylchromen-2-ol*, m. p. 163°, is obtained, which

can also be prepared from magnesium phenyl bromide and 3 : 4-diphenyl-6-methylcoumarin, m. p. 208—209° (obtained by heating a mixture of sodium phenylacetate, phenylacetyl chloride, and *o*-benzoyl-*p*-cresol), and also by the hydrolysis of 2 : 3 : 4-triphenyl-6-methylbenzopyrylium perchlorate with sodium hydroxide. *Bis*-2 : 4-*diphenyl*-3 : 6-*dimethylchromenyl*, *bis*-2 : 4-*diphenyl*-6-*methyl*-3-*ethylchromenyl*, and *bis*-2 : 3 : 4-*triphenyl*-6-*methylchromenyl* are obtained from the respective pyrylium perchlorates, chromenols, or chromenol ethers by means of chromous chloride. Mol. wt. determinations in boiling toluene show that the degree of dissociation into free radicals in the last two chromenyls is 14—16% and 44—58%, respectively. Their cold benzene solutions when shaken in air exhibit alternating disappearance and reappearance of colour, the latter being due to the oxidation of the primarily formed peroxides. The limited dissociation under these conditions harmonises with the behaviour of their deep green solutions in boiling toluene or xylene, which become decolorised on cooling quickly in absence of air and re-develop colour on further heating. The isolation of the two forms of 2 : 3 : 4-triphenyl-6-methylchromenol appears to indicate that the stable position of the free valency is at the 2-carbon atom.

J. S. H. Davies.

Synthesis of anthocyanins. I. A. Robertson and R. Robinson (J.C.S., 1926, 1713—1720).—*p*-Acetoxybenzoyl chloride, b. p. 157°/20 mm., m. p. 30° (prepared by the action of thionyl chloride on *p*-acetoxybenzoic acid), and ethyl sodio-αγ-dimethoxyacetoacetate react in ethereal solution, and the product is hydrolysed to p-*hydroxy*-ω-*methoxyacetophenone*, m. p. 130—131°. Its *potassium* salt with tetra-acetyl-β-glucosidyl bromide (β-bromotetra-acetylglucose), in aqueous acetone solution, gives p-*tetra*-*acetyl*-β-*glucosidoxy*-ω-*methoxyacetophenone*, m. p. 125—126°. When this is treated with β-resorcylaldehyde and hydrogen chloride in formic acid solution, partial removal of the sugar group occurs, leading to 7 : 4′-*dihydroxy*-3-*methoxyflavylium chloride* [*ferrichloride*, m. p. 179—180°; *picrate*, m. p. 250—252° (decomp. from 220°)], whilst in ethereal solution the product is 4′-*tetra*-*acetyl*-β-*glucosidoxy*-7-*hydroxy*-3-*methoxyflavylium chloride*, m. p. 219—220° (decomp. from 200°) [picrate, m. p. 225—226° (decomp.)]. Treatment of the tetra-acetyl compound with ammonia in methyl alcohol at 0°, followed by the action of dilute hydrochloric acid, yields 4′-β-*glucosidoxy*-7-*hydroxy*-3-*methoxyflavylium chloride*, decomp. at about 300° [*picrate*, m. p. 199—220° (decomp.)]. Hydrolysis with hydrochloric acid converts this anthocyanin-like substance into the anthocyanidin, 7 : 4′-*dihydroxy*-3-*methoxyflavylium chloride*. By using orcylaldehyde instead of β-resorcylaldehyde in the condensations, the following have been prepared: 7 : 4′-*dihydroxy*-3-*methoxy*-5-*methylflavylium chloride* (*ferrichloride*, softens at 150°, decomp. 220—222°); 4′-*tetra*-*acetyl*-β-*glucosidoxy*-7-*hydroxy*-3-*methoxy*-5-*methylflavylium chloride* [*picrate*, m. p. 222—223° (decomp. from 218°)], obtained by condensation in formic acid, but better in ethereal solution; 4′-β-*glucosidoxy*-7-*hydroxy*-3-*methoxy*-5-*methylflavylium chloride* [*picrate*, m. p. 202—203° (decomp.)].

F. M. Hamer.

Substituted *spiro*benzopyrans. A. Löwenstein and W. Katz (Ber., 1926, **59**, [*B*], 1377—1383).—Ethyl methylacetoacetate and salicylaldehyde in ethereal solution in the presence of hydrogen chloride and perchloric acid afford 2-o-*hydroxystyryl*-3-*methylbenzopyrylium perchlorate*, m. p. 243°, which is transformed by ammonia into 3-*methyl*spiro-*dipyran*,  , m. p. 81°, converted by methyl alcohol and hydrochloric acid into 2-*methoxy*-2-o-*hydroxystyryl*-3-*methylchromene*, m. p. 233°. Similarly, ethyl or methyl benzylacetoacetate and salicylaldehyde yield 2-o-*hydroxystyryl*-3-*benzylbenzopyrylium perchlorate*, m. p. 234°, which, with ammonia, affords 3-*benzyl*spiro*dibenzopyran*, m. p. 121°. 2-*Phenyl*-3-*methylbenzopyrylium perchlorate*, m. p. 177°, is prepared analogously from ethyl methylbenzoylacetate and salicylaldehyde or propiophenone and salicylaldehyde. β-Naphthol-α-aldehyde and ethyl methylacetoacetate in formic acid solution in presence of perchloric acid yield 2-o-*hydroxy*-α-*benzostyryl*-3-*methyl*-β-*naphthapyrylium perchlorate*, m. p. about 320° (decomp.), and thence 3-*methyl*spiro*di*-2 : 2′-β-*naphthapyran*, m. p. 203°. 2-o-*Hydroxy*-α-*benzostyryl*-3-*benzyl*-β-*naphthapyrylium perchlorate*, m. p. 257° (decomp.), 3-*benzyl*spiro*di*-2 : 2′-β-*naphthapyran*, m. p. 207°, 2-o-*hydroxy*-α-*benzostyryl*-3-*phenyl*-β-*naphthapyrylium perchlorate*, and 3-*phenyl*spiro*di*-2 : 2′-β-*naphthapyran*, m. p. 240°, are described.

H. Wren.

Diazotisability of aminothiophens. W. Steinkopf and P. J. Müller (Annalen, 1926, **449**, 210—222).—Nitration of thiophen-2-carboxylic acid (cf. Römer, A., 1887, 362) gives 4-nitrothiophen-2-carboxylic acid, m. p. 146—147°, together with small amounts of the 5-nitro-isomeride, which is detected by decarboxylation in a current of steam, when a little 2-nitrothiophen, m. p. 46°, distils over. 4-Nitrothiophen-2-carboxylic acid and many of its salts resist decarboxylation, but 3-*nitrothiophen*, m. p. 64—67°, is obtained by heating the acid at 250—270° with a nickel catalyst. 4-*Aminothiophen*-2-*carboxylic acid hydrochloride* is obtained by reduction of the nitro-acid with tin and hydrochloric acid. The amino-acid (*acetyl* derivative, m. p. 272—273°) when diazotised (as the chlorostannite) in concentrated hydrochloric acid and coupled with β-naphthol gives 2-*carboxy*-4-*thiophenazo*-β-*naphthol*, isolated as the *acetyl* derivative, decomp. 204°.

When a solution of 2-aminothiophen chlorostannite in hydrochloric acid is diazotised, two solid products can be isolated, viz., the chlorostannite of aminoazothiophen and *thiophen*-2-*diazonium chloride* (?). The latter, not obtained pure, gives a yellow wool *dye* with *m*-phenylenediamine and on keeping becomes red, probably owing to coupling with 2-hydroxythiophen formed by decomposition.

C. Hollins.

Comparative behaviour of hydroxypyrroline- and pyrrolidone-carboxylic acids towards ozone. E. Abderhalden and E. Schwab (Z. physiol. Chem., 1926, **157**, 146—147; cf. this vol., 630).—When

treated with ozone in chloroform, hydroxypyrrolinecarboxylic acid affords a liquid *ozonide*, from which, on treatment with silver oxide by Tollens' method, the *silver* salt, $CHO{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2Ag$, decomp. 107°, was obtained. Pyrrolidonecarboxylic acid is not attacked by ozone under similar conditions.

F. G. WILLSON.

Action of sodioisatin on ethyl chloroformate. G. HELLER and H. LAUTH (J. pr. Chem., 1926, [ii], **113**, 225—232).—The work of Hantzsch (A., 1924, i, 420) criticising Heller (A., 1918, i, 309) is also inaccurate. Heller stated that ethyl isatin-1-carboxylate when boiled with water gave 2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylie acid. This was renamed formylisatoic acid by Hantzsch, but it is now found that mere addition of water occurs, to give *N*-carbethoxyisatoic acid (new m. p. 149—150°), as is shown by analysis and by the regeneration of the original ester on heating with acetic anhydride. The ethyl ester is similarly renamed, and the "phenylhydrazide" is found to be the phenylhydrazine salt of *N*-carbethoxyisatoic acid phenylhydrazone. 2 : 4-Dihydroxy-1 : 2 : 3 : 4-tetrahydroquinoline-2-carboxylic acid (Heller, *loc. cit.*) or formylanthranilic acid (Hantzsch) is actually *N*-carbethoxyanthranilic acid, already known (Ber., 1889, **22**, 1674).

The product of heating methyl isatin-1-carboxylate with water is N-*carbomethoxyisatoic acid*, yellow, m. p. 147°, which was previously confused with the carbethoxy-homologue under the name of 2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylic acid, of which the "methyl ester, m. p. 85°," is the methyl ester of this new acid. The new acid oxidises to *N*-carbomethoxyanthranilic acid.

Ethyl 5-bromo- and 5-chloro-2 : 3-dihydroxy-2 : 3-dihydroindole-2-carboxylic acids (Heller and Jacobsohn, A., 1921, i, 440) are to be renamed ethyl 5-bromo- and 5-chloro-*N*-carbethoxyisatoate.

The interaction of sodioisatin and benzoyl chloride in the presence of alcohol gives *ethyl* N-*benzoylisatoate*, m. p. 80—81° (*phenylhydrazone*, m. p. 95°; *oxime*, m. p. 103—104°), which is also obtained from the corresponding acid or from 1-benzoylisatin, and from which N-*benzoylisatoamide*, m. p. 215—216° (decomp.), is prepared. E. W. WIGNALL.

Synthesis of hydroxymethoxy-*N*-methyl-3 : 4-dihydro*iso*quinolinium salts. S. AKABORI (Bull. Chem. Soc. Japan, 1926, **1**, 96—102, 125—128).—Treatment of β-3-methoxy-4-benzyloxyphenylethylamine with benzaldehyde gives *benzylidene*-β-3-*methoxy*-4-*benzyloxyphenylethylamine*, m. p. 57—59°, the methiodide of which, when hydrolysed, yields *methyl*-β-3-*methoxy*-4-*benzyloxyphenylethylamine*, b. p. 200—202°/3·5 mm. (*hydrochloride*, m. p. 157—158°; *picrate*, m. p. 163·5—165°). The *formate* (m. p. 105—106°) of this compound gives, on heating, β-3-*methoxy*-4-*benzyloxyphenylethylformylmethylamide*, m. p. 78—80°, which can also be obtained from *formyl*-β-3-*methoxy*-4-*benzyloxyphenylethylformamide*, m. p. 69—71°. The formyl methyl compound, treated with thionyl chloride, yields 6-*methoxy*-7-*benzyloxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *chloride*, m. p. 135—138° (anhydrous), *picrate*, m. p. 177—178°. This last compound, on oximation, gives 4-*methoxy*-5-*benzyloxy*-2-ω-*methylaminoethyl*-1-*benzaldoxime*, m. p. 166—167°, and on hydrolysis yields 7-hydroxy-6-methoxy-2-methyl-3 : 4-dihydro*iso*quinolinium chloride (cf. Pyman, J.C.S., 1910, **97**, 268). Benzyl iodide acts on the phenolbetaine of 6 : 7-dihydroxy-2-methyl-3 : 4-dihydro*iso*quinolinium hydroxide to form 7-*hydroxy*-6-*benzyloxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *iodide*, m. p. 189—190°, with some 6 : 7-*dibenzyloxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *iodide*, m. p. 194—195°. Concentrated solutions of the former compound, treated with potassium carbonate, give 6-*benzyloxy*-7-(7-*hydroxy*-6-*benzyloxy*-2-*methyl*-3 : 4-*dihydro*isoquinoliniumoxy)-2-*methyl*-3 : 4-*dihydro*isoquinolinium *iodide* (?), m. p. 196—198°, and from this 7-*hydroxy*-6-*benzyloxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *picrate*, m. p. 176—177°, and *perchlorate*, m. p. 222—225°, are obtained. Partial hydrolysis of this perchlorate yields 6-*hydroxy*-7-*methoxy*-2-*methyl*-3 : 4-*dihydro*isoquinolinium *perchlorate*, m. p. 178—179·5°. *Methylhomovanillylamine hydrochloride*, $OH{\cdot}C_6H_3(OMe){\cdot}CH_2{\cdot}CH_2{\cdot}NH_2MeCl$, m. p. 149·5—151°, is obtained by the action of concentrated hydrochloric acid on methyl-β-3-methoxy-4-benzyloxyphenylethylamine. B. W. ANDERSON.

Synthesis of pyrrole- and pyrrolidone-carboxylic acids and of pyrrole-2-carbithionic acid. C. M. MCCAY and C. L. A. SCHMIDT (J. Amer. Chem. Soc., 1926, **48**, 1933—1939).—Attempts to synthesise proline by reduction of pyrrolidone-2-carboxylic acid and pyrrole-2-carboxylamide were unsuccessful. Reduction took place when pyrrole-2-carboxylic acid was treated with hydrogen in 50% alcohol containing hydrochloric acid in the presence of platinum oxide, but the product was not proline. The maximum yield (40%) of pyrrole-2-carboxylic acid is obtained when the magnesium pyrryl iodide is prepared with 1·4 mols. of magnesium methyl iodide to 1 mol. of pyrrole. Further excess of magnesium methyl iodide yields only acetic acid (cf. this vol., 506). Magnesium pyrryl iodide shows no luminescence when oxygen impinges on the surface of its solution. *Pyrrole*-2-*carbithionic acid* (*iron*, *lead*, and *mercury* salts), a dark brown oil which partly crystallises and is readily oxidised on exposure to air, is obtained by the action of pyrrole and carbon disulphide on an ethereal solution of magnesium methyl iodide. Pyrrolidone reacts normally with magnesium methyl iodide, and migration of the –MgX group to the 2-position does not occur.

R. BRIGHTMAN.

Pyridine and quinoline tartrates. PARISELLE (Compt. rend., 1926, **183**, 210—211).—From an examination of the rotatory powers of tartaric acid in various mixtures of pyridine and water, and quinoline and water, it is inferred that pyridine hydrogen tartrate does not exist in solution, but that dipyridine tartrate is formed and is completely ionised except in the presence of a large excess of pyridine. The case of quinoline is similar except that diquinoline *d*-tartrate is not totally ionised in aqueous solution, and is lævorotatory. Only *pyridine hydrogen* d-*tartrate*, m. p. about 150°, $[M]_{5780}$ +7·5° in cresol

solution, and *quinoline hydrogen* d-*tartrate*, m. p. 122°, $[M]_{5780}$ +9·7°, could be isolated in the solid state.

L. F. HEWITT.

Action of α-picoline on alkali hexachloroiridates. M. GUILLOT (Bull. Soc. chim., 1926, [iv], **39**, 852—864).—The action of α-picoline on alkali chloroiridates is more complicated than that of pyridine (cf. Delépine, A., 1923, i, 944), prolonged treatment leading to resinification. If aqueous ammonium hexachloroiridate is heated at 100° for a few minutes with hydrochloric acid and excess of picoline, the solution becomes cloudy and contains *iridium diaquotrichloropicoline*, $[IrCl_3(H_2O)_2(C_6H_7N)]$, pink leaflets, which is oxidised by aqua regia to *iridium tetrachlorodipicoline*, $[IrCl_4(C_6H_7N)_2]$. If the heating is continued for an hour, *iridium trichlorotripicoline*, $[IrCl_3(C_6H_7N)_3]$, yellow leaflets, is obtained. This yields the *salt* $(C_6H_8N)_2[IrCl_6]$ on oxidation. The mother-liquors from the preparation of iridium diaquotrichloropicoline contain the complex *salt*, $\{2[IrCl_6](NH_4)_3,[IrCl_5(C_6H_7N)](C_6H_8N)_2,(C_6H_8N)Cl,3NH_4Cl\}$, brownish-black, which may also be prepared by mixing solutions of the component simple salts. Potassium may partly replace ammonium in this compound. *Picolinium picolinopentachloroiridate*, $(C_6H_8N)_2[IrCl_5(C_6H_7N)]$, is obtained together with *picolinium hexachloroiridate*, $(C_6H_8N)_3[IrCl_6]$, when iridium diaquotrichloropicoline is heated with picoline hydrochloride in acid solution. *Silver* and *thallium picolinopentachloroiridates* form insoluble yellow powders.

H. E. F. NOTTON.

Structure of ammines of bivalent platinum. A. ROSENHEIM and W. HÄNDLER (Ber., 1926, **59**, [*B*], 1387—1390; cf. Reihlen and Nestle, this vol., 699).—Potassium chloroplatinite yields the *salts* $[Pt(C_7H_8ON_2)_2Cl_2]$ and $[Pt(C_5H_6N_2)_2Cl_2]$ with 2-amino-1-acetylpyridine and 3-aminopyridine, respectively, *m*-Tolylenediamine and potassium chloroplatinite afford the monotolylenediamine derivative, converted by an excess of base into the *compound* $[Pt(C_7H_{10}N_2)_2]Cl_2$ [corresponding *sulphate* (+$3H_2O$) and *dithionate*], which could not be resolved by means of silver bromocamphorsulphonate or ammonium *d*-tartrate (the *salt*, $2[Pt(C_7H_{10}N_2)_2]C_4H_4O_6,(NH_4)_2C_4H_4O_6,12H_2O$, is described).

H. WREN.

Two homologues of cinchomeronic acid and their degradation. O. MUMM and R. NEUMANN (Ber., 1926, **59**, [*B*], 1616—1624; cf. Mumm and Hüneke, A., 1918, i, 183; Mumm and Böhme, *ibid.*, 1921, i, 439).—6-Phenyl-2-methylpyridine-3 : 4-dicarboxylic acid is converted by acetic anhydride into the corresponding *anhydride*, m. p. 196°, transformed by ammonia into 6-*phenyl*-2-*methylpyridine* 4-*carboxylamide*-3-*carboxylic acid*, m. p. 199° (corresponding *imide*, m. p. 249°), and by boiling ethyl alcohol into 4-*carbethoxy*-6-*phenyl*-2-*methylpyridine*-3-*carboxylic acid*, m. p. 185°. The isomeric 3-*carbethoxy*-6-*phenyl*-2-*methylpyridine*-4-*carboxylic acid*, m. p. 145°, is converted through the *potassium* into the *silver* salt, which, when heated in a vacuum, affords *ethyl* 6-*phenyl*-2-*methylpyridine*-3-*carboxylate*, b. p. 185°/13 mm. (corresponding *acid*, m. p. 190—191°). Similarly, 4-carbethoxy-6-phenyl-2-methylpyridine-2-carboxylic acid affords successively a *potassium* and a *silver* salt, *ethyl* 6-*phenyl*-2-*methylpyridine*-4-*carboxylate*, b. p. 194°/16 mm., and 6-*phenyl*-2-*methylpyridine*-4-*carboxylic acid*, m. p. 272°, in a closed tube. Distillation of *potassium phenylmethylpyridine*-3 : 4-*dicarboxylate* with lime affords 6-phenyl-2-methylpyridine, b. p. 280—281° (corr.), d^0 1·0731.

2-*Methyl*-6-tert.-*butylpyridine*-3 : 4-*dicarboxylic anhydride*, m. p. 95°, is converted by ice-cold alcohol into 4-*carbethoxy*-2-*methyl*-6-tert.-*butylpyridine*-3-*carboxylic acid*, m. p. 105°, whereas the isomeric 3-*carbethoxy*-2-*methyl*-6-tert.-*butylpyridine*-4-*carboxylic acid*, m. p. 116°, is obtained by semihydrolysis of ethyl 2-methyl-6-*tert.*-butylpyridine-3 : 4-dicarboxylate. It is converted successively into the *potassium* and *silver* salts, *ethyl* 2-*methyl*-6-tert.-*butylpyridine*-3-*carboxylate*, b. p. 180°/17 mm., and 2-*methyl*-6-tert.-*butylpyridine*-3-*carboxylic acid* (+$2H_2O$), m. p. 137—138°. 4-Carbethoxy-2-methyl-6-*tert.*-butylpyridine-3-carboxylic acid gives a *silver* salt, *ethyl* 2-*methyl*-6-tert.-*butylpyridine*-4-*carboxylate*, b. p. 170—180°/14 mm., and 2-*methyl*-6-tert.-*butylpyridine*-4-*carboxylic acid*, m. p. 219°. 2-*Methyl*-6-tert.-*butylpyridine* has b. p. 179—180° (corr.), d^0 0·9158.

H. WREN.

Chlorides of simple pyridine- and quinoline-carboxylic acids. E. SPÄTH and H. SPITZER (Ber., 1926, **59**, [*B*], 1477—1486).—The acid is treated with thionyl chloride, generally purified by distillation over beeswax, in an apparatus which permits the distillation of excess of the reagent and distillation or sublimation of the product in a vacuum. The results differ in many respects from those of Meyer (A., 1901, i, 407). Picolinic acid and technical thionyl chloride afford *chloropicolinyl chloride*, m. p. 41—42°, transformed into *chloropicolinic acid*, m. p. 180° (decomp.) [*methyl* ester, m. p. 47°; corresponding *amide*, m. p. 152—153°], whereas the purified reagent gives *picolinyl chloride*, m. p. 45—47°. Nicotinic acid yields *nicotinyl chloride hydrochloride*, m. p. 155·5—156·5°, and, apparently, small amounts of nicotinyl chloride. Similarly, *iso*nicotinic acid gives *iso-nicotinyl chloride hydrochloride*, m. p. 164—165°, and, apparently, *iso*nicotinyl chloride. Cinchonic acid affords primarily *cinchonyl chloride hydrochloride*, m. p. 170°, which, when heated in a vacuum, yields *cinchonyl chloride*, m. p. 68°; the product obtained when cinchonyl chloride hydrochloride is preserved in a vacuum over alkali hydroxide is cinchonic acid hydrochloride, not cinchonyl chloride, as assumed by Meyer (*loc. cit.*).

H. WREN.

Quinoline derivatives. V. 4-Amino-2-phenylquinoline. H. JOHN [with V. GROSSMANN and V. FISCHL] (Ber., 1926, **59**, [*B*], 1447—1452).—Ethyl 2-phenylquinoline-4-carboxylate, m. p. 54°, is converted successively into the corresponding *hydrazide*, m. p. 222° (*benzylidene* derivative, m. p. 203°; *hydrochloride*), and *azide*, m. p. 87° (decomp.). From the latter substance 2-*phenyl*-4-*quinolylethylurethane* (-*carbamate*), m. p. 109° (*hydrochloride*), 2-*phenyl*-4-*quinolylcarbimide*, m. p. 231° (whence 4-amino-2-phenylquinoline), and *di*-2-*phenyl*-4-*quinolylcarbamide*, m. p. 273°, are obtained. Treatment of the urethane with boiling, concentrated hydrochloric acid affords

4-amino-2-phenylquinoline, m. p. 168° (*monohydrochloride*, m. p. 272°; *sulphate*; *nitrate*; additive *compound* with mercuric chloride; *chloroplatinate*, which does not melt below 270°; *tartrate*; *picrate*). 4-*Amino*-2-*phenylquinoline methiodide*, m. p. 274°, 4-*amino*-2-*phenylquinoline ethiodide*, m. p. 244°, 4-*formamido*-2-*phenylquinoline*, m. p. 275° (decomp.), 4-*acetamido*-2-*phenylquinoline*, m. p. 108°, and the corresponding *diacetyl* derivative, m. p. 117°, 4-*benzamido*-2-*phenylquinoline*, m. p. 182°, 4-*methyleneimino*-2-*phenylquinoline*, m. p. 188°, and 4-*benzylideneimino*-2-*phenylquinoline*, m. p. 240°, are described. H. WREN.

Colour reactions of certain heterocyclic compounds with aldehydes. F. LIEBEN and H. POPPER (Biochem. Z., 1926, **173**, 455—466).—The colour reactions between β-skatole, indole, pyrrole, furfuraldehyde, thiophen, tryptophan, and certain aldehydes in presence of sulphuric acid have been studied quantitatively. Usually, when either the aldehyde or the heterocyclic compound is present in excess of about 5 mols. : 1 mol. or greater, there is good proportionality between the colour developed and the amount of the less concentrated component. When the two are present in about equal molecular proportions, the colour intensity is quite untrustworthy quantitatively. Nevertheless, many exceptions to these rules have been observed. The authors are of opinion that most of the colour reactions described are not so much dependent on chemical reactions as on changes in the degree of dispersion in the reacting system. H. D. KAY.

Tryptophan–aldehyde reaction. IV and V. E. KOMM (Z. physiol. Chem., 1926, **156**, 161—201, 202—217).—IV. In presence of proline and its derivatives, or of polypeptides and proteins containing the pyrrole ring, the speed and intensity of colour formation in the reaction between tryptophan and aldehydes are markedly increased. Beyond a certain point, further addition of such proline derivatives does not influence the colour reaction. It is possible, using this observation, to make an approximate determination of the content of pyrrole rings in gelatin, or of the proline+hydroxyproline in protein hydrolysates.

V. Details are given, based on the findings recorded above, of an improved method for the colorimetric determination of the tryptophan content of a protein. An essential feature is the addition of sufficient gelatin to the tryptophan standard, and also in some cases to the protein under investigation, to ensure optimal colour development. The following figures are given for the percentage of tryptophan found: egg-albumin 1·43; albumin of yolk 1·67; vitellin 1·40; serum-albumin 2·66; serum-globulin 2·49; fibrin (from blood) 2·08; "plant fibrin" 0·40; legumin 1·35; crystalline protein from *Antiaris toxicaria* 5·29; myosin (from beef) 1·46; gelatin 0·0. H. D. KAY.

Synthesis of β-amino-9-ethylacridine [5-β-aminoethylacridine]. H. JENSEN and L. HOWLAND (J. Amer. Chem. Soc., 1926, **48**, 1988—1990).—Expecting to obtain an enhanced antiseptic effect, as compared with acridine, the authors have prepared 5-β-*aminoethylacridine*, yellow needles ($+1H_2O$), decomp. 225—230° (*benzoyl* derivative, m. p. 213°, *picrate*, m. p. 145°), from methyl acridine-5-propionate. The latter is converted by hydrazine hydrate into the *hydrazide*, m. p. 205—206° (*hydrochloride*, decomp. 270°), which, with amyl nitrite and alcoholic hydrogen chloride, affords the corresponding *carbamate*, m. p. 144—145° (*hydrochloride*, decomp. 217—218°, *picrate*, m. p. 195°); the latter with concentrated hydrochloric acid yields 5-β-aminoethylacridine. R. BRIGHTMAN.

Manufacture of diazotisable azo dyes and intermediate products. CHEM. WORKS, FORMERLY SANDOZ, and M. BÖNIGER.—See B., 1926, 657.

Yellow monoazo dyes. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1926, 658.

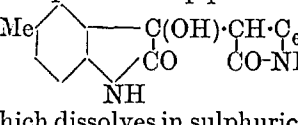
Isomeric forms of 2 : 5-diketopiperazines. Action of ozone on the enol and keto forms of 2 : 5-diketopiperazines and on dipeptides. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1926, **157**, 140—145).—When treated with ozone in chloroform, leucylglycine anhydride is partly converted into a pungent-smelling, liquid *ozonide* of the enol form, which affords valeric acid on hydrolysis, whilst 30—40% of the anhydride is recovered as the keto form, which is unattacked by ozone. Liquid *ozonides* were obtained similarly from the enol, but not from the keto, forms of alanine anhydride and glycyl-*d*-alanine anhydride. Whilst both forms of glycine anhydride yield the ozonide, production of the latter is slower from the keto form. Under similar conditions, ozone was without action on several dipeptides. F. G. WILLSON.

Spectrographic investigation of amino-acids, 2 : 5-diketopiperazines, peptones, and proteins. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1926, **155**, 195—199).—The tautomeric forms of amino-acids and 2 : 5-diketopiperazines show clearly marked differences in refractive index and conductivity. A partial separation of the keto–enol forms of 2 : 5-diketopiperazines was effected, making use of the difference in refractive index of their solutions. The enolic solution shows the higher value. The specific gravity of an enolic solution of given concentration is higher than that of the corresponding keto-solution. Proteins and peptones show a strong absorptive capacity for ultra-violet light. 2 : 5-Diketopiperazines and their corresponding dipeptides show successively decreased absorption. The aliphatic amino-acids and the corresponding polypeptides show slight and similar absorptive capacity, little affected by the length of the chain. The absorption is increased in the dicarboxylic amino-acids. The bearing of these facts on the structure of proteins is discussed. Investigations of specimens of alanine prepared respectively by crystallisation from water and precipitation from aqueous solution with alcohol show small spectrographic differences, ascribed to the presence of tautomeric forms. The clearly-marked differences in absorption spectra of tautomeric forms of 2 : 5-diketopiperazines are illustrated by reference to *dl*-norleucyl-*dl*-leucine anhydride and *dl*-leucylglycine

anhydride. Complete conversion of the enolic form of the latter compound into the keto-modification takes place after 8 hrs. M. CLARK.

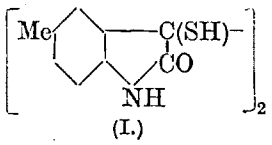
Physical behaviour of amino-acids, polypeptides, 2 : 5-diketopiperazines, in their tautomeric modifications, and proteins. II. E. ABDERHALDEN and R. HAAS (Z. physiol. Chem., 1926, **155**, 200—205).—The conductivity of aqueous solutions of the enolic form of 2 : 5-diketopiperazines is increased on conversion into the ketonic modification by long boiling. Electrolytic dissociation of the enolic form does not take place. The increase is ascribed to the presence of small quantities of neutral salts, which give more stable molecular compounds with the enolic than with the ketonic modification. Aqueous solutions of optically active dipeptides are unaltered by exposure to ultra-violet light or to *X*-rays. Solutions of the corresponding 2 : 5-diketopiperazines show diminished rotation, which soon reaches a constant value. Traces of ammonia and carbon dioxide can be detected after illumination. The change is ascribed to oxidation following ozone formation, since no change occurs in an atmosphere of nitrogen. Solutions of silk peptones show similarly altered rotations. Solutions of globulin and albumin containing sodium chloride, on illumination with ultra-violet light or *X*-rays, show slight increase in conductivity and in degree of buffering, accompanied by slight decrease in p_H, in capillary ascent, and in optical rotation. Diketopiperazines are more readily oxidised by atmospheric oxygen in presence of platinum-black than the corresponding dipeptides. The yield of dipeptide, obtained from the diketopiperazine by reversible reaction with water, is increased when the dipeptide is removed by precipitation with copper hydroxide or by fermentation with yeast. M. CLARK.

α-Amino-*N*-carboxylic anhydrides. II. F. SIGMUND and F. WESSELY (Z. physiol. Chem., 1926, **157**, 91—105; cf. A., 1925, i, 1151).—*Sarcosine-N-carboxylic anhydride*, m. p. 99—100° (decomp.) (rapidly heated), is obtained by the action of thionyl chloride on carbomethoxysarcosine (cf. Leuchs, A., 1906, i, 236). It sublimes almost without decomposition at 50°/10 mm., as does also *N*-phenylglycine-*N*-carboxylic anhydride at 100—130°/10 mm. Phenylalanine-*N*-carboxylic anhydride sublimes with partial decomposition into a non-volatile residue at 100—110°/0·5 mm. Glycine-*N*-carboxylic anhydride sublimes similarly at 70—80°/0·5 mm. Treatment of phenylalanine-*N*-carboxylic anhydride with alcoholic ammonia affords phenylalanineamide, m. p. 137—138° (cf. Königs and Mylo, A., 1909, i, 87). Ethylamine affords similarly, when applied in either aqueous or ethyl acetate solution, *phenylalanine-ethylamide* [*picrate*, m. p. 191—192° (decomp.)]. Aminoacetal, in aqueous solution, affords in the same way *phenylalanylaminoacetal*, liquid [*picrolonate*, m. p. 162° (decomp.)]. Phenylalanylglycine and phenylalanylglycylglycine (cf. Fischer, A., 1904, i, 890; 1905, i, 863) were obtained analogously. Condensation of phenylalanine-*N*-carboxylic anhydride with *l*-tyrosine ethyl ester in chloroform affords *phenylalanine-l-tyrosine anhydride*, $OH\cdot C_6H_4\cdot CH\cdot CO\cdot NH$ / $NH\cdot CO\cdot CH\cdot CH_2Ph$, m. p. 281° (decomp.) after turning brown at 277°. The action of aniline on phenylalanine-*N*-carboxylic anhydride affords a mixture from which only *phenylalanylphenylalanineanilide*, $CH_2Ph\cdot CH(NH_2)\cdot CO\cdot NH\cdot CH(CH_2Ph)\cdot CO\cdot NHPh$, m. p. 170° after sintering at 160° [*picrate*, m. p. 217° (decomp.) after turning brown at 214°], could be isolated. The formation of phenylalanineanilide (cf. Curtius and Sieber, A., 1922, i, 721) was not observed. Methylaniline affords similarly only an amorphous *product*. Pyridine is without action on *N*-phenylglycine-*N*-carboxylic anhydride, but causes elimination of carbon dioxide from glycine-*N*-carboxylic anhydride, sarcosine-*N*-carboxylic anhydride, and phenylalanine-*N*-carboxylic anhydride. Quinoline behaves analogously. F. G. WILLSON.

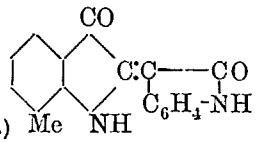
Methyl*iso*indigotins and methylindirubins. A. WAHL and T. FAIVRET (Ann. Chim., 1926, [x], **5**, 314—362).—7-Methylisatin, golden-yellow, m. p. 260°, prepared by oxidation of 7 : 7′-dimethylindigotin with chromic anhydride in glacial acetic acid, or, better, from *o*-toluidine by the method of Sandmeyer (A., 1919, i, 318), is reduced by sodium hyposulphite in aqueous solution to *7-methyldioxindole*, m. p. 212°. 5-Methylisatin, dark red, m. p. 187°, prepared in the same manner from *p*-toluidine, is reduced by the same reagent to *5-methyldioxindole*, m. p. 210°. Reduction of isatin by hydrogen in presence of colloidal platinum yields isatide, and 5-methylisatin in the same way furnishes 5 : 5′-*dimethylisatide*, m. p. 230—232°. Condensation of 5-methylisatin with dioxindole in presence of piperidine yields *5-methylisatide*, m. p. 230°, soluble in alkali hydroxides. 7-Methylisatin does not react in this way, nor will isatin condense with 5-methyloxindole. 5-Methylisatin condenses with oxindole in presence of piperidine, furnishing *5-methylisatan*,  , decomp. 195—200°, which dissolves in sulphuric acid with a blood-red colour. When this reaction is carried out in glacial acetic acid in presence of concentrated hydrochloric acid, a molecule of water is also eliminated and *5-methyliso*indigotin, dark red crystals yielding a *leuco*-compound soluble in alkalis, is produced. Concentrated sulphuric acid at the ordinary temperature converts this into *5-methyliso*indigotin-5′-*sulphonic acid* (*sodium* salt, $+3H_2O$, described). By analogous reactions, 7-methylisatin yields *7-methylisatan*, m. p. 259° (heated rapidly), and *7-methyliso*indigotin, reddish-brown crystals subliming with decomp. [*leuco*-compound, m. p. 310—312° (decomp.)], which when heated at 100° with sulphuric acid furnishes *7-methyliso*indigotin-5 : 5′-*disulphonic acid* (*sodium* salt, $+5H_2O$, *potassium* salt, $+3H_2O$, *barium* salt, $+6H_2O$, *silver* salt, $+\frac{1}{2}H_2O$, described).

5 : 5′-*Dimethyldisulphoisatide* (I) is obtained as an amorphous, white powder by the action of hydrogen sulphide on 5-methylisatin in alcohol, and is converted by sodium carbonate in alcohol into 5 : 5′-*dimethyliso*indigotin, dark red, produced in a purer condition

by the action of boiling pyridine (*leuco*-compound, m. p. 330°, soluble in alkalis). The corresponding



(I.)



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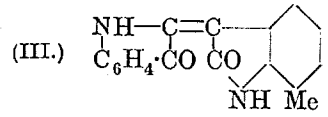


(III.)

7 : 7′-*dimethyldisulphoisatide* furnishes by similar reactions 7 : 7′-*dimethyl*iso*indigotin* (*leuco*-compound, soluble in alkalis), which is sulphonated by concentrated sulphuric acid at 100° to a *disulphonic acid* (*sodium* salt, $+6H_2O$, *potassium* salt, $+4H_2O$, *barium* salt, $+4H_2O$, *silver* salt, $+5H_2O$, described). The decomposition of disulphoisatide in presence of pyridine yields as by-products free sulphur and oxindole, and the above substituted disulphoisatides yield the corresponding 5-*methyloxindole*, m. p. 168° (*benzylidene* derivative, m. p. 182°), and 7-*methyloxindole*, m. p. 204° (*benzylidene* derivative, m. p. 224°).

7-*Methylindirubin* (II), violet needles with a coppery reflex, soluble in a solution of sodium hyposulphite, is obtained by the condensation of oxindole with a mixture of phosphorus pentachloride and 7-methylisatin in benzene, whilst 7′-*methylindirubin* (III) results from the condensation of 7-methylisatin with indoxylic acid in alcoholic solution in presence of sodium carbonate. 5-*Methylindirubin*, violet needles, and 5′-*methylindirubin*, dark needles yielding violet solutions, are obtained in the same way from 5-methylisatin. The indirubin derivatives do not dye cotton well.

Spectrophotometric observations of the absorption spectra of *iso*indigotin, indirubin, and the above methyl and dimethyl derivatives are recorded.

G. M. Bennett.

1 : 1′-Dialkyltetrahydro-4 : 4′-dipyridyls. O. Mumm and H. Ludwig (Ber., 1926, **59**, [*B*], 1605—1616).—Ethyl 1 : 2 : 6-trimethyl-4-*iso*butylpyridine-3 : 5-dicarboxylate methosulphate dissolved in aqueous acetic acid is reduced by sodium amalgam to *ethyl* 1 : 2 : 6 : 1′ : 2′ : 6′-*hexamethyl*-4 : 4′-*di*iso*butyltetrahydrodipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate*, m. p. 75°, which slowly decomposes in freezing benzene into *ethyl* 1 : 2 : 6-*trimethyl*-4-iso*butyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*, m. p. 78—79°, and ethyl 1 : 6-dimethyl-4-*iso*butyl-2-methylene-1 : 2-dihydropyridine-3 : 5-dicarboxylate. *Ethyl* 1 : 2 : 6 : 1′ : 2′ : 6′-*hexamethyl*-4 : 4′-*diethyltetrahydrodipyridyl*-3 : 5 : 3′ : 5′-*tetracarboxylate*, m. p. 72° (decomp.), is similarly prepared. The tendency of the di*iso*butyl derivative towards fission exceeds that of any homologous dialkyl derivative. In cold ether or alcohol or when heated at 85—90°, it gives equimolecular quantities of methide and dihydro-ester. Similarly, ethyl 1 : 2 : 6 : 1′ : 2′ : 6′-hexamethyl-4 : 4′-diethyltetrahydrodipyridyl-3 : 5 : 3′ : 5′-tetracarboxylate at 100° gives ethyl 1 : 6-dimethyl-4-ethyl-2-methylene-1 : 2-dihydropyridine-3 : 5-dicarboxylate and *ethyl* 1 : 2 : 6-*trimethyl*-4-*ethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*, m. p. 89°. The di*iso*butyl compound is converted by iodine in alcoholic solution into ethyl 2 : 6-dimethyl-4-*iso*butylpyridine-3 : 5-dicarboxylate methiodide, or, if excess of halogen is used, into a bimolecular *periodide*, $(C_{18}H_{28}O_4NI_3)_2$, m. p. 99—100°. Oxygen transforms it into a peroxide which decomposes with formation of hydrogen peroxide into ethyl 1 : 2-dimethyl-4-*iso*butyl-6-methylene-1 : 2-dihydropyridine-3 : 5-dicarboxylate. Hydrogen in the presence of colloidal palladium reduces it to ethyl 1 : 2 : 6-trimethyl-4-*iso*butyl-1 : 2-dihydropyridine-3 : 5-dicarboxylate, b. p. 140°/0·1 mm. In contrast to the isomeric 1 : 4-dihydro-ester, which is not affected by hydrogen in acetic acid solution in the presence of spongy platinum, the 1 : 2-dihydro-compound is reduced to *ethyl* 1 : 2 : 6-*trimethyl*-4-iso*butyltetrahydropyridine*-3 : 5-*dicarboxylate*, b. p. 130—135°/0·2—0·3 mm. (*styphnate*, m. p. 122—123°). The additive compound of methyl sulphate and ethyl 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate is reduced by sodium amalgam and aqueous acetic acid to *ethyl* 4-*phenyl*-1 : 2 : 6-*trimethyl*-1 : 4-*dihydropyridine*-3 : 5-*dicarboxylate*, m. p. 132°; the loosening influence of the phenyl group appears to inhibit the production of a dipyridyl derivative. A similar reaction is observed with ethyl 2 : 6-dimethylpyridine-3 : 4-dicarboxylate methosulphate, which affords *ethyl* 1 : 2 : 6-*trimethyl*-1 : 4-*dihydropyridine*-3 : 4-*dicarboxylate*, b. p. 184—186°/17 mm. H. Wren.

Mechanism of the formation of derivatives of 1 : 2-diazine and of 1-aminopyrrole in the reaction of hydrazine with 1 : 4-diketo-compounds. Absorption spectra of certain 1 : 2-diazine derivatives. J. V. Korschun and K. V. Roll (Sci. Mag. Chem. Cath. Katerinoslav, 1926, 19—30).—The authors discuss the different possible mechanisms for the reaction between hydrazine and 1 : 4-diketo-compounds and suggest formulæ for the intermediate compounds formed in the different cases. Experimental data are to be given later. T. H. Pope.

Interaction between chloroacetic acid, potassium cyanide, and benzaldehyde. M. Henze (J. pr. Chem., 1926, [ii], **113**, 212—224).—The acid $C_{20}H_{17}O_2N_3$ obtained by Lapworth (J.C.S., 1922, **121**, 1707) in this interaction forms slightly soluble heavy metal salts, *ammonium* salt, decomp. 138°, and *aniline* salt, m. p. 173°. It gives a pyrrole pine-chip reaction and a yellow precipitate with sodium nitrite. *Substances* are obtained: by hydrolysis, $C_{20}H_{15}O_3N_2$, decomp. about 185°; when heated, $C_{19}H_{17}N_3$, m. p. 238°, and an isomeride of m. p. 176°; reduction product, m. p. 168—169°, hydrolysed to a substance, m. p. 200—202°, and a ketonic acid, $C_{17}H_{16}O_3$, decomp. 180°. Other reduction products etc. are obtained for which formulæ are not calculated.

E. W. Wignall.

Aminopropyl-1 : 2 : 4-triazoles. J. Reilly and P. J. Drumm (J.C.S., 1926, 1729—1737).—The action of heat on aminoguanidine nitrate mixed with *n*- and with *iso*-butyric acid, respectively, gives 5-*amino*-3-n-*propyl*-1 : 2 : 4-*triazole* (I), m. p. 143° (*hydrochloride*; *nitrate*, m. p. 153°; *picrate*, m. p. 152°; *silver* salt), and 5-*amino*-3-iso*propyl*-1 : 2 : 4-*triazole*

(II), m. p. 112° (*hydrochloride*; *nitrate*, m. p. 176°; *picrate*, m. p. 193—194°; *silver* salt; *acetyl* derivative, m. p. 205°), which are isolated as the nitrates. Treatment of (I) with alkaline potassium permanganate gives 3 : 3′-*di*-n-*propyl*-5 : 5′-*azo*-1 : 2 : 4-*triazole* (decomp. on heating) (*silver* salt obtained), which may be reduced to the hydrazo-compound; reduction of the diazotised triazole with stannous chloride and treatment of the resulting hydrazine with benzaldehyde yields *benzaldehyde*-3-n-*propyl*-1 : 2 : 4-*triazolyl*-5-*hydrazone*, m. p. 239°, together with 5-chloro-3-*n*-propyltriazole. When an alcoholic solution of (I) is heated with salicylaldehyde in presence of piperidine, the *salicylidene* derivative, m. p. 173°, is obtained, but in the preparation of the *cinnamylidene* derivative of (II), the intermediate *hydrate* appears to be formed (white substance, softening at 100°, m. p. 120°, changes to yellow solid, softening at 125°, m. p. 130°). The diazonium nitrates of (I) and (II) are comparatively stable; the diazonium chlorides may be converted into 5-*chloro*-3-n-*propyl*-1 : 2 : 4-*triazole*, m. p. 90°, and 5-*chloro*-3-iso*propyl*-1 : 2 : 4-*triazole*, m. p. 133°. The action of sodium nitrite on the nitrate of (II), followed by treatment with sodium acetate, leads to 3-iso*propyl*-1 : 2 : 4-*triazole*-5-iso*diazohydroxide*, whilst 3-n-*propyl*-1 : 2 : 4-*triazole*-5-iso*diazohydroxide* ($+\frac{1}{2}H_2O$) is similarly obtained. From the diazonium nitrates are prepared 5-*diazo*-3-n-*propyl*-1 : 2 : 4-*triazole chloroaurate*, m. p. 135° (decomp.), 5-*diazo*-3-iso*propyl*-1 : 2 : 4-*triazole chloroaurate* (decomp. on heating), 3-n-*propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine*, m. p. 267° (decomp.), 3-iso*propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine*, m. p. 254—255° (decomp.), and 3-iso*propyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthol*, m. p. 186° (decomp.), whilst the products obtained by coupling with acetylacetone are regarded as 3-n-*propyl*-1 : 2 : 4-*triazole*-5-*azoacetylacetone*, m. p. 172—173°, and 3-iso*propyl*-1 : 2 : 4-*triazole* 5-*azoacetylacetone*, m. p. 200—202° (*sodium* salt), and those obtained by coupling with ethyl acetoacetate as *ethyl* 3-n-*propyl*-1 : 2 : 4-*triazole*-5-*azoacetoacetate*, m. p. 156°, and *ethyl* 3-iso*propyl*-1 : 2 : 4-*triazole*-5-*azoacetoacetate*, m. p. 168—170°. F. M. HAMER.

5-Amino-4-hydroxy-4 : 5-dihydrouric acid and uric acid glycol, with a review of the corresponding ψ-uric acid derivatives. H. BILTZ and W. KLEMM (Annalen, 1926, **448**, 134—163).—5-Amino-4-hydroxy-4 : 5-dihydrouric acid, prepared from uric acid by way of 5-chloro-ψ-uric acid, 5-hydroxy-ψ-uric acid, and 5-amino-ψ-uric acid (overall yield, 30%), is unchanged by nitrosyl chloride or bromide, but is converted by nitrogen trioxide into uric acid glycol (4 : 5-dihydroxy-4 : 5-dihydrouric acid), obtained as hemihydrate in the presence of water, or anhydrous in the presence of alcohol. The following salts of the aminohydroxydihydrouric acid are described: *ammonium*, decomp. 110—115° ($+H_2O$), m. p. 120—130° (anhyd.; decomp.); *potassium*, decomp. 140—145° ($+H_2O$); 1 : 9-*disilver* ($+2H_2O$); *cupridiammine* (dibasic; $+2H_2O$); *perchlorate*, decomp. 156—157°; *nitrate*, decomp. 137—145° ($+H_2O$). Uric acid glycol gives the following salts: *ammonium*, decomp. 60—70° ($+H_2O$); *potassium*, decomp. 148—155° ($+H_2O$); 1 : 9-*disilver*; no cuprammonium salt is formed. From *spiro*dihydantoin the following salts are obtained: *diammonium* ($+2H_2O$); *dipotassium* ($+2H_2O$); *cupridiammine*.

Uric acid glycol is stable to weak acids, but with strong acids yields carbamide and alloxanic acid; with condensing agents (sulphuric acid, phosphoryl chloride, hydrogen chloride), the hydantoylcarbamide first formed is converted into *spiro*dihydantoin. Aminohydroxydihydrouric acid is much less stable to acids, being converted by acetic acid into *spiro*dihydantoin. There is a similar difference in stability towards alkalis and boiling water, the aminohydroxy-acid giving *spiro*dihydantoin when boiled with ammonia, and carbamide, oxalic acid, carbon dioxide, and ammonia when boiled with water. Boiling acetic anhydride converts both the glycol and the aminohydroxy-compound into OO-*diacetyl*spiro*dihydantoin*, m. p. 246° (after loss of $1H_2O$ at 150°), which with diazomethane gives tetramethyl*spiro*dihydantoin. *Diacetyl*-3 : 7-*dimethyl*spiro*dihydantoin*, m. p. 172°, is obtained by acetylation of 3 : 7-dimethyl*spiro*dihydantoin.

Uric acid glycol, treated with diazomethane, takes up 4 methyl groups, the hydroxyl in position 5 being etherified. Aminohydroxydihydrouric acid is decomposed during methylation, and gives tetramethyl*spiro*dihydantoin. Decomposition or rearrangement under the influence of diazomethane is also found to occur with 5-amino-ψ-uric acid and 5-methylamino-ψ-uric acid (to tetramethyl*spiro*hydantoin), 5-anilino-ψ-uric acid (to 5-*anilino*-4-*hydroxy*-1 : 3 : 9-*trimethyl*-4 : 5-*dihydrouric acid*, m. p. 167—168°), 5-hydroxy-ψ-uric acid and 5-methoxy-ψ-uric acid (to 1 : 3 : 9-trimethyluric acid glycol monomethyl ether), and 5-hydroxy-1 : 3-dimethylhydantoylcarbamide (to trimethylcaffolide).

In the preparation of the aminohydroxyuric acid from 5-amino-ψ-uric acid by dissolving in ammonia and acidifying, ring-closure occurs in the alkaline solution, since it yields the cuprammonium salt of the aminohydroxyuric acid without acidification. 5-Methoxy-ψ-uric acid similarly yields with ammonia the ammonium salt of uric acid glycol monomethyl ether, but ring-closure takes place only on acidification in the case of 5-hydroxy-ψ-uric acid. The facilitation of ring-closure in the presence of bromine is observed with 5-methoxy-ψ-uric acid (to uric acid glycol monomethyl ether) and 5-amino-ψ-uric acid (to *spiro*dihydantoin).

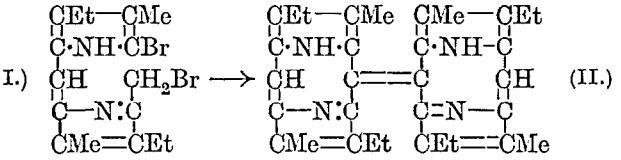
5-Amino-ψ-uric acid is converted by 15% hydrochloric acid at the ordinary temperature into carbamide and an additive *compound* of alloxan and ammonium chloride.

The behaviour of 5-amino- and 5-hydroxy-ψ-uric acid shows that in this series a 5-amino-group is less loosely bound than a 5-hydroxyl group.

C. HOLLINS.

Synthesis of ætioporphyrin, ætiohæmin, and ætiophyllin. H. FISCHER and J. KLARER (Annalen, 1926, **448**, 178—193).—Cryptopyrrole (2 : 3-dimethyl-4-ethylpyrrole), when brominated in cold acetic acid, yields a *compound*, $C_{16}H_{20}N_2Br_2$, probably (I), which is converted by concentrated sulphuric acid into

ætioporphyrin (crystallographic data by STEINMETZ). The product is spectroscopically identical with Willstätter's ætioporphyrin from natural sources, and reasons are advanced for the formula (II). The synthetic substance gives with copper acetate a

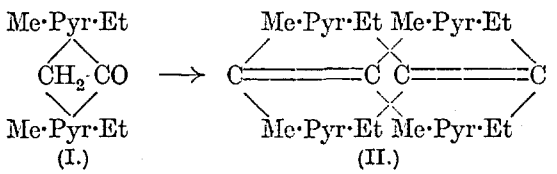


complex *copper* salt; with ferric chloride and sodium acetate, ætiohæmin; with magnesia and methyl-alcoholic potassium hydroxide, ætiophyllin.

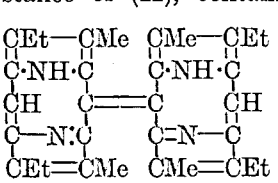
Complex *iron* salts are also prepared from bis(4-methyl-2-ethylpyrrole)methene, bis(3-propionyl-4-methyl-2-ethylpyrrole)methene, ethyl bis(2 : 4-dimethylpyrrole)methene-3 : 3′-dicarboxylate, and bis-(2-methyl-4-ethylpyrrole)methene; the respective m. p. are 190°, 184—185°, 195°, and 165°.

C. HOLLINS.

Synthesis of *iso*ætioporphyrin, its "hæmin," and its "phyllin." H. FISCHER and P. HALBIG (Annalen, 1926, **448**, 193—204; cf. preceding abstract).—*Ethyl bis(4-methyl-3-ethylpyrryl)methane-5 : 5′-dicarboxylate*, m. p. 126°, is prepared from ethyl 4-methyl-2-bromomethyl-3-ethylpyrrole-5-carboxylate by boiling with methyl alcohol, no hydrogen bromide being necessary. The free *acid*, m. p. 170° (decomp.), readily loses carbon dioxide at 100° in a vacuum, forming *isoætioporphyrin*, $C_{32}H_{36}N_4$, m. p. 350° (crystallographic data by STEINMETZ), the spectrum of which very closely resembles that of Willstätter's ætioporphyrin. In the formation of this compound, the acid loses 1 mol. of carbon dioxide, and the remaining carboxyl group probably condenses with the unsubstituted α-CH group to give (I), which then by self-condensation with loss of $2H_2O$ yields *iso*ætioporphyrin (II) ["Pyr"=the quadrivalent (2 : 3 : 4 : 5) pyrrole nucleus]. The



name "porphin" is suggested for the parent substance of (II), containing no β-substituents. This structure, with possible isomerism to (III), explains the existence of a large number of isomeric porphyrins, and is preferred to Küster's formula.

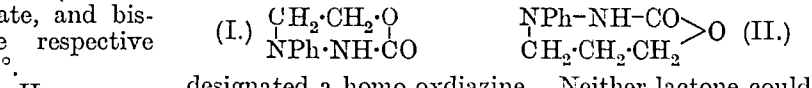


When boiled with ferric chloride and sodium acetate in acetic acid, the porphyrin is converted into the corresponding *isoætiohæmin* (crystallographic data by STEINMETZ). A complex *copper* salt is described, and *isoætiophyllin* is prepared by an application of the Grignard reaction (cf. Willstätter and Forsén, A., 1913, i, 499).

Hydrolysis of ethyl bis(4-methylpyrryl)methane-3 : 3′ : 5 : 5′-tetracarboxylate (this vol., 621) with aqueous-alcoholic sodium hydroxide yields the free *acid* (unmelted at 350°), which loses carbon dioxide at 160° in a vacuum, giving the porphyrin, *tetramethylporphin*.

C. HOLLINS.

Ring closure in chloroalkyl phenylcarbazates. Six- and seven-membered hydrazolactones [oxdiazines and "homo-oxdiazines"]. A. W. DOX (J. Amer. Chem. Soc., 1926, **48**, 1951—1954; cf. A., 1923, i, 483).—*β-Chloroethyl phenylcarbazate*, m. p. 89°, and *γ-chloropropyl phenylcarbazate*, m. p. 72°, undergo ring closure when treated with sodium ethoxide in absolute alcohol, yielding *2-keto-4-phenyltetrahydro-1 : 3 : 4-oxdiazine* (lactone of β-hydroxyethylphenylcarbazic acid) (I), m. p. 120°, and the *lactone* of γ-hydroxypropylphenylcarbazic acid (II), m. p. 146°, respectively. The latter is provisionally



designated a homo-oxdiazine. Neither lactone could be alkylated. The second lactone on hydrolysis and reduction yielded a secondary amine. Neither lactone showed appreciable pharmacological action when administered orally to dogs. The chloroalkyl phenylcarbazates were obtained by the action of the appropriate alkyl chloroformate on phenylhydrazine in pyridine. *n-Butyl phenylcarbazate*, m. p. 70°, was similarly prepared; *n-butyl hydrazine-s-dicarboxylate*, m. p. 47°, was obtained from butyl chloroformate and hydrazine hydrate.

R. BRIGHTMAN.

Reduction of thionine by various organic substances in absence of air and light. E. AUBEL and L. GENEVOIS (Compt. rend., 1926, **183**, 94—95).—Lævulose reduces thionine in the dark in a vacuum in presence of phosphates, the speed of the reaction being proportional to the concentration of lævulose and of phosphate and to the square root of the hydroxyl-ion concentration. Glycerol, mannitol, dulcitol, sorbitol, dextrose, galactose, and arabinose have a similar but less vigorous reducing power, glyceraldehyde a more vigorous one. Asparagine, alanine, tyrosine, and pyruvic, aspartic, and uric acids have a reducing power which has a maximum at p_H 7. Acetic acid and glycine have no reducing power.

G. M. BENNETT.

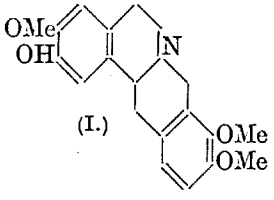
Alipine hydrochloride. J. SEVILLA (Anal. Asoc. Quím. Argentina, 1926, **14**, 5—37; cf. this vol., 744).—The author describes the principal reactions whereby alipine may be distinguished from cocaine, stovaine, and novocaine. Alipine may be determined quantitatively by means of bromine water, which it decolorises. *Alipine nitrate* is microcrystalline and has m. p. 159°. Alipine is twice as powerful as cocaine in its anæsthetic effect.

G. W. ROBINSON.

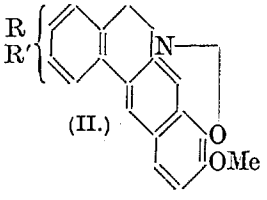
Yocca, a new caffeine drug. A. PERROT and A. ROUHIER.—See B., 1926, 644.

Alkaloids of the *Calumba* root. V. New base from the *Calumba* root and the constitution of berberrubine and palmatrubine. E. SPÄTH and G. BURGER (Ber., 1926, **59**, [*B*], 1486—1496).—The mother-liquors obtained during the separation of crude tetrahydrojatrorrhizine as the hydrochloride

yield a *base*, $C_{17}H_{14}ON(OMe)_3$, m. p. 223—224°, for which the name tetrahydrocolumbamine is proposed (the name becomes available since the alkaloid designated previously columbamine has been found identical with palmatine). It is converted by diazomethane into *r*-tetrahydropalmatine. Diazoethane affords *tetrahydrocolumbamine ethyl ether*, which is oxidised successively to 1-keto-6-methoxy-7-ethoxy-1 : 2 : 3 : 4-tetrahydro*iso*quinoline and a mixture of hemipinic acid and the methyl ethyl ether of nor-*m*-hemipinic acid, whereby the constitution (I) is established.



(I.)



(II.)

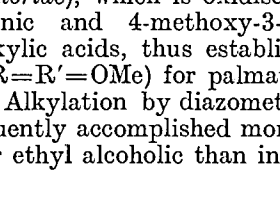
Berberrubine (cf. Frerichs and Stoepel, A., 1913, i, 1094) is transformed successively into tetrahydroberberrubine and tetrahydroberberrubine ethyl ether, m. p. 128°. Oxidation of the latter substance affords hydrastic acid and 4-*methoxy*-3-*ethoxybenzene*-1 : 2-*dicarboxylic* (4-*methoxy*-3-*ethoxyphthalic*) *acid*, m. p. 175° (decomp.) (*anhydride*, m. p. 105°; *ethylimide*, m. p. 82—83°), identified by preparation from 3-hydroxy-4-methoxybenzene-1 : 2-dicarboxylic acid. The constitution (II) is therefore established for berberrubine ($RR'=CH_2O_2$).

Palmatrubine (Feist and Dschu, A., 1925, i, 830) is converted by zinc dust in acid solution into *tetrahydropalmatrubine*, m. p. 148—149° (*hydrochloride*), and the latter substance is transformed into *tetrahydropalmatrubine ethyl ether*, m. p. 115° (*hydrochloride*), which is oxidised to a mixture of *m*-hemipinic and 4-methoxy-3-ethoxybenzene-1 : 2-dicarboxylic acids, thus establishing the constitution (II) (R=R'=OMe) for palmatrubine.

Alkylation by diazomethane or diazoethane is frequently accomplished more easily in absolute methyl or ethyl alcoholic than in ethereal solution.

H. WREN.

Synthesis of cryptopine and protopine. R. D. HAWORTH and W. H. PERKIN, jun. (J.C.S., 1926, 1769—1784).—*iso*Dihydrocryptopine chloride and *iso*dihydroprotopine chloride have been synthesised and have been converted into cryptopine and protopine, respectively, by the method applied to β-homochelidonine (this vol., 417). 3 : 4-Methylenedioxyhomophthalic acid condenses at 165—175° with β-veratrylethylamine (prepared from β-3 : 4-dimethoxyphenylpropionamide), yielding N-β-*veratrylethyl*-3 : 4-*methylenedioxyhomophthalimide* (I), m. p. 181—182° (N-β-*veratrylethyl*-4 : 5-*methylenedioxyhomophthalimide* has m. p. 162°), which is hydrolysed by sodium hydroxide to N-β-*veratrylethyl*-3 : 4-*methylenedioxyhomophthalamic acid* (II), m. p. 185—186° (also obtained by condensing 3 : 4-methylenedioxyhomophthalic anhydride with β-veratrylethylamine). Its *methyl* ester, m. p. 131—132°, is converted by phosphorus oxychloride into oxy*epi*berberine (III), m. p. 240° (*acetate* isolated), identical with that obtained from *iso*cryptopine chloride (cf. Perkin, J.C.S., 1918, **113**, 518). (III) is reduced electrolytically in alcoholic sulphuric acid solution to tetrahydro*epi*berberine (IV), m. p. 170° (*hydrochloride* prepared), [which Perkin (*loc. cit.*) has oxidised to *epi*berberinium



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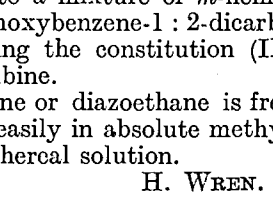

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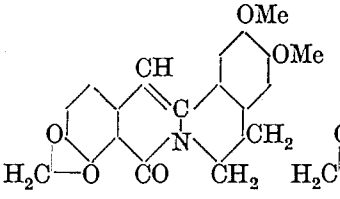

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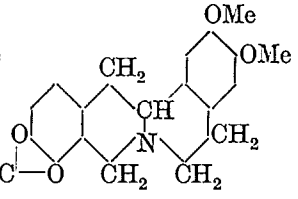
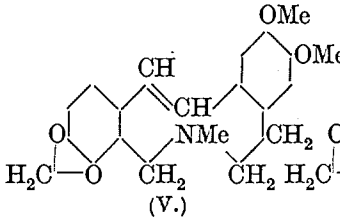
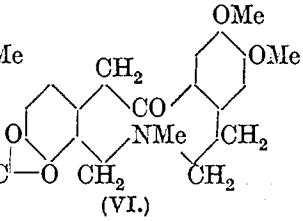


(IV.)

chloride], but a modification of the electrolytic reduction yields *iso*oxy*epi*berberine, m. p. 370° (decomp. from 300°). (IV) is converted into a methiodide and that into a *methochloride*, which occurs in two forms, identical with the α- and β-forms of *iso*dihydrocryptopine chloride, obtained by reducing *iso*cryptopine chloride either with sodium amalgam or electrolytically. By decomposing *iso*dihydrocryptopine α- or β-chloride, from either source, with silver hydroxide there are obtained anhydrodihydrocryptopine-A (V) and anhydrodihydrocryptopine-B (cf. Perkin, J.C.S., 1916, **109**, 937); oxidation of (V) by perbenzoic acid, in ether–chloroform solution, yields *anhydrodihydrocryptopine oxide* ($+1H_2O$), m. p. 135° (decomp.) [*hydrochloride*, m. p. 215° (decomp.)]. By heating with acetic and hydrochloric acids, the amine oxide is converted into cryptopine (VI), m. p. 220—221° (corr.).



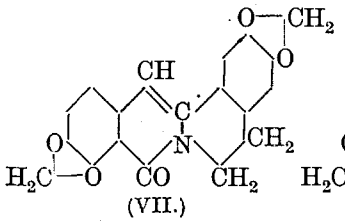
(V.)

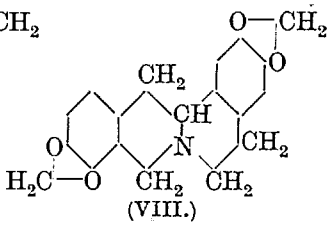


(VI.)

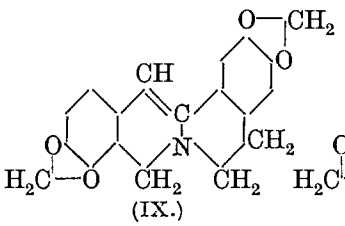
3 : 4-Methylenedioxyhomophthalic acid and β-piperonylethylamine condense at 180° to N-β-*piperonylethyl*-3 : 4-*methylenedioxyhomophthalimide*, m. p. 214—215°, which is hydrolysed to N-β-*piperonylethyl*-3 : 4-*methylenedioxyhomophthalamic acid*, m. p. 194—195° (also prepared by condensation of 3 : 4-methylenedioxyhomophthalic anhydride with β-piperonylethylamine). Its *methyl* ester, m. p. 170—171°, is converted by phosphorus oxychloride into 2 : 3 : 9 : 10-*bismethylenedioxyoxyprotoberberine* (VII), m. p. 292° (*acetate* prepared), which is reduced electrolytically to 2 : 3 : 9 : 10-*bismethylenedioxytetrahydroprotoberberine* (VIII), m. p. 218—219° [*hydrochloride*, m. p. 275—278° (decomp.)]. On heating *iso*protopine chloride

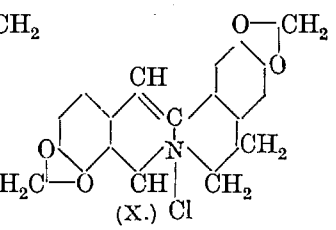
in a vacuum, it loses methyl chloride, giving 2:3:9:10-*bismethylenedioxydihydroprotoberberine* (IX),


(VII.)

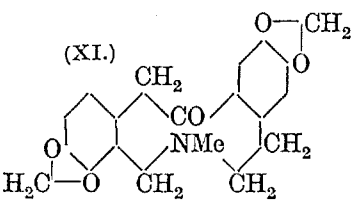

(VIII.)

m. p. 194—196° (decomp.) (*hydrochloride* described), which is reduced by zinc dust and dilute sulphuric acid to (VIII). Mercuric acetate oxidises (IX) to 2 : 3 : 9 : 10-*bismethylenedioxyprotoberberinium chloride* (X) ($+1H_2O$), m. p. 300° (decomp. from 280°) [2 : 3 : 9 : 10 - *bismethylenedioxyanhydroprotoberberine - acetone* has m. p. 195° (decomp.)]. On heating with sodium hydroxide, (X) gives a mixture of (IX) and


(IX.)


(X.) Cl

(VII). The methiodide of (VIII) is converted by silver chloride into iso*dihydroprotopine α-chloride* [($+1H_2O$), m. p. 90°, and anhyd., softening at 155°, m. p. 175° (decomp.)] and iso*dihydroprotopine β-chloride*, m. p. 270° (decomp.); these chlorides are also obtained by reduction of *iso*protopine chloride. Decomposition of *iso*dihydroprotopine chloride, from either source, with silver hydroxide yields *anhydrodihydroprotopine-A*, m. p. 118—120° [which hydrochloric acid converts into *iso*dihydroprotopine β-chloride, indicating that its structure is similar to (V)]. Its oxidation gives *anhydrodihydroprotopine oxide*, m. p. 140° (decomp.) [*hydrochloride*, m. p. 221° (decomp.)], which on heating with hydrochloric and acetic acids yields protopine (XI), m. p. 207° (corr.).


(XI.)

F. M. Hamer.

Alkaloids of *Corydalis cava*. Synthesis of *d*-tetrahydropalmatine. E. Späth and E. Mosettig (Ber., 1926, **59**, [*B*], 1496—1500).—*r*-Tetrahydroberberine is converted by phloroglucinol and aqueous sulphuric acid into the corresponding phenolic *base*, m. p. 260—262° (decomp.) (*hydrochloride*; *hydriodide*), which affords *r*-tetrahydropalmatine when methylated. Similarly, *d*-tetrahydroberberine affords successively a *phenolic base*, m. p. 249—250°, $[\alpha]_D^{13}$ +307·7° in ethyl alcohol, and *d*-tetrahydropalmatine, m. p. 141—142°, $[\alpha]_D^{14}$ +288·9° in ethyl alcohol, identical with the alkaloid obtained from *Corydalis cava*, whereas *l*-tetrahydroberberine yields the phenolic base, m. p. 249—250°, and *l*-tetrahydropalmatine.

H. Wren.

Basic (dissociation) constant of morphine etc. C. Morton.—See B., 1926, 644.

Colour reactions of morphine. L. Ekkert (Pharm. Zentr., 1926, **67**, 498).—Benzidine in sulphuric acid solution gives with morphine and several related alkaloids a series of colour changes, extended by diluting, adding ammonia, etc. Similar colour changes are obtained if citric acid is used instead of benzidine. S. I. Levy.

Reactions of certain nitro-compounds with alkaloids. E. Navarro (Anal. Fís. Quím., 1926, **24**, 283—296).—Nitro-compounds generally form additive compounds with alkaloids when they contain a negative group in the *ortho* or *para* position. In the case of the corresponding *meta* compounds, precipitates are formed which are considered to be salts. The reactions of 1-chloro-2 : 4-dinitrobenzene, 1 : 3 : 5-trinitrobenzene, *p*-nitrophenol, *p*-hydroxybenzoic acid, *p*-nitrobenzoic acid, 3 : 5-dinitrobenzoic acid, 2 : 4-dinitrophenol, 4 : 6-dinitro-2-aminophenol, and picric acid with the more important alkaloids are described. The best-defined precipitates are given by the strong bases. 3 : 5-Dinitrobenzoic acid gives well-defined, crystalline precipitates with some of the principal alkaloids and is recommended as a reagent for the recognition of alkaloids. Photomicrographs are given of the precipitates with brucine, quinidine, morphine, codeine, papaverine, strychnine, pilocarpine, and antipyrine. G. W. Robinson.

Synthesis of iodine compounds of the salvarsan group. A. D. Macallum (J.C.S., 1926, 1645—1647).—5-Iodo-3-nitro-4-hydroxyphenylarsinic acid is reduced by hyposulphite or by titanous or ferrous oxide to 5-*iodo*-3-*amino*-4-*hydroxyphenylarsinic acid* (*zinc* and *lead* salts described); the action of acetic anhydride and ethyl chloroformate, respectively, gives 5-*iodo*-3-*acetamido*-4-*hydroxyphenylarsinic acid*, m. p. 158—159°, 190—191°, and 5-*iodo*-3-*carbethoxyamino*-4-*hydroxyphenylarsinic acid*, m. p. 182—183° (decomp.). Warm hyposulphite reduces the acetamido-compound to 5 : 5′-*di-iodo*-3 : 3′-*diacetamido*-4 : 4′-*dihydroxyarsenobenzene*, decomp. from 180°, m. p. 194°, which is trypanocidally active. 5-Iodo-3-nitro-4-hydroxyphenylarsinic acid is converted by hypophosphorous acid into 5 : 5′-*di-iodo*-3 : 3′-*dinitro*-4 : 4′-*dihydroxyarsenobenzene*, decomp. about 200°. Oxidation of 5 : 5′-di-iodo-3 : 3′-diacetamido-4 : 4′-dihydroxyarsenobenzene with iodine, followed by hydrolysis of the arsine di-iodide, yields 5-*iodo*-3-*acetamido*-4-*hydroxyphenylarsenious oxide*, m. p. 182—183°, and, similarly, 5 : 5′-di-iodo-3 : 3′-dinitro-4 : 4′-dihydroxyarsenobenzene gives 5-*iodo*-3-*nitro*-4-*hydroxyphenylarsenious oxide*, m. p. 170—210°. F. M. Hamer.

Introduction of the selenocyano-group into aromatic compounds. F. Challenger, A. T. Peters, and J. Halévy (J.C.S., 1926, 1648—1655).—Cyanogen triselenide and triphenylbismuthine react in ether, giving phenyl selenocyanate, selenium, and diphenylselenocyanobismuthine. Diphenylbromobismuthine and potassium selenocyanate give triphenylbismuthine, but no diphenylselenocyanobismuthine. Potassium selenocyanate with triphenylbismuthine dichloride and tri-*p*-tolylbismuthine di-

chloride gives, respectively, phenyl selenocyanate and p-*tolyl selenocyanate*. From triphenylstibine dichloride and potassium selenocyanate, or from triphenylstibine and cyanogen triselenide, the product is *triphenylstibine hydroxyselenocyanate*, or possibly the corresponding *oxide*. Tellurium dicyanide and triphenylbismuthine form diphenylcyanobismuthine and a red *solid*, m. p. 54°, which is regarded as diphenyl ditelluride. Cyanogen triselenide with aniline and dimethylaniline yields, respectively, p-*aminophenyl selenocyanate*, m. p. 93·5°, and p-*dimethylaminophenyl selenocyanate*, m. p. 105°, which may be converted into p-*dimethylaminophenyl methyl selenide*. p-*Tolyl selenocyanate*, m. p. 55—56° (together with di-*p*-tolyl selenide), p-*bromophenyl selenocyanate*, m. p. 70·5—71·5°, and *p*-chlorophenyl selenocyanate, m. p. 53·5—54·5°, have been prepared by the diazo-reaction.

F. M. HAMER.

Aryl bismuth derivatives. J. SUPNIEWSKI (Rocz. Chem., 1926, **6**, 97—109).—The following aryl derivatives of bismuth are described: *methyl* ester of *tri*-(p-*carboxyphenyl*)*bismuthine dichloride*, m. p. 107°, *tri*-(p-*carboxyphenyl*)*bismuthine*, m. p. 162°, *tri*-o-*tolylbismuthine*, m. p. 129° (*dichloride*, m. p. 160°; *dinitrate*, decomp. 60°), *tri*-(3-*nitro*-2-*methylphenyl*)*bismuthine dichloride*, m. p. 147—149°, *tri*-(o-*carboxyphenyl*)*bismuthine dichloride*, m. p. 157—159°, its *methyl* ester, m. p. 135—137°, 4-*sulpho*-2-*methylphenyldi*-o-*tolylbismuthine sulphate*, $SO_4Bi(C_6H_4Mc)_2(C_6H_3Me{\cdot}SO_3H)$, m. p. 166—167°, the corresponding *disulphonic acid*, m. p. 174°, *tri*-m-*xylylbismuthine*, m. p. 159—161° (*dichloride*, m. p. 142—157°), *tri*-(p-*methoxyphenyl*)*bismuthine*, m. p. 190° (*dichloride*, m. p. 133°), *tri*-o-*methoxyphenylbismuthine*, m. p. 168—171°. p-*Bromobenzyl methyl ether*, b. p. 201°, and o-*bromobenzyl methyl ether*, b. p. 215—230°, do not yield bismuth derivatives.

R. TRUSZKOWSKI.

Mercuration of o-nitrotoluene. H. BURTON, F. HAMMOND, and J. KENNER (J.C.S., 1926, 1802—1804).—Interaction of mercuric acetate and *o*-nitrotoluene at 150°, followed by treatment with bromine, gives 4-bromo-2-nitrotoluene together with 3-bromo-2-nitrotoluene; this is (*a*) reduced to 3-bromo-*o*-toluidine, of which the *acetyl* derivative, m. p. 166°, is oxidised to 3-*bromo*-2-*acetamidobenzoic acid*, m. p. 212°, and (*b*) converted into 6-*bromo*-o-*tolunitrile*, m. p. 99° (also prepared from 2-cyano-*m*-toluidine). Oxidation of the crude bromonitrotoluene with potassium permanganate in presence of magnesium sulphate yields 4-bromo-2-nitrobenzoic acid, together with 3-bromo-2-nitrobenzoic acid, the *ethyl* ester of which, m. p. 132°, is converted by copper powder at 180° into *ethyl* 2 : 2′-*dinitrodiphenyl*-3 : 3′-*dicarboxylate*, m. p. 113°, hydrolysable to 2 : 2′-*dinitrodiphenyl*-3 : 3′-*dicarboxylic acid*, m. p. 286° (decomp.).

F. M. HAMER.

Behaviour of the colloidal acetates of tetra- and penta-mercuriacetanilide. A. BERNARDI (Gazzetta, 1926, **56**, 337—357; cf. A., 1895, i, 357; 1912, i, 931; 1914, i, 610).—Experiments on the halogenation of the acetates of tetramercuriacetanilide and pentamercuriacetanilide are described, and the results are tabulated and discussed. *Pentabromoacetanilide*, m. p. 284—285°, was prepared by the action of bromine on acetanilide pentamercuriacetate, and from acetanilide-2 : 4 : 6-trimercuriacetate one atom of bromine was introduced by treatment with the calculated amount, with production of the *compound* $C_6H_2Br(HgOAc)_2{\cdot}NHAc$. The action of sodium chloride, sodium bromide, sodium iodide, copper chloride, and barium chloride on the same mercury derivatives was also studied; a certain quantity of halogen can be introduced by these salts, with production of such compounds as $C_6Hg_5Cl(OAc)_4{\cdot}NHAc$, $C_6Hg_5Cl_1(OAc){\cdot}NHAc$, but it is not possible to obtain pure compounds by this means. Large quantities of the salts used are adsorbed, increasing with the concentrations. The experiments are in agreement with the theory of Rossi (A., 1922, i, 605; 1924, i, 459) that the particles which react in colloidal solutions are not derived simply from the dispersion of the dissolved substance, but are formed by the union of the dissolved substance with any ions arising from the dissociation of the electrolytes present, so that in nearly all colloidal solutions there exist, not particles of the pure substances, but rather complexes of the latter and adsorbed ions. This complex exists only under certain experimental conditions, so that by variation of these conditions the complex itself alters and by consequence changes its properties and those of the solution in which it is dispersed.

S. B. TALLANTYRE.

Effects of radiations from quartz mercury-vapour arc on some properties of proteins. H. L. STEDMAN and L. B. MENDEL (Amer. J. Physiol., 1926, **77**, 199—210).—In the case of twelve purified proteins, exposure to the quartz mercury-vapour lamp resulted in a lowering of the coagulation temperatures, the assumption of a characteristic odour, and a yellow tint. These changes were independent of water, electrolytes, or oxygen. The specific rotations of edestin, gliadin, and diluted egg-albumin and, under certain conditions, the acidity of the protein solutions, were increased by irradiation. A surface film was not always formed nor did coagula always appear.

R. K. CANNAN.

Action of hypochlorites on amino-acids and proteins. N. C. WRIGHT (Biochem. J., 1926, **20**, 524—532).—On addition of increasing quantities of neutral caseinogen or neutral gelatin to solutions of hypochlorite, the available chlorine of the solutions falls as the quantities of the protein are increased. Beyond a certain stage, however, the addition of increased quantities of protein destroys less available chlorine than the preceding smaller quantities. Eventually, on the introduction of still larger quantities of protein, the available chlorine begins to decrease again permanently. When glycine is added to hypochlorite, the available chlorine falls to zero as the quantity of the amino-acid is at first increased. By further increasing the added glycine, some available chlorine is again demonstrated. The latter increases as the quantity of the amino-acid is increased until it equals its original strength, and remains at this level even if still larger quantities are added. This phenomenon is due to the fact that

the available chlorine acts as an oxidising agent only with small quantities of glycine, but as the quantities of the amino-acid are increased, it acts both as an oxidising and as a chlorinating agent and eventually as a chlorinating agent alone, producing a stable chloroamino-compound capable of liberating iodine from potassium iodide. Other amino-acids behave similarly towards hypochlorite except that their chloroamino-compounds are less stable. On adding mixtures of two amino-acids one of which yields a very stable chloroamino-derivative (glycine) and the other an unstable chloroamino-derivative (cystine) to hypochlorite, the behaviour of the available chlorine is similar to that observed in the case of proteins. It is therefore assumed that the anomalous results obtained with proteins are due to the sodium hypochlorite acting as an oxidising and chlorinating agent and to the variable stability of the chloroamino-derivatives formed by the latter reaction. The quantitative difference in the behaviour of caseinogen and gelatin towards hypochlorite may be due to the difference in their relative content of glycine and cystine. S. S. ZILVA.

Determination of arginine and histidine. A. KOSSEL and W. STAUDT (Z. physiol. Chem., 1926, **156**, 270—274).—Arginine in fairly acid solution is precipitated quantitatively by flavianic acid (2 : 4-dinitro-α-naphthol-7-sulphonic acid) even in presence of histidine. A micro-method based on this observation is described for the determination of arginine and histidine in small quantities of protein hydrolysates. Results agree well with those given by the usual macro-technique, although obtained with less expenditure of time and material. H. D. KAY.

Determination of small quantities of water in methyl alcohol. M. M. RISING and J. S. HICKS (J. Amer. Chem. Soc., 1926, **48**, 1929—1933).—Small quantities of water in methyl alcohol may be determined (cf. Crismer, A., 1903, ii, 10; 1907, ii, 134) by measuring the solution temperature of the sample with hexane and reference to a curve previously determined by density measurements. The range of solution temperatures is 15° for 3% of water. Light petroleum gives a wider range, but its use is not recommended owing to its variable composition. R. BRIGHTMAN.

Analysis of glacial acetic acid. H. D. RICHMOND and E. H. ENGLAND.—See B., 1926, 645.

Analysis of acetic anhydride. H. D. RICHMOND and J. A. EGGLESTON.—See B., 1926, 645.

Determination of very small quantities of guanidine by means of the nephelometer. R. RITTMANN (Biochem. Z., 1926, **172**, 36—39).—Guanidine can be determined in water or Ringer solution by measuring with the nephelometer the turbidity produced when Nessler solution is added, but the method cannot be used for determining guanidine in blood or serum. H. I. COOMBS.

Thalleioquinine reaction. G. W. HARGREAVES (J. Amer. Pharm. Assoc., 1926, **15**, 100—105).—Saturated bromine water is added drop by drop to 3—5 c.c. of an aqueous solution of quinine or a quinine salt until a faint yellow colour appears; with 0·1% solutions, a yellowish-white precipitate is formed temporarily. Aqueous alcoholic phenylhydrazine hydrochloride solution (3—5 c.c.) is then added, and, after shaking, a slight excess of 10% ammonia solution, when a pink to deep red wine colour is produced. The reaction is not given by other common alkaloids, but is inhibited by alkalis, morphine, codeine, and an excess of bromine or phenylhydrazine. CHEMICAL ABSTRACTS.

Electrometric titration of alkaloids. Application of the quinhydrone electrode. L. R. WAGENER and W. J. MCGILL (J. Amer. Pharm. Assoc., 1925, **14**, 288—294).—With the quinhydrone electrode, equilibrium is rapidly attained, and the danger of reduction of the alkaloid is decreased; the results are reproducible, but it is not yet certain whether the electrometric or the colorimetric method of titration is the more accurate. The end-point as indicated by methyl-red is always reached before the electrometric end-point, giving results nearer to the theoretical values, but no absolute criterion of the purity of the samples was available. Details are given of the procedure employed. CHEMICAL ABSTRACTS.

Analytical use of the difference in the ease of oxidation of organic substances. G. BOTSTIBER (Biochem. Z., 1926, **174**, 68—83).—An investigation of the rate of oxidation of the products of protein hydrolysis with a view to their determination by differential combustion. Amino-acids are readily oxidised by potassium permanganate in acid solution, but they are resistant to hydrogen peroxide, whereas the reverse is the case with polypeptides and basic substances. The differentiation is not sufficiently marked for use in analysis. E. C. SMITH.

Biochemistry.

Chemical regulation of respiration. II. Accumulation of lactic acid in the isolated brain during anaërobic conditions and the rôle of lactic acid as a continuous regulator of respiration. D. A. MCGINTY and R. GESELL (Amer. J. Physiol., 1925, **75**, 70—83).—Lactic acid accumulates rapidly in the isolated dog's brain, the initial concentration being doubled in 4 min. Carbon monoxide anoxæmia in the living animal considerably increased the lactic acid content of the brain and blood. It is believed that lactic acid is an important regulator of respiration. CHEMICAL ABSTRACTS.

Respiratory exchange of the mussel (*Mytilus edulis*, L.). J. R. Bruce (Biochem. J., 1926, **20**, 829—846).—Taking into consideration the effect of temperature and oxygen pressure on the rate of gaseous metabolism, it was found that the oxygen uptake of a normal full-grown mussel was profoundly affected by the condition of reproductive maturity. The influence of the annual temperature wave is approximately three times that attributable to the sexual cycle. The rising respiratory quotient from July to March corresponds with the period when the storage of glycogen takes place preparatory to fat formation, whilst the low respiratory quotient corresponds with the period from March onwards to the actual spawning period in May. S. S. Zilva.

Variations in loosely-bound carbon dioxide of the blood. H. Tangl (Biochem. Z., 1926, **172**, 355—357).—During digestion there is a 10% increase in the carbon dioxide content of the blood, synchronous with the rise of carbon dioxide in the alveolar air. It can be correlated with the secretion of acid by the stomach, but may also, in part, be derived from the increased metabolism of the glands.
C. Rimington.

Ammonia content and formation in blood. V. Ammonia content of normal human blood. A. Klisiecki (Biochem. Z., 1926, **172**, 442—446).—The venous blood of 44 normal individuals, determined by the method of Parnas and Heller, contained an average of 0·026 mg. of ammonia-nitrogen per 100 c.c., with extreme fluctuations of 0·011 mg. and 0·037 mg., respectively. C. Rimington.

Do ammonium salts exist in the blood? G. Fontès (Bull. Soc. Chim. biol., 1926, **8**, 497—500).—Polemical against Parnas and Klisiecki (this vol., 536). The author reaffirms that blood contains inappreciable amounts of ammonium salts, which can play no part in the production of urea.
C. P. Stewart.

Composition of ox blood. III. Blood of calves on diet of milk, with or without supplements. C. F. Huffman and C. S. Robinson (J. Biol. Chem., 1926, **69**, 101—112).—Calves fed on a diet of whole milk alone or of whole milk supplemented with cod-liver oil or with various inorganic salts, developed convulsions of the type observed in parathyroidectomised animals; the only change in the composition of the blood observed under these conditions was a reduction in the concentration of calcium.
C. R. Harington.

Effect of age on the hæmoglobin of the rat. C. S. Williamson and H. N. Ets (Amer. J. Physiol., 1926, **77**, 480—482).—The concentration of hæmoglobin in the blood steadily falls during the first fifty days of life, rises again to a maximum about the 150th day, and thence falls somewhat to a steady value. R. K. Cannan.

Action of salts of quinine, strychnine, morphine, and caffeine on leucocytes. G. Forti (Arch. Farm. sper., 1926, **41**, 102—112).—Quinine hydrochloride exhibits a paralysing action on leucocytes, and similar effects, diminishing in order, are produced by strychnine nitrate, morphine hydrochloride, and free caffeine. The initial exciting effect which some authors consider that these alkaloids have on the activity of the cellular protoplasm could not be detected. T. H. Pope.

Porphyrins from oxyhæmin anhydride. A. Hamsik (Z. physiol. Chem., 1926, **156**, 218—230).—Nencki's hæmatoporphyrin may be obtained by shaking oxyhæmin anhydride with excess of hydrobromic acid in glacial acetic acid solution and keeping for 24 hrs. By shaking the anhydride with stannous chloride in acetone solution and adding concentrated hydrochloric acid to the cooled solution, a series of *porphyrins* is obtained which have not yet been identified with any known pigments. Elementary analysis of one of these agrees with the formula $(C_{34}H_{34}O_4N_4)_2O$ or $C_{31}H_{34}O_4N_4,0{\cdot}5H_2O$. Preliminary experiments are described in which, in place of acetone, glacial acetic acid and methyl alcohol have been successfully employed as solvents.
H. D. Kay.

Naturally occurring porphyrins and porphyratins. VIII. Spectrochemical reaction of iron porphyratins with potassium hydroxide, sodium cyanide, and hydrazine hydrate. O. Schumm (Z. physiol. Chem., 1926, **156**, 268—269; cf. this vol., 751).—When iron-porphyratin is dissolved in a small quantity of water and $\frac{1}{3}$ vol. of 15% potassium hydroxide, the addition of $\frac{1}{2}$ vol. of concentrated sodium cyanide solution followed by a few drops of hydrazine hydrate or, better, ammonium sulphide solution yields a solution giving a characteristic two-banded absorption spectrum. H. D. Kay.

Possible significance of hexosephosphoric esters in ossification. VI. Phosphoric esters in blood-plasma. M. Martland and R. Robison (Biochem. J., 1926, **20**, 847—855).—The presence of small amounts of acid-soluble phosphoric esters in blood-plasma has been confirmed. They are present in quantities greater than could be accounted for by their production from the laking of the corpuscles. Bone phosphatase hydrolyses these esters. Several modifications in the determination of phosphorus by the Briggs method are given. S. S. Zilva.

Blood sugar. II. Initial rise. J. C. Bock, H. Schneider, and M. Gilbert (J. Biol. Chem., 1926, **69**, 9—16; cf. this vol., 635).—Following ingestion of 1·75 g. of dextrose per kg. body-weight, in normal individuals, the rise in concentration of dextrose in the blood was apparent within 5 min. and reached its first maximum in about 30 min. This indicates that the response of the glycogenic function of the body to influx of dextrose is a fairly slow process.
C. R. Harington.

Effect of calcium and potassium ions on the blood-sugar. E. Sterkin (Biochem. Z., 1926, **174**, 1—17).—A slight rise or fall of blood-sugar may occur after the administration of calcium or potassium chloride, but usually no change occurs. The salts have no effect on adrenaline hyperglycæmia. Pilocarpine and atropine, either alone or in the presence of calcium or potassium, have no effect on the blood-sugar. E. C. Smith.

Reducing power of blood *in vitro*. E. SLUITER and J. KOK (Arch. Néerland. Physiol., 1926, **11**, 189—199).—Fluctuations in the quantity of reducing substances in the blood *in vitro* may be explained by the formation of intermediate reducing substances formed from the decomposition of dextrose.

H. I. COOMBS.

Electro-dialysis of human blood-serum. A. BERNHARD and J. J. BEAVER (J. Biol. Chem., 1926, **69**, 113—124).—Electro-dialysis of blood-serum shows that sodium, potassium, and probably chlorine are completely diffusible, whereas calcium, magnesium, and phosphorus are only partly so; the proportion of the total calcium and magnesium which is diffusible shows marked variations, the highest figures obtained being 28% for calcium and 42% for magnesium.

C. R. HARINGTON.

Dependence of the surface tension of the blood on the hydrogen-ion concentration. L. JENDRASSIK and J. GELDRICH (Biochem. Z., 1926, **174**, 99—105).—The surface tension of hæmolysed blood decreases slightly with increase of hydrogen-ion concentration, and *vice versa*. In the absence of hæmolysis, there is no effect. E. C. SMITH.

Equations applicable to simple hæmolytic reactions. E. PONDER (Proc. Roy. Soc., 1926, **B**, **100**, 199—222).—The velocity of the reaction between the lysin and the cell component on which it acts, the distribution of the resistances of the cells in suspension, and the fact that the reaction occurs only in the region of the surfaces of the cells must be taken into account in an analysis of the kinetics of simple hæmolytic systems. The expression describing the reaction between the lysin and the cell component is of the first order, but contains also a term relating to the surface upon which the lysin can act. The sigmoid nature of the percentage hæmolysis–time curves is completely explained by the assumption that the resistances of the cells are distributed according to a symmetrical frequency curve, the distribution being altered in some cases by secondary reactions. There is round each cell a " zone of action " extending for about 6 μ from the cell surface within which the molecules of lysin enter into combination with the cell surface. Simple hæmolysins do not produce their effect by solvent action of the red cell membrane.

P. W. CLUTTERBUCK.

Inorganic composition of bones. J. HOWLAND, W. McK. MARRIOTT, and B. KRAMER (J. Biol. Chem., 1926, **68**, 721—728).—The ratio of calcium to phosphorus in bones, normal or rachitic, indicates that these elements are combined in the form of tertiary calcium phosphate; further, the precipitate obtained by mixing an acid solution of calcium and magnesium chlorides with one of sodium hydrogen carbonate, chloride, and phosphate, so that the concentrations of the various ions were similar to those obtaining in serum, and aërating the solution until the p_H was about 8·0, consisted of tertiary calcium phosphate. The ratio of calcium phosphate to calcium carbonate is lower in rachitic than in normal bones.

C. R. HARINGTON.

Nature of the sugar residue of the cerebrosides of ox-brain. J. PRYDE and R. W. HUMPHREYS (Biochem. J., 1926, **20**, 825—828).—The mixed cerebrosides from ox-brain (see A., 1914, i, 225) were exhaustively methylated, the products hydrolysed with acid methyl alcohol at 100°, and the tetramethylgalactosides were obtained by fractional distillation in a high vacuum. The tetramethylgalactose obtained by hydrolysing the methylgalactoside had an equilibrium value of $[\alpha]_D$+115° in water. It is therefore concluded that the sugar residue of the cerebrosides is homogeneous and that it has the amylene oxidic structure of the normal stable galactose. S. S. ZILVA.

Mineral content of skin. H. BROWN (J. Biol. Chem., 1926, **68**, 729—736).—Dried human skin has on the average Ca 0·046, Mg 0·030, Na 0·36, K 0·24%; dog skin, Ca 0·043, Mg 0·027, Na 0·20, K 0·24%; rabbit skin, Ca 0·074, Mg 0·035, Na 0·18, K 0·15%.

C. R. HARINGTON.

Cholesterol and phospholipin content of human cutaneous epithelium. H. C. ECKSTEIN and U. J. WILE (J. Biol. Chem., 1926, **69**, 181—186).—The cutaneous epithelium of man yields 2·4—9·9% of " total lipins " in which 13—24% of cholesterol is contained; 2·5—3·15% is phospholipin. The content of cutaneous fat in cholesterol and in phospholipins is therefore much greater than that of subcutaneous fat. C. R. HARINGTON.

Iodine partition in the thyroid. H. E. MEYER (Z. physiol. Chem., 1926, **156**, 231—249).—Rabourdin's method (Annalen, 1850, **76**, 375) with slight modification is recommended as particularly useful for biochemical iodine determinations. Substances containing iodine may be extracted from the thyroid with ether, alcohol, or water, but in all cases the greater part of the iodine remains unextracted. Water extracts more iodine than the other two solvents. Methods are described in detail for fractional extraction of the gland, whereby it is possible to divide the iodine into inorganic, lipin, and protein fractions.

H. D. KAY.

Existence of a characteristic level of nucleic phosphorus of tissues. M. JAVILLIER and H. ALLAIRE (Compt. rend., 1926, **183**, 162—164).—The following amounts (mg./100 g. of dry tissue) of nucleic phosphorus were found for the various organs of the horse: thymus 1296, pancreas 643, spleen 390, liver 204, thyroid 139, kidney 169, heart 61, brain 75, muscle 25, spinal cord 20, and the values with other species are not very different. G. M. BENNETT.

Amount of cobalt in organs of animals. G. BERTRAND and M. MÂCHEBŒUF (Bull. Soc. chim., 1926, [iv], **39**, 942—945).—See A., 1925, i, 996.

H. E. F. NOTTON.

Existence of α- and β-philothione. J. DE REY PAILHADE (Bull. Soc. Chim. biol., 1926, **8**, 518—522).—α-Philothione, acting on sulphur with production of hydrogen sulphide, but giving no coloration with sodium nitroprusside, appears to be identical with ovalbumin. β-Philothione, reacting with sulphur and

with sodium nitroprusside, is present in living tissues and can be produced from α-philothione by the action of heat or of weak acids. Philothione is not identical with glutathione. C. P. STEWART.

"Lecitiburin," a lecithin obtained from the eggs of the shark. H. P. PONCE (Rev. Fac. Cienc. Quím., 1925, **3**, 77—88; cf. A., 1925, i, 97).—The following additional data are given for "lecitiburin": m. p. 70°, iodine value 55·88, total fatty acids 1·74. It contains 2·11% of nitrogen and 3·43% of phosphorus. G. W. ROBINSON.

Constituents of the mussel (*Mytilus edulis*). R. J. DANIEL and W. DORAN (Biochem. J., 1926, **20**, 676—684).—Taurine and mytilitol were extracted by aqueous alcohol from mussel powder and from wet mussel flesh. Experimental evidence is produced confirming the methyl*cyclo*hexanehexitol structure given to mytilitol by Ackermann (A., 1921, i, 764) as opposed to Jansen's *cyclo*pentitol formula (Arch. Néerland., 1917, III, **B 2**, 130; A., 1913, i, 791). The tissues of *Mytilus* contain a substance resembling glutathione, cholesterol, and probably highly unsaturated fatty acids. S. S. ZILVA.

Determination of globulin increase in [cerebro-] spinal fluid. G. E. ROCKWELL (J. Lab. Clin. Med., 1925, **10**, 578—579).—When 1 c.c. of a reagent composed of 1 part of concentrated nitric acid and 4 parts of water, saturated with magnesium sulphate and sodium chloride, is introduced under 0·5—1 c.c. of cerebrospinal fluid, an increase in globulin content is indicated by the appearance of a ring.
CHEMICAL ABSTRACTS.

Phosphorus compounds of milk. II. Liberation of phosphorus from caseinogen by enzymes and other agents. C. RIMINGTON and H. D. KAY (Biochem. J., 1926, **20**, 777—790).—Pepsin does not liberate inorganic phosphorus from caseinogen in 9 days, and a large proportion of this element is found in the paranuclein produced during this digestion. Trypsin in sufficient concentration hydrolyses the organic to inorganic phosphorus, and hydrolysis with 1% sodium hydroxide at 37° for 24 hrs. converts all of the organic phosphorus into inorganic phosphorus. Hydrolysis with 1% sulphuric acid at 37° has no action on caseinogen in this respect. Bone phosphatase does not hydrolyse caseinogen, whilst kidney phosphatase does so very slightly. The separation of phosphorus from phosphopeptone by the action of trypsin is more rapid than from caseinogen, and hydrolysis with 1% alkali at 37° liberates all of the organic phosphorus, as also does the action of kidney phosphatase; bone phosphatase eliminates about two thirds of the organic phosphorus. No inorganic phosphorus is produced from the peptone by digestion with pepsin for 71 hrs. or with 1% sulphuric acid at 37° for 48 hrs. The whole of the organic phosphorus of paranuclein was converted into the inorganic state by hydrolysis with 1% sodium hydroxide at 37°. With trypsin, there was slow hydrolysis, whilst neither phosphatase had any action on it.
S. S. ZILVA.

Effect of heat on milk. I. Physico-chemical changes. II. Influence of diets of fresh and treated cow's milk on the calcium, phosphorus, and nitrogen metabolism of the young pig. H. E. MAGEE and D. HARVEY (Biochem. J., 1926, **20**, 873—884, 885—891).—I. When proteins are precipitated with colloidal ferric hydroxide, 85% of the total calcium is found in solution in the case of whole fresh milk and 71% in that of whole milk heated for 30 min. at 65°. When the caseinogen is coagulated by rennin, the average loss in pasteurised milk is 2% and in boiled milk 4% of soluble calcium expressed as percentage of the total calcium. About 26% of the total calcium is in diffusible form in fresh milk, about 20% in pasteurised milk, and about 15% in boiled milk. There is a lowering of the p_H on boiling milk. Heat progressively lessens the stability of the colloids of milk and increases the size of the protein particles. Pasteurisation for 30 min. causes a slight fall in viscosity, but boiling for 1 hr. causes a marked increase. There is no difference in the rates of tryptic digestion of milk before and after heating.

II. A young pig on a diet of cow's milk and cereals showed signs of rickets after 30 days. The addition of a soluble calcium salt to this diet enabled young pigs to thrive for 60 days. On a diet of cereals and milk, the retention of calcium, phosphorus, and nitrogen was lower with heated milk than with fresh and sour milk. The addition of soluble calcium to a ration containing heated milk raised the retention of calcium, phosphorus, and nitrogen by more than the weight of the calcium added. Reduction of the soluble calcium of the diet increased the urinary phosphorus and nitrogen. S. S. ZILVA.

Carbohydrate of normal urine. J. PATTERSON (Biochem. J., 1926, **20**, 651—655).—The osazone of urinary sugar differs from that of dextrose. It is without definite m. p., gradually decomposing between 170° and 182°, and passing into a viscous, tarry mass at 182—184°. It differs in crystalline form from phenylglucosazone and is also more soluble in hot water. The osazone of the urinary sugar and the sugar itself are unstable to acids. The hydrolysis of the complex carbohydrate frequently found in normal urine liberates a reducing sugar which is fermentable.
S. S. ZILVA.

Neutral salts in high-tension fields. I. Electrical factor in urinary secretion. II. R. KELLER and J. GICKLHORN (Biochem. Z., 1926, **172**, 233—241, 242—248).—I. In high-tension electric fields, in addition to water, colloids, and ions, neutral salts also suffer a displacement towards the cathode. This may be due to the establishment of an electric polarity or to the mechanical effect of the moving water and may be of importance in biological processes.

II. Blood undergoes a process of ultrafiltration through the glomerular membrane, and the latter becomes thereby negatively charged. The epithelium of the convoluted tubules is, in the main, strongly negative with positive granules and here electro-osmotic reabsorption of water and sodium chloride occurs. Carbamide, which migrates towards the anode, is not reabsorbed. C. RIMINGTON.

Determination of the amount and composition of the fat of fæces. F. S. Fowweather (Brit. J. Exp. Path., 1926, 7, 7—14, 15—21).—Saxon's wet method gives higher results for total and neutral fat than Cammidge's dry method. In general, but not always, there is a transference of fatty acids from the free to the combined state by the dry as compared with the wet method. When the total fat exceeds 28% of the total dry matter, abnormality is probable. When the neutral fat exceeds 12% of the total dry matter or 60% of the total fat, deficient fat-splitting is indicated. When the free and combined fatty acids exceed 20% of the dry matter or 75% of the total fat, deficient fat-absorption is indicated.
Chemical Abstracts.

Nickel, cobalt, and diabetes. G. Bertrand and M. Mâchebœuf (Compt. rend., 1926, **183**, 257—259; cf. this vol., 869).—Injection or oral administration of nickel and cobalt salts has a favourable influence in alleviating the symptoms in some cases of diabetes. L. F. Hewitt.

Effect of nickel and cobalt salts on certain diabetics. F. Rathery and L. Levina (Compt. rend., 1926, **183**, 326—328; cf. preceding abstract).—Subcutaneous injection of a solution containing nickel and cobalt salts into some diabetics resulted in temporary disappearance of glycosuria and increased sugar tolerance, but in other cases no effect was observed. L. F. Hewitt.

Chemical composition of normal and luetic sera. A. A. Solari (Rev. Fac. Cienc. Quím., 1925, **3**, 1—63).—See A., 1925, i, 858.

Metabolic aspects of calcium therapy. A. P. Briggs (Arch. Intern. Med., 1926, **37**, 440—444).—The partition of phosphorus is only slightly influenced by potassium acetate and magnesium acetate, whilst calcium acetate and chloride cause considerable diversion of phosphorus from the urine into the fæces. The relief from the phosphorus load with calcium acetate is followed by reduced ammonia synthesis by the kidneys; potassium, sodium, and magnesium excretion is not appreciably affected. The theory that sodium excretion following the administration of calcium chloride is caused, not by ion antagonism, but by residual hydrochloric acid from calcium excretion in the fæces is thereby supported. The phosphorus retention of nephritis can be corrected by calcium acetate without causing alkali retention and œdema peculiar to sodium hydrogen carbonate therapy. Chemical Abstracts.

Urinary proteins. Crystalline proteins of nephritis. W. A. Welker, W. A. Thomas, and L. Hektoen (J. Amer. Med. Assoc., 1926, **86**, 1333—1334).—Globular or acicular crystals of urinary protein obtained in nephritis consisted of serum-albumin, euglobulin, and pseudoglobulin.
Chemical Abstracts.

Nitrogen retention and kidney function. H. Berglund (Svenska Läkartidningen, 1924, **21**, 953—968).—Normal whole blood contains 32·1 mg. of total residual nitrogen, consisting of 6·4 mg. of amino-, 11·5 mg. of urea-, and 13·7 mg. of undefined residual nitrogen. The residual nitrogen for plasma and erythrocytes and the creatine–creatinine partition are also given. Administration of creatine causes an increase of plasma creatine, whilst the creatinine remains unaltered. Chemical Abstracts.

Significance of blood chemical changes in pertussis. J. C. Regan and A. Tolstouhov (J. Amer. Med. Assoc., 1926, **86**, 1116—1119).—In pertussis, an uncompensated acidosis occurs. Cure by administration of alkali is associated with a rapid rise of inorganic phosphorus and a change in the p_H of the blood. Chemical Abstracts.

Pathogenesis of tetany. V. Prevention and control of parathyroid tetany by calcium lactate. VI. By strontium lactate. VII. By oral administration of kaolin. VIII. Effect of guanidine intoxication on the blood calcium of parathyroidectomised dogs. L. R. Dragstedt and A. C. Sudan (Amer. J. Physiol., 1926, **77**, 296—306, 307—313, 314—320, 321—325).—V. Thyreoparathyroidectomised dogs were kept free from tetany by daily doses of 1·5—4·4 g. of calcium lactate per kg. Young or pregnant animals required up to three times this dose. Milk in daily amounts as great as 2 litres did not prevent tetany. The value of milk in infantile tetany is probably to be ascribed to the lactose rather than to the calcium present.

VI. The life of parathyroidectomised dogs was prolonged at least 24 days by administration of strontium lactate. That it is less effective than the calcium salt may be due to irritant effects on the gastric mucosa.

VII. Feeding 50—200 g. of kaolin per day was effective in controlling tetany and preserving the dogs. It is suggested that tetany is an intoxication of gastro-intestinal origin and that the kaolin serves to remove the toxic products and to modify the intestinal flora.

VIII. In parathyroidectomised dogs which had been kept free from tetany for several months by lactose there was no notable fall in the concentration of calcium in the blood following guanidine intoxication. R. K. Cannan.

Inorganic constituents of blood-serum in disease. J. B. Pincus, H. A. Peterson, and B. Kramer (J. Biol. Chem., 1926, **68**, 601—609).—Comparison of the fluid obtained by filtering blood-serum through collodion sacs shows that in infantile tetany and in experimental parathyroid tetany the proportion of filterable calcium is much reduced; in chronic nephritis it is normal unless uræmic convulsions occur, when it is reduced. In all these conditions the inorganic phosphorus of the serum is increased, but in infantile tetany the increase is small; the proteins of the serum are unchanged during tetany. At p_H 4·7 (the isoelectric point of the serum proteins) the calcium of the serum is completely filterable. Irradiation with ultra-violet light caused no change in the calcium of the blood of parathyroidectomised animals, but raised the blood calcium of children with infantile tetany. C. R. Harington.

Oxidative mechanisms of tumour tissue. I. Anaërobic habit of tumour tissue. B. E. Holmes (Biochem. J., 1926, **20**, 812—815).—The tissues of

rat sarcoma, rat carcinoma, and human mammary carcinoma contain abnormally small amounts of reduced glutathione. The first two tissues show very slight activity in reducing added glutathione and are found spectroscopically deficient in the respiratory pigment, cytochrome. S. S. ZILVA.

Ketosis in pregnancy. V. J. HARDING and K. D. ALLIN (J. Biol. Chem., 1926, **69**, 133—151).—During pregnancy there is no tendency to develop ketosis more readily than under normal conditions. C. R. HARINGTON.

Permeability of polarised membranes in relation to the permeability of the nucleus and the proportions of the various amino-acids which are contained in proteins. T. B. ROBERTSON (Austral. J. Exp. Biol., 1926, **3**, 105—113).—The properties of nuclear membranes are discussed, very largely from the point of view of the work of Collip (J. Biol. Chem., 1920, **42**, 227). In order to conform with the results of this and other work, the nuclear membrane must be electrically polarised. The proportions of the various amino-acids present in gelatin, caseinogen, and lactalbumin afford further indication that such a polarised membrane exists within the cell and governs the availability of amino-acids for protein synthesis. A. G. POLLARD.

Economy of nutrition under different oxygen pressures. L. DRASTICH (Bull. Soc. Chim. biol., 1926, **8**, 508—517).—Larvæ of *Salamandra maculosa*, kept in water with an atmosphere of varying oxygen content, show that the greater the oxygen content of the atmosphere, the less is the food consumption required for a given increase of body-weight. C. P. STEWART.

Copper, manganese, and zinc as factors in the metabolism of animals. J. S. MCHARGUE (Amer. J. Physiol., 1926, **77**, 245—255; cf. *ibid.*, 1925, **72**, 583).—The growth of rats on a synthetic diet was much improved by the addition to the diet of compounds of manganese and, to a less degree, of copper and of zinc. Analyses are given of the mineral matter in the carcases of the rats on the various diets. R. K. CANNAN.

Uncombined sugar in the white and yolk of the hen's egg during autogenesis. I. D. GADASKIN (Biochem. Z., 1926, **172**, 447—450).—The sugar content of the white decreases from 0·5% at the commencement of incubation to 0·03% on the 11th day, after which it entirely disappears. The yolk contains 0·33% of sugar, the amount decreasing during incubation to 0·07% on the 11th day and then disappearing. C. RIMINGTON.

Metabolism of aromatic acids. X. Fate of *m*-nitro-, *m*-amino-, *m*-hydroxy-, and *m*-chlorophenylacetic acids. J. B. MUENZEN, L. R. CERECEDO, and C. P. SHERWIN (J. Biol. Chem., 1926, **68**, 503—511).—*m*-Nitrophenylacetic acid (*chloride*, m. p. 77°; *ethyl* ester, b. p. 39°/12 mm.) was excreted unchanged after feeding, as the sodium salt, to men and rabbits, but was converted by the dog into m-*nitrophenaceturic acid*, m. p. 176°; *m*-aminophenylacetic acid was excreted unchanged by man and the dog, but in the rabbit gave rise to m-*acetamidophenylacetic acid*, m. p. 122—124°; *m*-hydroxyphenylacetic acid was excreted unchanged in all cases; *m*-chlorophenylacetic acid was converted in all cases into m-*chlorophenylaceturic acid*, m. p. 144—145°. C. R. HARINGTON.

Benzoylated amino-acids in the animal organism. III. Determination of hippuric acid. Synthesis of hippuric acid in rabbits. W. H. GRIFFITH (J. Biol. Chem., 1926, **69**, 197—208).—Acidified urine is extracted continuously with ether for 1 hr.; the residue obtained on evaporation of the ethereal extract consists of the whole of the hippuric acid together with some carbamide; the latter is destroyed with sodium hypobromite and the residual (hippuric acid) nitrogen determined by the Kjeldahl method.

After oral administration of sodium benzoate to rabbits in doses of 0·25—1·0 g. per kg. body-weight, the hippuric acid excreted amounted to 65—90% of the total combined benzoic acid of the urine; appreciable amounts of benzoic acid must therefore have been excreted as benzoylglycuronic acid. C. R. HARINGTON.

Absorption from the isolated, surviving intestine. III. Influence of saponin on the resorption of sugar solutions. F. LASCH and S. BRÜGEL (Biochem. Z., 1926, **172**, 422—427).—Saponin facilitates very markedly the resorption of isotonic dextrose solutions. C. RIMINGTON.

Relation of solubility to absorption of calcium salts from the intestine. L. IRVING (J. Biol. Chem., 1926, **68**, 513—520).—The changes in concentration of calcium in the blood, following injection of solutions of various calcium salts into the intestine of dogs, indicate that the rate of absorption is considerably greater in the case of the chloride and acetate than in the case of the less soluble lactate and citrate; the rate of absorption of the acetate and lactate was accelerated by the addition of acetic and lactic acids, respectively, to bring the p_H of the solution to about 3·5. C. R. HARINGTON.

Nitrogen and fat deposition in growing pigs fed on a diet containing glycine and ammonium acetate as a substitute for protein. H. BUCKENAUER (Biochem. Z., 1926, **174**, 188—231).—The nitrogen balance of growing pigs is maintained by the substitution of either glycine or ammonium acetate for about 25% of the fish protein of the basal diet, but in spite of the substitution of potato flake for the starch of the diet, fat deposition is less than in the control animals. E. C. SMITH.

Soft pork. II. Influence of food on composition of body fat of hogs. III. Effect of food fat on body fat as shown by separation of individual fatty acids. N. R. ELLIS and H. S. ISBELL (J. Biol. Chem., 1926, **69**, 219—238, 239—248).—Alterations in the physical constants and of the percentages of individual fatty acids of the fat of hogs, following alterations in the diet, indicate that the nature of the latter has a marked influence on the composition of the body fat. C. R. HARINGTON.

Intermediary fat metabolism. I. Effect of a fat diet on carbohydrate metabolism. II. Influence of ions on formation and excretion of acetone substances. T. TAKAO (Biochem. Z., 1926, **172**, 272—279, 280—295).—I. No evidence could be obtained for the transformation of fat into carbohydrate in starving, phloridzinised dogs, rabbits rendered glycosuric by adrenaline, or in rats, either from the urinary excretion or from the glycogen content of the livers. The formation of sugar from glycerol occurs to some extent.

II. Ketosis in dogs was increased by ammonium lactate and chloride, whereas Wigglesworth (A., 1925, i, 191), working with rats, found the opposite effect. Potassium and magnesium increase and calcium decreases the acetone substances in both blood and urine, whilst no regular behaviour could be observed in the case of sodium.

There is no connexion between the excretion of sugar and of acetone substances, but a parallelism exists between acetone substances and β-hydroxybutyric acid. C. RIMINGTON.

Importance of fat in the action of the thyroid gland on metabolism. Theory of the action of the thyroid gland. I. ABELIN, E. GOLDENER, and B. KOBORI (Biochem. Z., 1926, **174**, 232—256).—The liver of animals fed on thyroid gland is incapable of storing glycogen from fed carbohydrate unless considerable excess fat is added to the diet. Egg-yolk, cod-liver oil, and higher fatty acids have the same action, but brain substance, although rich in lipins, is inactive. The higher alcohols are much less effective than the corresponding acids. The glycogen deposited is formed from carbohydrate, not from fat. Thyroid feeding also inhibits the formation of glycogen from dihydroxyacetone. The action of adrenaline on the glycogen metabolism of the liver is very different from that of the thyroid gland, since, although it causes glycogenolysis, it does not inhibit the new formation of glycogen, but may actually stimulate it. E. C. SMITH.

Physiological behaviour of glucosan. H. J. DEUEL, S. S. WADDELL, and J. A. MANDEL (J. Biol. Chem., 1926, **68**, 801—820).—Administration of a preparation of glucosan to normal or phloridzinised dogs caused no change in the respiratory quotient; when given by mouth it was absorbed to the extent of about 30% only, and the absorbed fraction was excreted unchanged in the urine. It is therefore unlikely that, as has been suggested, the substance can be profitably included in the diet of human diabetics. C. R. HARINGTON.

***Rigor mortis* and *post mortem* acid formation in different organs under the action of poisons.** J. DE NITO (Biochem. Z., 1926, **174**, 131—142).—Rigor supervenes more rapidly in animals killed by a quick-acting poison such as strychnine and potassium thiocyanate than in those killed by bleeding or by a blow. In all organs an increase in acidity occurs after death, which is greatest in skeletal muscle, decreasing in magnitude in heart, liver, kidney, and lungs. The increase is particularly marked after ammonium chloride poisoning, and is least in animals dying from hunger and insulin poisoning. In animals poisoned with phloridzin and those dying from hunger, rigor sets in rapidly, but is not very marked. E. C. SMITH.

Can purines, creatinine, or creatine replace histidine in the diet? Availability of synthetic glyoxalines in supplementing diets deficient in histidine. G. J. COX and W. C. ROSE (J. Biol. Chem., 1926, **68**, 769—780, 781—799).—Addition of adenine, guanine, creatine, and creatinine, separately or together, to the food of young rats on a basal diet, the sole deficiency of which was lack of histidine, failed to induce satisfactory growth in the animals. The rate of growth of rats on a histidine-deficient diet was not affected by administration of glyoxaline, 4-methylglyoxaline, 4-hydroxymethylglyoxaline, glyoxaline-4-aldehyde, or of glyoxaline-4-carboxylic, -acetic, -propionic, and -acrylic acids; addition to the diet of *dl*-glyoxaline-4-lactic acid, however, was almost as effective in promoting growth as addition of histidine itself. C. R. HARINGTON.

Creatinine and uric acid metabolism. H. ZWARENSTEIN (Biochem. J., 1926, **20**, 743—750).—There are marked variations in the daily excretion of creatinine in man. When nuclear-rich materials such as thymus and pancreas are ingested, there is an increased output of uric acid, but not of creatinine. When uric acid is ingested by man, there is an increase in creatinine excretion whenever the uric acid is absorbed. A transformation, therefore, of the glyoxaline nucleus in uric acid to creatinine probably takes place. Uric acid given to a dog *per os* causes an increase in the allantoin excretion, the excretion of creatinine remaining unaltered. In man, the ratio of uric acid to creatinine is about 1 to 4. In dogs, the ratio of allantoin to creatinine is about 2·4 to 1, and similar ratios were found in the cat, rat, guinea-pig, and rabbit. S. S. ZILVA.

Nuclein metabolism. XIV. Uricolysis and uric acid excretion. S. J. THANNHAUSER, L. LURZ, and P. VON GARA (Z. physiol. Chem., 1926, **156**, 251—267).—Pus from three sources, (*a*) sterile, from a dog, (*b*) from a tuberculous abscess, (*c*) from a case of empyema, was found to have no uricolytic power. After intravenous injection of sodium urate into dogs, the kidneys are found to have taken up most of the injected acid. A kidney was found still to possess the power of specifically taking up uric acid from the blood-stream even after all nervous connexion with the rest of the body had been cut; the amount taken up was, however, less than that taken up by the intact organ. No evidence was obtained of any uric acid excretion by way of the intestine. H. D. KAY.

Metabolism of women. II. Cyclic variations in uric acid and non-protein nitrogen of blood. R. OKEY and S. E. ERIKSON (J. Biol. Chem., 1926, **68**, 687—709).—The uric acid of the blood of normal women is slightly increased just before and reduced during menstruation; the non-protein nitrogen is increased during and immediately after menstruation; the latter increase cannot be accounted for by any of the known constituents of blood, and is therefore ascribed to the "rest nitrogen." C. R. HARINGTON.

Dietetic value of oatmeal proteins. G. A. HARTWELL (Biochem. J., 1926, **20**, 751—758).—The proteins of oatmeal are of good value as regards growth in rats. A diet of oatmeal, butter, and salt mixture, however, is inadequate for gestation and lactation. The addition of food casein, gluten, gelatin, and egg-albumin to the oatmeal produces better growth in the suckling rat. S. S. ZILVA.

Proteins of wheat bran. III. Nutritive properties. J. C. MURPHY and D. B. JONES (J. Biol. Chem., 1926, **69**, 85—99).—As was anticipated from their relatively high content of those amino-acids known to be essential for growth (A., 1925, i, 1027), the proteins of bran have been found to be considerably more efficacious than those of wheat endosperm in promoting the growth of young rats. C. R. HARINGTON.

Effect of histamine on the acid-base balance. Effect of histamine on protein catabolism. A. HILLER (J. Biol. Chem., 1926, **68**, 833—846, 847—864).—Subcutaneous injection into dogs of 1·3 mg. of histamine per kg. body-weight caused a mild acidosis which was partly accounted for by increased urinary excretion of hydrogen carbonate. Injections of 1·8 mg. of histamine per kg. body-weight caused, in fasting dogs, an increase in protein catabolism, as indicated by increases in the urea of the blood and urine, which was proportional to the magnitude of the dose of histamine. C. R. HARINGTON.

Action of morphine on protein metabolism. H. VÖLKER (Biochem. Z., 1926, **174**, 55—67).—After feeding with meat, an increase was observed in the oxygen consumption and non-protein nitrogen of the blood of a dog, which reached a maximum in 2—4 hrs. Injection of morphine caused a delay, proportional to the intensity of its action, in the attainment of the maximum, which did not occur until more than 6 hrs. after the meal. Introduction of the meat into the duodenum caused a hastening of the processes, and the injection of morphine had no effect. The action of the morphine is therefore to cause delayed emptying of the stomach. E. C. SMITH.

Effect of light on creatinine and creatine excretion and on basal metabolism. M. EICHELBERGER (J. Biol. Chem., 1926, **69**, 17—28).—Exposure of normal women and children to direct summer sunlight, or to the light of the electric (carbon) arc, caused an increase in the excretion of creatinine during the period of irradiation, followed by decreased excretion during the first few hours afterwards; no effect was observed on the excretion of creatine or on the basal metabolic rate. C. R. HARINGTON.

Effects of caffeine and theobromine on the formation and excretion of uric acid. G. W. CLARK and A. A. DE LORIMIER (Amer. J. Physiol., 1926, **77**, 491—502).—The concentration of uric acid in the blood tends to increase after ingestion of either caffeine or theobromine. This is probably due, not to direct oxidation of these substances, but to increased production of uric acid, in the case of caffeine, and to diminished excretion, in the case of theobromine. Prolonged administration of either substance tends to impair active excretion by the kidney. R. K. CANNAN.

Physiological action of 1 : 3 : 7 : 9-tetramethylxanthine compared with that of caffeine. C. PADERI (Arch. Farm. sper., 1926, **41**, 92—101).—Experiments with frogs show that the introduction of a methyl group into the caffeine molecule to form 1 : 3 : 7 : 9-tetramethylxanthine results in diminution of the activity, the new compound exhibiting the spinal action, but not the muscular action of caffeine. T. H. POPE.

Effects of asphyxia and isletectomy on the blood-sugar of *Myxocephalus* and *Ameiurus*. W. W. SIMPSON (Amer. J. Physiol., 1926, **77**, 409—419).—The average blood-sugar of *Myxocephalus* (sculpin) immediately after catching the fish was 0·03%. On exposure to air this rose to about 0·12% in an hour. Removal of the principal islets resulted in a hyperglycæmia far exceeding that attributable to the exposure during the operation. The blood of *Ameiurus* (fresh-water cat-fish) behaved in the same way in asphyxia. It is suggested that the hyperglycæmia thus occurring is due to the breakdown of "combined sugar" of the blood, since the increase in reducing power of the blood on hydrolysis is relatively less after than before asphyxia. R. K. CANNAN.

Effect of ethylcarbylamine on the Pasteur reaction. O. WARBURG (Biochem. Z., 1926, **172**, 432—441).—Ethylcarbylamine had no effect on the respiration of rat tissues, the carbon dioxide assimilation of *Chlorella*, or the anaërobic fermentation of yeast and tumour cells; all these processes are strongly inhibited by hydrogen cyanide in the same concentration (10^{-3} *N*). Aërobic respiration was found by Pasteur to inhibit the process of fermentation, and the chemical reaction relating the two processes may be termed the "Pasteur reaction." Ethylcarbylamine has no effect on the anaërobic lactic acid fermentation of Jensen-sarcoma, but in presence of oxygen the fermentation coefficient is as high as that characteristic of anaërobiosis. The effect is reversible, the normal quotient returning when the tissue is transferred to Ringer solution; it is specific for ethylcarbylamine. C. RIMINGTON.

Chemical constitution and physiological action. I. Position isomerism in relation to the miotic activity of some synthetic urethanes. E. STEDMAN (Biochem. J., 1926, **20**, 719—734).—Since the miotic activity of physostigmine (eserine) is due to the urethane grouping in the molecule, the following urethanes and their derivatives have been synthesised for physiological tests: p-*Dimethylaminophenyl methylcarbamate*, m. p. 131° [*hydrochloride*, m. p. 157°; *methiodide*, m. p. 170° (decomp.); *picrate*, m. p. 179° (decomp.)]; *ethylcarbamate*, m. p. 123° [*hydrochloride*, m. p. 77°; *methiodide*, m. p. 160° (decomp.); *picrate*, sinters 145°, m. p. 158°]; *phenylcarbamate*, m. p. 163° [*hydrochloride*, m. p. 182° (decomp.); *methiodide*, m. p. 169°; *picrate*, m. p. 177° (decomp.)]. m-*Dimethylaminophenyl methylcarbamate*, m. p. 85—86° [*hydrochloride*, sinters 164°, m. p. 170° (decomp.); *methiodide*, m. p. 165° (decomp.); *picrate*, m. p. 177°

(decomp.)]; ethylcarbamate, m. p. 99—100° [*hydrochloride*; *methiodide*, m. p. 152° (decomp.); *picrate*, m. p. 95°]; *phenylcarbamate*, m. p. 159° [*hydrochloride*, m. p. 180° (decomp.); *methiodide*, m. p. 160° (decomp.)]; *carbamate*, m. p. 137° [*hydrochloride*, m. p. 174° (decomp.)]. o-*Dimethylaminophenyl methylcarbamate*, m. p. 76° [*hydrochloride*; *methiodide*, m. p. 78—80° (decomp.); *picrate*, m. p. 152° (decomp.)]; *ethylcarbamate*, m. p. 61° [*hydrochloride*; *methiodide*, m. p. 119° (decomp.); *picrate*, m. p. 124°]; *phenylcarbamate*, m. p. 144°. The hydrochloride of the *methylcarbamido-derivative of hordenine* has m. p. 161°; the *phenylcarbamido-derivative of hordenine*, m. p. 119° [*hydrochloride*, m. p. 194° (decomp.)]; the *methylcarbamido-derivative of* 8-*hydroxyquinoline* sinters at 152°, m. p. 161° [*hydrochloride*, m. p. 168° (decomp.)], *ethylcarbamido-derivative of* 8-*hydroxyquinoline*, m. p. 150° (decomp.), (hydrochloride, m. p. 84°).

Miotic action was shown by dimethylaminophenyl methylcarbamate, *m*-dimethylaminophenyl carbamate, *o*-dimethylaminophenyl ethylcarbamate, and the methylcarbamido-derivative of hordenine; *m*- and *p*-dimethylaminophenyl ethylcarbamate were inactive. The basic group modifies the action of the urethane grouping. By converting the tertiary basic group in the urethane derived from the isomeric dimethylaminophenols into a quaternary ammonium group, the activities of the *m*-compounds are intensified, whilst those of the *o*- and *p*-compounds are abolished. Amongst the isomeric urethanes those compounds derived from phenols which according to the polarity theory should be the most acidic are the least active.

S. S. Zilva.

Toxicity of organic compounds to spores of *Phytophthora colocasiæ*, Rac. B. N. Uppal (J. Agric. Res., 1926, **32**, 1069—1097).—The toxicity of the normal aliphatic alcohols increased with the mol. wt.; the normal alcohols were more toxic than their isomerides. Aldehydes owe their toxicity mainly to the aldehyde group, the radical to which it is attached having little influence, although substitution of a nitro- or hydroxyl group in benzaldehyde increased the toxicity. Formaldehyde is exceptional and was highly toxic; so also was glyoxal. The lower members of a homologous series of organic acids were, in general, more toxic than the higher members. The nature and position of a substituent in an aromatic acid affected the toxicity. The results are considered in relation to the dissociation constants of the acids. C. T. Gimingham.

Mode of absorption and mechanism of action of bismuth in experimental syphilis. C. Levaditi, S. Nicolau, R. Schoen, A. Girard, and Y. Manin (Ann. Inst. Pasteur., 1926, **40**, 541—573).—When insoluble bismuth compounds are injected intramuscularly, phagocytes absorb the metallic bismuth liberated in the tissues, fix it, and assist in its conversion into a soluble bismuth–protein complex, in which form it is very gradually liberated over a long period of time from the muscle and circulated in the blood in amounts sufficient to destroy the spirochæte, but insufficient to damage the kidney. Soluble compounds, on injection, are too rapidly absorbed and cause renal disturbances. Most of the insoluble bismuth remains for some time near the point of injection, and of that circulated, the kidney, lungs, and spleen contain most. Lysis of the spirochæte requires only infinitesimal traces of bismuth (1—2 μg. in the case of chancre of rabbit), the metal acting as a catalyst and the process being analogous to many enzymic processes (cf. A., 1924, i, 691, 1016; 1925, i, 463, 1005, 1117). P. W. Clutterbuck.

Pharmacology of bismuth salts. I. Determination of bismuth. II. Toxicity and urinary elimination of soluble bismuth salts. C. S. Leonard. **III. Toxicity and urinary elimination of potassium bismuth tartrate.** C. S. Leonard and J. L. O'Brien. **IV. Toxicity and urinary elimination of bismuth oleate and bismuth metal.** C. S. Leonard (J. Pharm. Exp. Ther., 1926, **28**, 81—87, 89—108, 109—119, 121—130).—I. The material is oxidised by wet combustion, potassium iodide added, and the bismuth determined as potassium bismuth iodide by colorimetry. In the case of blood, liver, and fæces, citric acid is added to mask the effect due to iron. Interference is caused by heavy metals, arsenic, lead, and copper, but these are usually present in amounts insufficient to cause disturbance.

II. Sodium and potassium bismuth tartrates, sodium bismuth citrate, and sodium bismuth thiosulphate are toxic to rabbits, producing necrosis of the tubules with all the usual nephritic and uræmic symptoms. The maximum tolerated doses given intramuscularly are 100, 150, and 300 mg. per kg., respectively, corresponding with bismuth doses of 40, 50, and 200 mg. per kg. The tartrate displays the greatest initial rate of urinary excretion, and as with the other salts, the rate diminishes until death. In sublethal doses, the tartrate excretion shows a series of crises and stoppages in bismuth excretion, the other salts show variations only. The higher the dose, the lower is the initial rate of excretion. Sodium bismuth thiosulphate is equal in toxicity to the tartrate; it is excreted more slowly than the latter, but more rapidly than the insoluble bismuth salts. The detoxicant action of thiosulphates may be explained as a mobilisation of local insoluble depôts.

III. Dipotassium bismuth tartrate is nephrotoxic, the maximum tolerated dose for rabbits (intramuscular) being 150 mg. per kg. (containing 75 mg. of bismuth) and the minimum nephropathic dose 100 mg. per kg. (in a 2-week period). Its rate of excretion is fairly uniform, not diminishing, as in the case of the soluble tartrate, but the excretion is less the higher the dose given. The therapeutic ratio is 1/75.

IV. Bismuth oleate is toxic to rabbits, causing necrosis of the kidney and all symptoms of uræmic poisoning. The maximum tolerated dose (intramuscular) is about 200 mg. Bi per kg. The excretion resembles that of sodium bismuth citrate. Precipitated bismuth ("neo-trepol") is less toxic, the maximum tolerated dose lying between 400 and 500 mg. per kg., but 85 mg. per kg. was still partly nephrotoxic. As with the above, the heavier the dose the less is the urinary excretion.

The toxic effect of tartrobismuthates is an additive effect of the tartrate and bismuth ions.

C. Rimington.

Hæmochromatosis and chronic poisoning with copper. F. B. MALLORY (Arch. Intern. Med., 1926, **37**, 336—363).—Injection of copper powder or feeding of copper acetate causes the deposition in rabbit's liver of hæmofuscin; excess of copper causes hæmoglobinuria. Hæmofuscin is not a copper compound of hæmoglobin, but an intermediate between hæmoglobin and hæmosiderin. CHEMICAL ABSTRACTS.

Elimination of mercurials. L. W. ROWE (J. Amer. Pharm. Assoc., 1925, **14**, 317—325).—A study of the distribution and the rapidity and manner of elimination of mercuric chloride, mercury salicylate, mercury succinimide, and "mercurosal" after injection into dogs. CHEMICAL ABSTRACTS.

Autolysis. IV. Effect of iodine on autolysis. V. Effect of iodine on autolysis *in vivo*. O. STEPPUHN and A. TIMOFEJEVA (Biochem. Z., 1926, **174**, 84—89, 90—98).—IV. The effect of iodine on the autolysis of liver tissue is determined by the method of its administration. Addition of iodine to the protein suspension at p_H 3·8—7·6 gives the usual result, viz., acceleration or inhibition of proteolysis according to the magnitude of the dose, but addition of the emulsion to the same volume of iodine solution has no effect at p_H 7·1 and 7·6, and inhibition only at p_H 3·8. No conclusion can be reached by this method as to the part played by the individual proteases in tissue autolysis.

V. The addition of iodine to the liquid perfusing an organ causes an increase in the proteolysis of the tissues. Injection of iodine into the intact animal results in an increase in the non-protein nitrogen of the blood. Iodides are without effect on this process, and the presence or absence of the thyroid gland is immaterial. The rate of autolysis of mice previously treated for a considerable period with small doses of iodine is increased, but with large doses is diminished. The increased nitrogen metabolism following the administration of iodine is probably due to the direct stimulation of proteolytic enzymes. Thyroidectomised animals autolyse less rapidly than normal, and iodine has less effect on the former. Iodides are without action in either case. E. C. SMITH.

Effect of temperature on the catalase reaction. I. Effect of concentration of hydrogen peroxide. II. Loss of catalase activity. III. Effect of p_H. IV. Theory of catalase reaction. S. MORGULIS, M. BEBER, and I. RABKIN (J. Biol. Chem., 1926, **68**, 521—533, 535—545, 547—557, 557—563).—I. The activity (measured by the total oxygen liberated) of catalase prepared from ox-kidney is at a maximum at about 8°, although the speed of the actual reaction is greater at higher temperatures; the reduction in activity of catalase at higher temperatures is due to destruction of the enzyme by hydrogen peroxide and is therefore more marked the higher the concentration of the latter. In presence of high concentrations of hydrogen peroxide and at low temperatures, the reaction is at first rapid and then exhibits a quiescent period. The temperature coefficient varies with the concentration of hydrogen peroxide.

II. Catalase will withstand heating at temperatures up to 40° for 1 hr. without loss of activity; heating at higher temperatures for the same period causes progressively greater loss of activity, until at 58° inactivation is complete; the course of inactivation by heat is that of a bimolecular reaction, whereas the inactivation by hydrogen peroxide is a unimolecular reaction. Exposure to −15° for 1 hr. results in only 12% loss of activity.

III. Catalase acts best at p_H 5·0—9·0; the loss of activity is more rapid on the acid than on the alkaline side of this range, from which it is concluded that catalase may be a weak acid. The rate of destruction of catalase by rising temperature is greatest at the optimum p_H for the action of the enzyme and least on the acid side of this range. The latent period at the beginning of the reaction is increased by preliminary partial inactivation of the catalase by heat and also when the p_H is less than 5·0.

IV. A theoretical discussion of the above results. C. R. HARINGTON.

Adsorption of diastase. Z. UNNA (Biochem. Z., 1926, **172**, 392—410).—Adsorption of diastase from pancreas extract by animal charcoal is irreversible and increases as the temperature is raised. At 0° and the ordinary temperature, the adsorption curve reaches a maximum, after which it slowly falls, but at 37° no subsequent fall occurs. The adsorption curves for enzyme and accompanying impurities intersect. Neither surface-active alcohols nor phenylurethane interfere with the adsorption. Adsorbed diastase is, however, practically inactive. C. RIMINGTON.

Separation of the enzymes of barley malt. II. Lichenase and cellobiase. H. PRINGSHEIM and A. BEISER (Biochem. Z., 1926, **172**, 411—421).—Treatment of barley malt, freed from maltose and dextrins by dialysis, with aluminium hydroxide at p_H 11, removed 60—70% of the cellobiase by adsorption; the remainder, together with some lichenase, was removed by treatment with aluminium hydroxide at p_H 3. It was recovered by washing off at p_H 3. Lichenase free from cellobiase was thus obtained. C. RIMINGTON.

Optimum p_H for glycogenase and its bearing on regulation of dextrose concentration in the body. M. B. VISSCHER (J. Biol. Chem., 1926, **69**, 3—7).—The optimum p_H for the action of glycogenase from the rabbit's liver, whether in presence or in absence of adrenaline, is 6·5. This is in agreement with the depletion of the glycogen stores of the body known to occur in conditions involving a tissue acidosis. The results of Langfeldt (A., 1921, i, 473) were not confirmed. C. R. HARINGTON.

Protein nature of invertase. R. WILLSTÄTTER (Ber., 1926, **59**, [*B*], 1591—1594).—The occasional isolation of invertase preparations which are free from tryptophan is not in harmony with von Euler and Josephson's conception (this vol., 865) that tryptophan is an essential component of the enzyme molecule. Reproducible methods of freeing invertase from tryptophan cannot be given. A probable method consists in subjecting to ageing the autolysates from invertase-rich yeasts, whereby the tryptophan carrier is replaced by other materials;

after very prolonged dialysis further purification is effected by adsorption. H. WREN.

Hydrolysis of sucrose solutions by invertase. P. ACHALME (Bull. Soc. Chim. biol., 1926, **8**, 565—567).—Polemical against Ingersoll (this vol., 641). C. P. STEWART.

Connexion between degree of dispersion of substrate and enzyme action. Determination of enzymic lipolysis. P. RONA and H. KLEINMANN (Biochem. Z., 1926, **174**, 18—42).—A comparison of the rates of hydrolysis by lipase of two emulsions of triolein of the same concentration, but of different degrees of dispersion, showed no difference until the hydrolysis had proceeded to 25%, after which the finer emulsion hydrolysed slightly more rapidly. The degree of dispersion of the substrate is therefore of very little significance. The determination of the triolein concentration depends on the formation of an emulsion of a known degree of dispersion by treatment with ammoniacal ammonium oleate and nephelometric examination. E. C. SMITH.

Synthetic action of pancreatic and intestinal lipases. J. GROEN (Arch. Néerland. Physiol., 1926, **11**, 169—183).—The reversible action of enzymes is well demonstrated by lipases and carbohydrases. This is especially the case in the esterification of a fatty acid with glycerol in the presence of lipase. This reversibility is important in the absorption of fats by the intestine. H. I. COOMBS.

Effect of p_H on the proteolytic activity of papain. W. E. RINGER and B. W. GRÜTTERINK (Z. physiol. Chem., 1926, **156**, 275—324).—The activity–p_H curve for the action of crude papain on fibrin shows two maxima, one at p_H 2·5 and the other about 11. The proteolytic activity of the gastric juice of *Astacus fluviatilis* towards fibrin also has an optimum at p_H 11. There are, in addition, smaller maxima in the papain–fibrin curve; one is at 4·5, and, in presence of phosphate, which powerfully activates papain, there is a second at 7·0. Papain thus displays both peptic and tryptic properties, but it has not been possible to separate it into a pepsin- and a trypsin-like enzyme. With either serum-protein or secondary albumose as substrate, papain displays one optimum only, at p_H 3·75 for the former and p_H 4 for the latter protein. With either fibrin, serum-protein, or albumose as substrate, sodium cyanide strongly activates papain with increasing but not with decreasing p_H. The cyanide ion is the activating agent. Papain is held to be a single enzyme, and the various pecularities of its activity are ascribed to changes in the state either of the enzyme or of the substrate. H. D. KAY.

Kidney phosphatase. H. D. KAY (Biochem. J., 1926, **20**, 791—811).—The kidney contains a phosphatase which liberates inorganic phosphate from hydrolysable organic phosphorus compounds in the *post mortem* changes of the kidney. The rate of this liberation is increased by mechanical injury to the organ. The optimum reaction for the enzymic hydrolysis is p_H 8·8—9·2. The phosphatase is present in greater quantity in the cortex than in the medulla of the kidney. It is low per g. of tissue in the fœtal stage, but increases markedly just before and soon after birth. The activity of bone phosphatase, on the other hand, which is much more active than the kidney enzyme in the ossifying zone of the fœtal cartilage, is correlated with bone growth. The kidney phosphatase extract hydrolyses a variety of organic phosphorus compounds such as hexosediphosphate, hexosemonophosphate, glycerophosphate, etc. It hydrolyses the organic phosphorus in the plasma, but not the organic esters within the corpuscles when acting on whole blood. The red cells contain a substrate for kidney phosphatase. The action of the enzyme is inhibited by the presence of certain alcohols. Kidney extracts contain a feeble lecithinase which has an optimum p_H of 7·0—7·4. The inorganic phosphate and to a less degree the acid-soluble organic phosphorus in the kidney remain constant during the adult life of the animal. S. S. ZILVA.

Purification of oxydoreductase (Schardinger enzyme, perhydridase). B. SBARSKY and D. MICHLIN (Biochem. Z., 1926, **174**, 116—119).—The enzyme preparation (A., 1925, i, 472) is further purified by adsorption on kaolin, elution with ammonium hydroxide, and evaporation to dryness in a vacuum. It may be kept under light petroleum indefinitely without loss of activity. E. C. SMITH.

Xanthine oxydase. VII. Specificity of the system. M. DIXON (Biochem. J., 1926, **20**, 703—718).—Xanthine oxydase shows a high degree of specificity towards the hydrogen donator, but none towards the hydrogen acceptor. Using the methylene-blue technique, hypoxanthine, xanthine, aldehydes, and possibly adenine to a slight extent, were oxidised by xanthine oxydase of milk out of thirty-five substances tested. Out of a large number of substances tested, all, including Clark's "reduction potential indicators," acted as hydrogen acceptors in oxidising hypoxanthine by the above enzyme. S. S. ZILVA.

Tyrosinase–tyrosine reaction. V. Production of *l*-3 : 4-dihydroxyphenylalanine from tyrosine. H. S. RAPER (Biochem. J., 1926, **20**, 735—742).—*l*-3 : 4-Dihydroxyphenylalanine has been isolated in small amounts as a product of the action of tyrosinase on *l*-tyrosine. This dihydroxy-compound is oxidised more rapidly by tyrosinase than tyrosine, giving rise to the same unstable red pigment (A., 1923, i, 1146; this vol., 434). Its presence also increases the oxidation of tyrosine by the enzyme in the initial stages of the reaction. *l*-3 : 4-Dihydroxyphenylalanine is readily oxidised by tyrosinase when added to a borate buffer with a reaction of p_H 8 (cf. McCance, this vol., 203). It is considered to be the first product in this enzyme reaction, which is then oxidised further to the red pigment. S. S. ZILVA.

Formation of polysaccharides by yeast preparations. H. NAGANISHI (Biochem. J., 1926, **20**, 856—864).—Harden and Young's observation of the enzymic production of polysaccharides in yeast juice and similar preparations (A., 1914, i, 237) is confirmed. The formation of these substances is irregular and conditions favouring their formation could not be ascertained. There is no relation between the

amount of phosphoric esters formed and the degree of polysaccharide formation. Among the compounds formed are substances which are probably dextrins possessing about twice the rotatory power and about 36% of the reducing power of the dextrose formed from them by hydrolysis. There is no definite evidence of the production of glycogen.

S. S. Zilva.

Function of phosphates in the dissimilation of hexoses. A. J. Kluyver and A. P. Struyk (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 322—333).—A new theory of the catalysing action of mineral phosphates on the fermentation of sugars is developed, and is shown to agree with known experimental facts. The scheme suggested postulates the intermediate formation of unstable hexose monophosphoric ester due to the attachment of the phosphate residue to the ε-carbon atom. This subsequently breaks up into carbon dioxide, alcohol, and the phosphate, on account of the transference of hydrogen from the δ- to the γ-carbon atom under the combined activating action of the phosphate group and the protoplasm of the enzyme.

M. S. Burr.

Effect of organic substances on the glycolysis of yeast. W. Schoeller and M. Gehrke (Biochem. Z., 1926, **172**, 358—372).—The inhibition of glycolysis due to members of the quinine group and the organic mercury compounds is probably a result of adsorption; of the other alkaloids investigated, only strychnine and veratrine had a powerful effect, whilst nicotine and coniine produced no inhibition. In a group, activity increases with the number of alkyl groups. Among the dyes, by far the greater activity is shown by the basic dyes, the introduction of lipin-soluble groups again resulting in increased inhibitory activity. Whereas choline and guanidine are without effect, acetylcholine and diphenylguanidine are powerful inhibitors, probably owing to their greater adsorbability. C. Rimington.

Pyruvic acid in alcoholic fermentation. F. Traetta-Mosca (Annali Chim. Appl., 1926, **16**, 167—169).—The acidity developing during the fermentation of dextrose solution by a pure culture of brewers' yeast was gradually neutralised by additions of brucine. Filtration of the fermented solution, followed by concentration to crystallisation, yielded crystals of a compound, m. p. 194°, agreeing in composition and mol. wt. with brucine pyruvate. T. H. Pope.

Simpler nitrogenous constituents of yeast. I. Choline and nicotinic acid. H. B. Vickery (J. Biol. Chem., 1926, **68**, 585—592).—Brewers' yeast was extracted with boiling water and the solution fractionated by the method previously described for lucerne juice (A., 1924, i, 1275, 1393); the filtrate from the precipitate obtained with mercuric acetate and sodium carbonate, containing 3·35% of the total nitrogen of the crude extract, was treated with phosphotungstic acid; after recovery from the phosphotungstates, the bases were precipitated with mercuric chloride; the solution obtained on recovery from this precipitate contained 2·41% of the total nitrogen of the crude extract; from this solution were isolated, as picrates, choline and nicotinic acid, representing 2·07 and 0·28%, respectively, of the total nitrogen of the crude extract. No indication of the presence of betaines was found.

C. R. Harington.

Determinations of permeability with *Saccharomyces cerevisiæ*. N. L. Söhngen and K. T. Wieringa (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 353—358).—In determinations of the amount of a substance penetrating into a cell, the measurement of water-transport into and out of the cell offers difficulty. This difficulty has been overcome by the use of gelatin. Since it does not raise the osmotic pressure of the liquid appreciably, nor penetrate the cell wall, and is not adsorbed by the cell, the variations in its concentration, combined with the variations in the concentration of the substance entering the cell, indicate the movements of the water. It has thus been found that, in 48 hrs., about 0·25 mg. of sodium chloride and 3·2 mg. of ureum (urea?) diffuse per g. of yeast of surface area about 1 m.^{2} With ureum (urea?) 2·2 mg. diffuse during the first 24 hrs., and during the last 24 hrs. 1 mg. per g. of yeast. With 1% sodium chloride, the amount of water withdrawn from the protoplasm was 8% and the imbibition water 12% or more. The behaviour of lactose resembles that of sodium chloride rather than that of ureum (urea?).

M. S. Burr.

Enzymic decomposition in lactic acid bacteria and yeast. R. Nilsson and E. Sandberg (Biochem. Z., 1926, **174**, 106—115).—*Thermobacterium helveticum* is without action on pyruvic acid, hence does not contain carboxylase. The lactic acid formed by fermentation of dextrose is dextrorotatory. Pyruvic acid is fermented by yeast completely free from co-zymase, and the addition of co-zymase does not affect the rate of fermentation. Since the rate of pyruvic acid fermentation is greater than that of dextrose, the possibility that the former is an intermediate in the fermentation of the latter is not excluded by its absence from the products of fermentation. E. C. Smith.

Acid production by *Aspergillus niger*. I. Processes of acid production. II. Gluconic acid formation. III. Citric acid formation. K. Bernhauer (Biochem. Z., 1926, **172**, 296—312, 313—323, 324—349).—I. The formation of gluconic and citric acids can be controlled by regulation of the temperature, oxygen supply, composition, and reaction of the medium.

II. In presence of lime, a practically theoretical yield of gluconic acid from sugar is obtainable. Alkali exerts a stimulating influence, but in time a tendency to produce oxalic acid arises.

III. Small quantities of mycelium in a medium containing chalk, but devoid of nitrogen, form chiefly gluconic acid, but with larger quantities of *Aspergillus* citric acid is formed exclusively. Abundant supplies of nitrogen in the culture fluid favour citric acid production, whilst inhibiting that of gluconic acid. In acid solutions, citric acid is formed more readily than is gluconic acid. At lower temperatures, relatively more gluconic acid, and at higher tem-

peratures more citric acid is formed, but the influence of temperature is much more pronounced on the formation of the latter. The optimum for acid production is 30—35°.

The processes giving rise to the two acids appear to be independent and citric acid production to be more closely related to nitrogenous metabolism.

C. RIMINGTON.

Determination of catalase and peroxydase in bacterial investigations. O. KIRCHNER and H. NAGELL (Biochem. Z., 1926, **174**, 167—181).—The catalase of *Diplococcus gonorrhœæ*, in contradistinction to that of *Staphylococcus aureus* and *Bacillus coli* and all tissue catalases, is very sensitive to changes of p_H. The determination of peroxydase by the pyrogallol method is dependent on the oxygen content of the medium, and is therefore not trustworthy in the presence of catalase. The substitution of ethyl hydrogen peroxide for hydrogen peroxide in the determination gives inconclusive results. The catalase activities of *D. gonorrhœæ*, *S. aureus*, and *B. coli* are in the proportions 30 : 10 : 1, their peroxydase activities in the proportions 10 : 10 : 1.

E. C. SMITH.

Preparation and properties of purified diphtheria toxoid. A. F. WATSON and E. LANGSTAFF (Biochem. J., 1926, **20**, 763—776).—By treating the filtrates of *C. diphtheriæ* with formaldehyde and acidifying them with acetic acid, a highly-active toxoid fraction is precipitated. This fraction can be purified further by reprecipitation with acetic acid or alcohol or by dialysis. Purified toxoid is stable to heat up to nearly 100°, to alkalinity up to about p_H 10, to mechanical shaking, and to aëration, and does not deteriorate on storage for considerable periods of time in the absence of preservatives. It is protein in nature and contains sulphur and occasionally phosphorus. S. S. ZILVA.

Losses of nitrogen caused by soil bacteria in pure cultures. M. LEMOIGNE and P. L. DOPTER (Compt. rend., 1926, **183**, 160—162).—Numerous bacteria normally present in soils and manures are able, in pure culture, to cause loss of nitrogen, the loss occurring after the initial development of the organism is over. G. M. BENNETT.

Variations of some forms of nitrogen in a pure culture of infusoria. A. LVOV and N. ROUKHELMAN (Compt. rend., 1926, **183**, 156—158).—The growth of *Glaucoma piriformis* in a culture medium causes a fall in peptone nitrogen at first owing to a tryptic enzyme which diffuses out into the medium and also shows its presence in cultures on gelatin by the liquefaction of the latter. At the same time, there occurs a rise in amino-nitrogen partly masked for a time by the absorption of these substances by the organism. Nitrogen as ammonia or amide increases throughout the growth. Urea does not occur, and if introduced is not affected. Uric acid is not excreted. Death of the organisms occurs after 20—40 days while abundant food is still present, and is presumably due to some substance not yet identified. This organism therefore resembles bacteria in its chemical behaviour. G. M. BENNETT.

Insulin convulsions and recovery. L. B. WINTER (Biochem. J., 1926, **20**, 668—675).—Rabbits at the moment of insulin convulsions, or even one hour after, have about the same amount of reducing sugar available in the liver and muscles as have normal animals. The minimum quantity of dextrose necessary for a rabbit of approximately 1 kg. to recover from insulin convulsions is about 0·5 g. A rise in the blood-sugar and a recovery from insulin convulsions are brought about by the injection of glucal in doses similar to those of dextrose. Glucosan administered subcutaneously in such doses does not relieve the convulsions or restore the animal to normal, although a rise in the blood-sugar takes place. S. S. ZILVA.

Variations in the blood-sugar content following the administration of insulin. H. J. JOHN (J. Lab. Clin. Med., 1926, **11**, 548—560).—The amount of insulin administered intravenously bears no regular relation to the fall of blood-sugar. In some cases a rise follows. The level of the blood-sugar is not *per se* a criterion of the probability that a reaction will follow the administration of insulin.

CHEMICAL ABSTRACTS.

Effect of dihydroxyacetone on insulin hypoglycæmia. W. R. CAMPBELL and J. HEPBURN (J. Biol. Chem., 1926, **68**, 575—583).—Symptoms of insulin hypoglycæmia in man and in the rabbit can be relieved by administration of dihydroxyacetone, although the effect is not so rapid as that of dextrose. The falling off in the concentration of dihydroxyacetone in the blood, after intravenous injection into rabbits, is accompanied by a simultaneous rise in the concentration of dextrose; dihydroxyacetone is thus to be regarded as a possible precursor of dextrose.

C. R. HARINGTON.

Carbohydrate metabolism. I. Influence of insulin on lævulose and dextrose administered intravenously. M. WIERZUCHOWSKI (J. Biol. Chem., 1926, **68**, 631—652).—When either dextrose or lævulose is injected intravenously into normal dogs at a rate similar to that of the absorption from the intestine after a large oral dose, each sugar is excreted unchanged to the extent of about 10%. If insulin be administered at the beginning of the sugar injection, the excretion of sugar is much decreased in the case of dextrose, but is not altered in that of lævulose; the magnitude of the effect of insulin is independent of the dose of the latter between the limits 1·9—8·5 units per kg. body-weight. C. R. HARINGTON.

Separation of an internal secretion of the parathyroid glands. L. BERMAN (J. Lab. Clin. Med., 1926, **11**, 412—413).—Parathyroidectomised animals were kept alive and normal by daily injection of a crystalline substance obtained after removal of lipins and proteins from an acidified-alcoholic extract of parathyroid glands of the ox. The blood calcium increased; injections made 3—4 hrs. after parathyroidectomy prevented the retention of phosphate in the body. CHEMICAL ABSTRACTS.

Preparation, properties, and source of the parathyroid hormone. I. D. T. DAVIES, F. DICKENS, and E. C. DODDS (Biochem. J., 1926, **20**, 695—702).—The parathyroid hormone of Collip and Clark (A., 1925, i, 713, 754, 1017; this vol., 206) yields a picrate which is insoluble in water but is soluble in 70% acetone, and can be converted into a hydrochloride by Dudley's method (A., 1924, i, 585). The hormone can also be obtained from the parathyroid gland by the acetone–picric acid method used in the preparation of insulin (Dodds and Dickens, Brit. J. Exp. Path., 1924, **5**, 115). Insulin and, to a less extent, pituitrin also raise the serum-calcium, but when the latter is administered simultaneously with the former, it inhibits the calcium elevating power and blood-sugar lowering activity of the pancreas hormone. Preparations made from the pancreas by Collip and Clark's method also raise the blood calcium, but, like the parathyroid hormone, they have no action on the blood-sugar. The parathyroid hormone is destroyed by pepsin and trypsin.

These pharmacological tests were carried out on rabbits. The serum-calcium of these animals varies only within 1 mg. per 100 c.c. throughout the 24 hrs., and it rises during the period of the experiment when the rabbits are injected with large doses of Collip and Clark's parathyroid preparation at 4-hourly intervals. S. S. ZILVA.

Stability towards acid of the oxytocic principle of the infundibulum. A. STASIAK (J. Pharm. Exp. Ther., 1926, **28**, 1—7).—Short boiling with acetic acid in concentrations from 0·05 to 6·0% (p_H of extract 7·0—3·4) or hydrochloric acid 0·05% (p_H 4·6) in preparing the extracts leads to no loss in activity. With 0·5% hydrochloric acid (p_H 2·6), destruction is practically complete. Stability depends on p_H irrespective of the nature of the acid employed. No histamine formation occurs under the above conditions. The activity of the extracts is destroyed by alkali. C. RIMINGTON.

Unsaponifiable fraction of fish oil. G. WEIDEMANN (Biochem. J., 1926, **20**, 685—691).—Batyl alcohol and selachyl alcohol (A., 1922, i, 297) were obtained from the unsaponifiable fraction of the liver oil of the Greenland shark, *Somniosus microcephalus*, the former by separation from the hot alcoholic extract of the unsaponifiable fraction on cooling, and the latter from the mother-liquor. "Batyl diphthalic ester acid," $C_{20}H_{40}O_3,2C_8H_5O_3$, m. p. 97°, was prepared by treating the alcohol with phthalic anhydride in pyridine at the ordinary temperature. "Selachyl diphthalic ester acid" was prepared in a similar way and was purified by liberation from its lead and copper salts. In pure condition, the above alcohols showed neither growth-promoting nor antirachitic properties and did not give a colour reaction with sulphuric acid. There is a close resemblance between the ester acids of the alcohols which are present in cod-liver oil and selachyl diphthalic ester acid, the former alcohols being more unsaturated. S. S. ZILVA.

Photoactivity. I. Effect of cod-liver oil and other vitamin-containing substances on the photographic plate. H. VOLLMER (Biochem. Z., 1926, **172**, 467—482).—Cod-liver oil is able to affect a photographic plate, and this activity is increased by exposure of the oil to sunlight either in open or hermetically closed vessels. Irradiation for 3 hrs. produces maximal activity, which is not increased by longer exposure. No loss of photoactivity occurs during 1 hr. at 100°, but direct heating destroys it. Exposure to sunlight reactivates the oil. Hydrogen peroxide increases the activity of cod-liver oil. Addition of formaldehyde or sulphurous acid to the mixture destroys the activity irreversibly. Cod-liver oil liberates iodine from potassium iodide, and a parallelism exists between this property and the intensity with which it affects the photographic plate. There is thus a possibility of determining physiological activity iodometrically. Ether extracts of the oil are active, alcohol extracts practically inactive. If cod-liver oil is shaken out with water, some activity is shown by the water phase, whilst that of the oil is decidedly increased. Salt solutions extract no active material.

Lard and butter fat are inactive, but show activity after irradiation. Many plant oils are active and also liberate iodine with corresponding intensity.

Milk, blood, and some fruit juices are devoid of activity, but sawdust, shavings, and wood can be activated by irradiation.

The unsaponifiable fraction of cod-liver oil is not photoactive and cannot be rendered so by irradiation. C. RIMINGTON.

Photoactivity. IV. Specific colour-reaction of photoactive substances. H. VOLLMER (Biochem. Z., 1926, **174**, 143—145).—Aqueous extracts of photoactive oils give, in lesser degree, the same yellow coloration with alkali as the oils themselves. The reaction with the oil is stronger after irradiation with ultra-violet light. The substance responsible for the reaction is not the same as that to which the photoactivity is due, since some of the extracts which give a positive reaction are not photoactive. The reaction fails when the extracts are shaken with animal charcoal. The alkalinity at which the colour appears is different for different extracts, hence the substances responsible are not identical. E. C. SMITH.

Fearon's "pyrogallol" test as a possible basis for the determination of vitamin-*A*. S. G. WILLIMOT and T. MOORE (Biochem. J., 1926, **20**, 869—872).—Fearon's test for vitamin-*A* (this vol., 207) as modified by the authors is considered to be capable of quantitative application. S. S. ZILVA.

Solubility of vitamin-*B* in benzene. R. R. WILLIAMS and R. E. WATERMAN (J. Biol. Chem., 1926, **68**, 499—501).—The statement of McCollum and Simmonds (*ibid.*, 1918, **33**, 55), that vitamin-*B* can be extracted by means of benzene, holds good only when the raw material is moist with 95% alcohol; the vitamin is therefore not soluble in benzene, but is soluble in a mixture of benzene, alcohol, and water. C. R. HARINGTON.

Chemical studies of vitamin-*B* in Japan. U. SUZUKI (Sci. Papers Inst. Phys. Chem. Res., 1926, **4**, 295—302).—A review of recent work.

Antirachitic substances. IV. Polymerisation of cholesterol. C. E. Bills and F. G. McDonald (J. Biol. Chem., 1926, **68**, 821—831; cf. this vol., 645).—By moderating the course of the reaction previously described (*loc. cit.*) and in particular by arresting it at an earlier stage, there was obtained a *substance*, $C_{81}H_{138}O_3$, m. p. 203° (secondary m. p. 209° and 196°), $[\alpha]_D^{29}$ −40·8° in carbon tetrachloride; the substance appears to be a polymeride of 3 mols. of cholesterol; it gives the colour reactions of cholesterol, but does not yield an acetyl derivative; it has itself no antirachitic properties nor does it acquire such properties on exposure to ultra-violet light, but it is an intermediate product in the formation of the antirachitic resin which results from more prolonged boiling of cholesterol with fuller's earth (*loc. cit.*). C. R. Harington.

Dietary requirements for reproduction. V. Rôle of vegetable and fruit oils in fertility and lactation. VI. Types of sterility produced on a reproduction-deficient diet. VII. Lactation-promoting factor in unsaponifiable matter from wheat oil. B. Sure (J. Biol. Chem., 1926, **69**, 29—40, 41—51, 53—74; cf. A., 1924, i, 455).—V. Addition to a basal diet consisting of dried skimmed milk and cod-liver oil, of wheat oil, cottonseed oil, maize oil, or palm oil rendered possible a normal reproductive cycle in rats, the wheat oil being the most efficacious; addition of peach kernel, soya-bean, peanut, or olive oil sufficed to prevent sterility, but not to promote normal lactation, whilst linseed, coconut, sesamé, palm-kernel, rape-seed, mustard-seed, sweet almond, and commercial maize oils were unable to prevent sterility. The primary effect of reducing the allowance of the first group of oils was to increase the mortality of the young.

VI. On diets deficient in vitamin-*E* there were observed two types of sterility in rats; the first, occurring in females of the first generation, consisted of resorption of the fœtus; the second, occurring in the second generation, is of unknown character, but could be corrected by administration of a mixture of equal amounts of alum, sodium fluoride, sodium silicate, and manganese sulphate equal to 0·05% of the diet.

VII. From the unsaponifiable matter of wheat oil, after removal of sitosterol, was prepared a fraction which, when added in amounts of 4 mg. per diem to a diet deficient in vitamin-*E*, sufficed for a normal reproductive cycle in rats. Exposure of the active material to heat and oxidation gave preparations which prevented sterility but did not permit normal lactation; this observation, together with results obtained by changing rats from a normal to a vitamin-*E*-deficient diet at different stages of the reproductive cycle, suggests the possible existence of two factors, one concerned with gestation and the other with lactation. C. R. Harington.

Gases in the body of certain plants. S. A. Gaerlan (Philippine Agric., 1926, **14**, 557—567).—With advancing age, the amount of carbon dioxide decreases, and that of oxygen increases, in the air cavities of the bamboo stem. The ratio is greatest at noon. In the stems of one variety of bamboo the gases contained 5·42% CO_2, 13·07% O_2, and 81·51% N_2, but the proportions differed for closely related plants. Chemical Abstracts.

Physiological rôle of tannins. Michel-Durand (Compt. rend., 1926, **183**, 312—314; cf. A., 1924, i, 477).—Tannins are synthesised in the growing seedling of *Quercus pedunculata* until the food reserves fail. The quantity of acetone-soluble tannins present in the cotyledons follows the quantity of simple carbohydrates, whilst the acetone-insoluble, water-soluble tannins in the cotyledons remain constant until the starch stores are nearly depleted, when they increase in quantity. L. F. Hewitt.

Phloridzin. I. Significance of phloridzin in apple and pear tissue. II. Hydrolysis and determination of phloridzin. E. M. Harvey (Oregon Agric. Exp. Sta. Bull., 1925, [215], 1—23).—Apple and pear trees contain the greatest quantity (up to 20% of the total solids) of phloridzin in the early summer. Pear shoots contain more water and slightly more sugar than the apple, and twice as much phloridzin. Phloridzin is always most abundant at the tip of the shoot; at the tip it is present in maximal quantity early in the growing season, but in other parts of the shoot it decreases from earliest observation to the end of the season. It is suggested that the phenol acids, on which the synthesis of phloridzin depends, are by-products of metabolic activity, and that phloridzin serves as a protection against the accumulation of these substances or as a temporary repository of them for future use by the tissue. Chemical Abstracts.

***Ochna pulchra* berries.** A. W. Facer (Rhodesia Agric. J., 1925, **22**, 566—572).—The berries contain 8·4% of water and 32·9% of oil. The whole berry oil, d_{15}^{15} 0·9121, m. p. 22·5—25·5°, had acid value, 13·8; saponification value, 199·7; iodine value, 67; titre, 41·4°. The expressed cake contained water, 10·0; protein, 12·65; oil, 7·0; carbohydrates, 58·0; fibre, 9·8; ash, 2·55%. Chemical Abstracts.

New Zealand pepper-plant. H. J. Finlay (New Zealand J. Sci. Tech., 1926, **8**, 107—108).—From the leaves of the New Zealand pepper-plant, *Wintera colorata*, there have been extracted an essential oil (of which the main constituent appears to be a limpid, colourless oil, b. p. 169—174°, *d* 0·8449, *n* 1·47, [α] +10·15° in chloroform), and a pyrocatechol *tannin* which appears to differ from any yet recorded. Attempts to isolate the pungent principle were unsuccessful. W. O. Kermack.

Flower waxes: rose wax. H. Prophète (Compt. rend., 1926, **182**, 1559—1561).—Rose wax, green, m. p. 55—58·5°, saponification number 29·8, iodine value 13, Reichert–Meissl value 1·35, Hehner value 97·4, acetyl value (Lewkowitsch) 31·9, acid value (Leys) 3·15, after saponification yielded 80·2% of unsaponifiable matter (m. p. 54°, iodine value 8·6, acetyl value 33·3, containing 56·5% of hydrocarbons, 20·2% of alcohols, and 3·2% of hydroxy-acids), 17% of insoluble fatty acids, m. p. 56—57°, iodine value 32, neutralisation value 129, and 1·6% of soluble fatty acids, m. p. 57—59°. L. F. Hewitt.

Scyllitol from flowering dogwood (*Cornus florida*). R. M. HANN and C. E. SANDO (J. Biol. Chem., 1926, **68**, 399—402).—The alcoholic extract of the fat-free flowers and bracts of *Cornus florida* yielded, on concentration and long keeping, a small amount of scyllitol, identified by analysis of the substance itself and of its hexa-acetyl derivative and by crystallographic measurements. C. R. HARINGTON.

Inositol from the blackberry (*Rubus argutus*, Link) and flowering dogwood (*Cornus florida*). C. E. SANDO (J. Biol. Chem., 1926, **68**, 403—406).—Together with scyllitol (cf. preceding abstract), inositol was obtained from the flowers and bracts of *Cornus florida*; the latter substance was also obtained exclusively by similar treatment of the leaves of *Rubus argutus*, Link. C. R. HARINGTON.

Quercimeritrin from *Helianthus annuus*. C. E. SANDO (J. Biol. Chem., 1926, **68**, 407—414).—By alcoholic extraction of the dried and ether-extracted corollas of *Helianthus annuus*, there was obtained, in a maximum yield of 0·266%, a glucoside, $C_{21}H_{20}O_{12},3H_2O$, m. p. 247—249°, which was identified with the quercimeritrin of Perkin (J.C.S., 1909, **95**, 2181). C. R. HARINGTON.

Constituents of the corn-cockle seed. I. Githagenin, the "endsapogenin" of *Agrostemma githago*. E. WEDEKIND and R. KRECKE (Z. physiol. Chem., 1926, **155**, 122—136).—Ground corn-cockle seeds, freed from fats by extraction with light petroleum, yield 5—6% of a typical saponin on extraction with methyl alcohol. This product forms a yellowish-white, hygroscopic powder; its aqueous solutions behave as protective colloids, and show marked resistance to coagulation by electrolytes, and the colloidal particles are negatively charged. On hydrolysis with dilute sulphuric acid, it yields a prosapogenin, $C_{34}H_{54}O_{11}$, decomp. 222° (cf. Sänger, Diss., München, 1904; Brandl, Mayr, and Vierling, A., 1906, i, 526; Brandl, A., 1908, i, 818), for which the name *githagin* is adopted. When treated with dilute sulphuric acid under pressure at 140—150°, githagin is hydrolysed to the "endsapogenin," *githagenin*, $C_{25}H_{40}O(CO)(CH{\cdot}OH)_2$, m. p. 286—287° (decomp.) after becoming yellow at 280°, $[\alpha]_D^{18}$ +77·3° in alcohol [*diacetyl* derivative, m. p. 187—188° after sintering at 180°; *oxime*, m. p. 255—257° (decomp.); *semicarbazone*, m. p. 290° (decomp.)], together with a trace of an alkali-soluble *substance*. Oxidation of githagenin with chromic acid in glacial acetic acid affords *githaginic acid*, $C_{25}H_{40}O(CO)(CO){\cdot}CO_2H$, m. p. 223—224° [*dioxime*, m. p. 222° (decomp.)]. F. G. WILLSON.

Plant phosphatides. II. Lecithin, kephalin, and so-called cuorin of soya bean. P. A. LEVENE and I. P. ROLF (J. Biol. Chem., 1926, **68**, 285—293; cf. A., 1925, i, 487).—The lecithin previously obtained (*loc. cit.*) from soya beans gave, on hydrogenation, a derivative with $[\alpha]_D^{20}$ +6·9°. The barium glycerophosphate, obtained by hydrolysis of the lecithin with barium hydroxide, had $[\alpha]_D^{20}$ −0·63°; from the products of acid hydrolysis of the lecithin, oleic acid was isolated. From the crude phosphatides, after removal of all alcohol-soluble material, there was obtained a fraction, insoluble in glacial acetic acid, which resembled in its composition the cuorin of Erlandsen (A., 1907, i, 371); this, on hydrolysis, yielded palmitic, stearic, linoleic, and linolenic acids, aminoethanol, and barium glycerophosphate, $[\alpha]_D^{20}$ −1·00°. C. R. HARINGTON.

Enzymes of *Stereum purpureum*. J. K. MAYO (New Phyt., 1925, **24**, 162—171).—Diastase, inulase, glycogenase, invertase, raffinase, emulsin, pectinase, tyrosinase, and oxydase were detected. CHEMICAL ABSTRACTS.

***iso*Phytosterol in chewing-gum.** I. LIFSCHÜTZ and O. VIETMEYER (Z. physiol. Chem., 1926, **155**, 240—244).—Spectroscopical investigation of the alcohol-soluble constituent of chewing-gum, after treatment in chloroform solution with acetic anhydride and concentrated sulphuric acid, shows the presence of a substance resembling in its properties *iso*-cholesterol from wool-fat. The presence of an iso*phytosterol* in the vegetable product is inferred. A method is described for preparing pure *iso*cholesterol from wool-fat. M. CLARK.

Preparation of adenine nucleotide from tea leaves. H. O. CALVERY (J. Biol. Chem., 1926, **68**, 593—599).—Tea leaves were hydrolysed for 24 hrs. at the ordinary temperature with 2·5% sodium hydroxide; after acidification of the resulting solution with acetic acid, the nucleotides were precipitated as lead salts; the crude nucleotides were fractionated with ammonia and 50% alcohol, and from the soluble fraction was obtained adenine nucleotide in a yield of 0·011—0·016% of the original tea leaves. C. R. HARINGTON.

Pollen of tiger lily, *Lilium tigrinum*. E. H. DUCLOUX (Rev. Fac. Cien. Quím., 1925, **3**, 23—32).—The pollen of *Lilium tigrinum* contains an orange-yellow colouring matter which appears to be an anthoxanthin and may be a xanthone derivative, and a crystalline active principle of alkaloidal nature which is considered to be closely related to colchiceine. G. W. ROBINSON.

Strophanthin. X. Kombe-strophanthin-*B* and other Kombe-strophanthins. W. A. JACOBS and A. HOFFMANN (J. Biol. Chem., 1926, **69**, 153—163; cf. this. vol., 618).—By extraction of the seeds of *Strophanthus courmonti* there was obtained an enzyme ("strophanthobiase") which hydrolysed Kombe-strophanthin-*B* (*loc. cit.*) to cymarin and dextrose; the previous assumption that Kombe-strophanthin-*B* is a glucoside of strophanthin with a disaccharide of cymarose and dextrose has therefore been confirmed. The action of the same enzyme on amorphous Kombe-strophanthin yielded similarly cymarin and dextrose; it is suggested that the amorphous strophanthin may be a mixture of glucosides of strophanthidin with tri- and tetra-saccharides of cymarose with 2 and 3 mols. of dextrose. C. R. HARINGTON.

Composition of *Scilla* and its tonicardiac principle. F. HENRIJEAN and W. KOPACZEWSKI (Compt. rend., 1926, **183**, 376—377; cf. A., 1914, i, 913; 1915, i, 351).—Some physical and chemical properties of the active principle of *Scilla maritima*

are described, and the formula $C_{11}H_{22}O_{11}$ is assigned to it ($M=352\pm15$). It is soluble in water to the extent of 4%, but not in alcohol or ether. It has very little reducing power towards Fehling's solution, and does not produce dextrose when hydrolysed. It is toxic to dogs and rats, but less so to rabbits.

J. GRANT.

Asperuloside in plants. Extraction of the glucoside from *Galium aparine*, L. H. HÉRISSEY (Bull. Soc. Chim. biol., 1926, **8**, 489—496).—See this vol., 547.

Composition of *Salix triandra*, L. Rutoside, asparagine, and a new glucoside, salidroside. M. BRIDEL and C. BEGUIN (Compt. rend., 1926, **183**, 231—233).—Rutoside (rutin) and *l*-asparagine have been isolated from the leaves of *Salix triandra*, L., and *salidroside*, a new glucoside giving a compound of rose-like odour and dextrose on hydrolysis with emulsin, from the cortex, especially of male plants.

L. F. HEWITT.

Presence of β-methylglucoside and of scabioside in *Dipsacus arvensis*. N. WATTIEZ (Bull. Soc. Chim. biol., 1926, **8**, 501—507).—Scabioside has been obtained from both the leaves and roots of *Dipsacus arvensis*. The leaves also contained β-methylglucoside.

C. P. STEWART.

Heterotropic phanerogams. VI. J. BRAUNHAUSER (Monatsh., 1926, **46**, 631—638; cf. Einleger, Fischer, and Zellner, A., 1924, i, 817).—From the fats and resins extracted from bird-lime from the berries of *Viscum album*, L., by means of light petroleum, the following substances were isolated: stearic, palmitic, myristic, and probably arachidic and oleic acids present originally as glycerides or esters of ceryl alcohol. The hydrocarbon, $C_{30}H_{62}$, previously obtained from *Loranthus europæus* (*loc. cit.*); ceryl alcohol (the substance $C_{24}H_{50}O$, to which the name loranthyl alcohol was previously assigned, is now shown to be a mixture of the hydrocarbon and ceryl alcohol); caoutchouc; two amorphous *resins* $(C_{10}H_{18}O)_n$ (m. p. 80—82° and 89—90°, respectively); a resinous *substance*, m. p. 115°; and a crystalline *resin alcohol*, $C_{24}H_{42}O$, m. p. 206—207° (*acetyl* derivative, m. p. 207°; *bromine additive* product, m. p. 150—151°; *methylation product*, m. p. 190—191°), which on oxidation with potassium permanganate yields a *substance*, m. p. 158°.

J. W. BAKER.

Comparative plant chemistry. XII. Chemistry of barks. III. J. ZELLNER (Monatsh., 1926, **46**, 611—630; cf. A., 1924, i, 814).—The barks of dog-wood (*Cornus sanguinea*, L.) contained: soluble in light petroleum, 3·69%; ether extract, 4·19%; alcohol extract, 21·81%; total water-soluble matter, 25·48%; water-soluble mineral matter, 1·50%; tannin, 12·97%; reducing sugars, 1·23%; polysaccharides, 4·94%; free acids (as KOH), 1·19%; total nitrogen, 1·81%; total ash, 6·18%. From the light petroleum extract was isolated a substance, $C_{30}H_{52}O$, m. p. 251° (*acetyl* derivative, m. p. 237°, *bromine additive* product, m. p. 202°), which may be identical with alnulin (*loc. cit.*), and the phytosterol, m. p. 132°, previously isolated from *Tussilago Farfara*, whilst hydrolysis of the fats yielded ceryl alcohol and an acid, m. p. 75°. The ether extract contained a *substance*, $C_{24}H_{40}O_3$, decomp. 288° (*acetyl* derivative, m. p. 260°; *bromine additive* compound, m. p. 213°).

Linden (*Tilia platyphyllos*, Scop.) contained: soluble in light petroleum, 3·85%; ether extract, 2·29%; alcohol extract, 12·27%; total water-soluble matter, 18·07%; water-soluble mineral matter, 0·60%; tannin, 7·29%; reducing sugars 1·90%; polysaccharides, 1·20%; free acids (as KOH), 1·46%; total nitrogen, 1·54%; total ash, 1·91%. From the light petroleum extract were obtained ceryl alcohol, a phytosterol, m. p. 132°, and a *substance*, $C_{28}H_{48}O$, m. p. 275° (*acetyl* derivative, m. p. 261°), whilst hydrolysis yielded sativic acid and a little azelaic acid. The ether extract contained a *substance*, $C_{22}H_{38}O_3$, m. p. 285° (decomp.) (*acetyl* derivative, m. p. 267°), which on reduction with sodium and alcohol yielded a *substance*, $C_{22}H_{40}O_3$. On hydrolysis, in addition to fatty acids, a small quantity of vanillin was detected. The substance $C_{21}H_{32}O_2$, isolated by Brautigam (A., 1901, i, 93), could not be detected.

Hornbeam (*Carpinus Betulus*, L.) contains: soluble in light petroleum, 3·00%; ether extract, 3·39%; alcohol extract, 11·39%; total water-soluble matter, 16·86%; water-soluble mineral matter, 1·96%; tannin, 7·92%; reducing sugars, 2·60%; polysaccharides, 1·25%; free acids (as KOH), 1·99%; total nitrogen, 1·71%; total ash, 7·14%. The light petroleum extract yielded ceryl alcohol, a *phytosterol*, $C_{28}H_{44}O$ ($+H_2O$ and anhydrous), m. p. 234—235° (*acetyl* derivative, m. p. 117°), and a substance, $C_{18}H_{34}O_2$ or $C_{17}H_{32}O_2$, m. p. 249—250° (*acetyl* derivative, m. p. 217°; *bromine additive* compound, m. p. 117°), which is probably identical with coryliresinol (*loc. cit.*). Hydrolysis yielded a mixture of liquid and solid fatty acids from which palmitic and stearic acids were isolated. The ether extract afforded a *substance*, $C_{22}H_{38}O_3$, decomp. 276—277° (*bromine additive* product, decomp. 262°). The alcohol and aqueous extracts in each case afforded products similar to those obtained in previous cases.

J. W. BAKER.

Hemicelluloses. IV. Hemicelluloses of beech wood. M. H. O'DWYER (Biochem. J., 1926, **20**, 656—664).—Two hemicelluloses are present in the extract when sawdust from beech wood is treated with 4% sodium hydroxide. One, hemicellulose-*A*, can be obtained from the extract by direct precipitation with acetic acid, and the other, hemicellulose-*B*, is precipitated from the acid filtrate by the addition of alcohol. Hemicellulose-*A* yields on hydrolysis xylose and an amount of carbon dioxide corresponding with 11% of glycuronic acid, whilst hemicellulose-*B* yields arabinose and an amount of carbon dioxide corresponding with 63% of galacturonic acid together with small amounts of galactose. The above sugar acids have been isolated and identified from the products of hydrolysis of the respective hemicelluloses. They are obtained only in small amounts, as they decompose during hydrolysis.

S. S. ZILVA.

Destruction of organic matter by hydrogen peroxide. C. A. GRAU (Rev. Fac. Cien. Quim., 1925, **3**, 131—132).—Sodium perborate in the presence

of an acid may be used instead of hydrogen peroxide for the destruction of organic matter.

G. W. ROBINSON.

Tryptophan-aldehyde reaction. E. KOMM.—See this vol., 959.

Method for determining the accuracy of analyses of ethyl iodide vapour for measurements of the circulation of the blood in man. Y. HENDERSON (Biochem. J., 1926, **20**, 865—868).—The ethyl iodide is aspirated through two sets consisting of a U-tube containing iodine pentoxide heated at 170° and a bottle containing potassium iodide connected in series. The collected iodine is titrated with sodium thiosulphate. The flow of air through the train is regulated by means of a graduated cylinder into which a large bottle of water which is connected with the apparatus is drained.

S. S. ZILVA.

Determination of chlorine in blood and tissues by micro-titration. P. B. REHBERG (Biochem. J., 1926, **20**, 483—485).—To destroy the proteins, 0·1 c.c. of whole blood or plasma is heated with a known quantity of silver nitrate, concentrated nitric acid, and hydrogen peroxide. The excess of silver nitrate is then titrated with thiocyanate under constant stirring by means of a current of air-bubbles. The blood and the silver nitrate are measured out by the author's micro-burette (A., 1925, i, 852). Duplicate analyses by this method will give results which seldom vary more than 2—3 mg. per 100 c.c. of plasma. On whole blood, the error is greater, but is seldom 10 mg. per 100 c.c.

S. S. ZILVA.

Comparison of Bang's and Benedict's methods of blood-sugar determination. K. GOTO and N. OSAWA (Chug. Ij. Shp. Tokyo, 1922, **42**, 1422).—The Mayer–Benedict method, although simple and convenient, is influenced by creatinine and acetone in the blood; also the increase of blood-sugar after administration of lævulose is higher than is indicated by Bang's method.

CHEMICAL ABSTRACTS.

Folin–Wu and new Benedict methods for determination of sugar. J. D. LYTTLE and J. E. HEARN (J. Biol. Chem., 1926, **68**, 751—757).—Parallel determinations of dextrose in blood and in cerebrospinal fluid by the above methods showed that in most cases the method of Folin and Wu (A., 1920, ii, 337) yielded higher results than did the recent method of Benedict (A., 1925, i, 994); the concentration of non-protein nitrogen bore no relation to the difference between the results yielded by the two methods.

C. R. HARINGTON.

New Benedict method for determination of blood-sugar. R. ROCKWOOD (J. Biol. Chem., 1926, **69**, 187—196).—Determinations of blood-sugar by the recent method of Benedict (A., 1925, i, 994) give, in nearly all cases, lower values than determinations by the method of Folin and Wu (A., 1920, ii, 337). The difference between the values is not increased in uræmia and is therefore not due to one of the nitrogenous constituents of blood, nor could it be related to any abnormal constituent of the blood in diabetes; the substance which causes the difference is present in larger amount in the red corpuscles than in the plasma.

C. R. HARINGTON.

Determination of sugar in blood and normal urine. S. R. BENEDICT (J. Biol. Chem., 1926, **68**, 759—767).—Certain modifications are given of the author's recent method (A., 1925, i, 994) for the determination of sugar, and an answer is made to the criticisms of Folin (this vol., 648).

C. R. HARINGTON.

Determination of dextrose in presence of phosphate buffers. M. B. VISSCHER (J. Biol. Chem., 1926, **69**, 1—2).—The presence of potassium dihydrogen phosphate causes the results of determinations of dextrose by the method of Shaffer and Hartmann (A., 1921, ii, 417) to be low.

C. R. HARINGTON.

Determination of glycogen. T. OHARA (Tohoku Ig. Z. Sendai, 1922, **6**, 124—132).—The results obtained by three methods are in the increasing order: Pflüger, Birry–Gurzewska, Yamakawa.

CHEMICAL ABSTRACTS.

Determination of acetone and its application to urine. P. FLEURY and Y. AWAD (J. Pharm. Chim., 1926, [viii], **3**, 406—414; Bull. Soc. Chim. biol., 1926, **8**, 550—564).—Acetone is precipitated from solution by treatment with either Nessler's or Denigès' reagent; the precipitate is dissolved in hydrochloric acid, and potassium iodide added. After adding excess of standard iodine and some sodium hydroxide, the solution is acidified and titrated with thiosulphate. When aldehyde is also present, the precipitate formed with Nessler's reagent is treated with hydrochloric acid and filtered, leaving the mercury salt, reduced by the aldehyde, on the filter. The acetone in the filtrate is determined as above, and the aldehyde by treating the residue on the filter with hydrochloric acid and standard iodine, and finally titrating with thiosulphate.

B. W. ANDERSON.

Method of Denigès for the determination of acetone. C. ALBIZZATI (Rev. Fac. Cien. Quím., 1925, **3**, 1—21).—A general discussion.

G. W. ROBINSON.

Determination of small quantities of bismuth in urine. C. A. HILL (Lancet, 1925, ii, 1281).—Organic matter is destroyed at a low temperature with nitric acid. To the aqueous solution containing nitric acid are added 0·3 g. of carbamide, 0·5 g. of phenazone, and, gradually while shaking, 0·05 g. of potassium iodide. The maximum colour is compared with that of a standard containing 0·05 mg. of bismuth and 1 drop of nitric acid in 50 c.c., treated as above.

CHEMICAL ABSTRACTS.

Microchemical determination of calcium in urine. T. INOUE (Tokyo Ig. Kw. Z., 1922, **36**, 461—467).—2 C.c. of urine, acidified with acetic acid, are treated at 100° with 0·3 c.c. of saturated ammonium oxalate solution and centrifuged after 10 min. After washing twice with 2 c.c. of water, the precipitate is acidified and titrated with 0·01*N*-permanganate solution. The error is 5—6%.

CHEMICAL ABSTRACTS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

OCTOBER, 1926.

General, Physical, and Inorganic Chemistry.

Spectrum of hydrogen. A. SOMMERFELD and A. UNSÖLD (Z. Physik, 1926, **38**, 237—241).—Recent measurements of the intensities of the lines in the fine-structure of H_α are not in agreement with the calculations in the former paper (this vol., 549), but are found to be in agreement with calculations based on Schrödinger's equations. The values for H_α and He^+ are tabulated and also represented graphically. E. B. LUDLAM.

Method for producing a discharge in hydrogen. R. W. LUNT (Phil. Mag., 1926, [vii], **2**, 743).—The attention of Gill and Donaldson (*ibid.*, 129) is directed to two prior papers by the author (A., 1925, ii, 579, 616) on the production of discharges in gases at frequencies of the order of 10^7 cycles per sec. A. E. MITCHELL.

Spectroscopic study of the discharge in helium. T. TAKAMINE (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 55—61).—When helium is electrically excited by the method of exploding wires (Anderson, Astrophys. J., 1920, **51**, 37) a depression of intensity in the middle of the line for 4922, 4472, and 3203 (ionised helium line) is observed. This is ascribed to the interatomic electric field produced by the very closely packed atoms at high current densities and not to self-reversal (cf. Holtsmark and Trumpy, A., 1925, ii, 338). A similar phenomenon is observed in the condensed discharge at pressures from 0·5 to 1 atm. for lines 6678, 5876, and 3889. It is probable that in this case also the effect may be due, at least in part, to the interatomic field (cf. Merton, Proc. Roy. Soc., 1918, **A**, **95**, 30). M. S. BURR.

Intensity relations of the components of the helium doublets. D. BURGER (Z. Physik, 1926, **38**, 437—439).—The so-called doublets have a ratio of intensities 1 : 8, instead of 1 : 2 as is to be expected for doublets; probably they are triplets with a ratio 1 : 3 : 5, but not easily separated. E. B. LUDLAM.

Absorption and resonance radiation in excited helium and the structure of the 3889 line. W. H. MCCURDY (Phil. Mag., 1926, [vii], **2**, 529—538).—See this vol., 549.

Series spectra of beryllium, Be I and Be II. I. S. BOWEN and R. A. MILLIKAN (Physical Rev., 1926, [ii], **28**, 256—258).—Tabulated data concerning the intensity, frequency, designation, and term values are given of 20 lines of Be II (14 being new) between 842·03 and 5274·28 Å., and 20 lines of Be I (6 being new) between 1943·60 and 3322·30 Å. The frequencies of series terms for stripped atoms Li I to C IV are compared. A. A. ELDRIDGE.

Oxygen spectral line 5577·35 Å. J. C. MCLENNAN, J. H. MCLEOD, and W. C. MCQUARRIE (Nature, 1926, **118**, 441).—The line is obtainable with pure oxygen, but not in its absence; conditions for maximal intensity are described. The intensity is enhanced by the presence of helium, neon, or argon, the enhancement factors being, respectively, 1·7, 4·6, and 84·2. No fine structure was observed. A study of the Zeeman effect suggests that the line has an atomic origin; it probably originates in an electron transition between atomic levels for oxygen provided by one or other of two new singlet–triplet schemes based on Hund's theory. A. A. ELDRIDGE.

Intensity variations in the spectrum of neon. (MRS.) M. R. JOHNSON and R. C. JOHNSON (Phil. Mag., 1926, [vii], **2**, 593—611).—The effects on the intensity, of the visual spectrum of neon, of current density, condensed and "bulb" discharge, high and low pressure, admixture of hydrogen, helium, argon, and carbon dioxide have been examined, together with the intensity distribution as a function of the distance from a flat cathode. The examination is limited chiefly to a comparison of the various principal series amongst themselves. A. E. MITCHELL.

Width of the absorption lines in sodium vapour. W. KUHN (Z. Physik, 1926, **38**, 440—442).—Light which was dispersed but not absorbed by sodium vapour was passed through the vapour and the width of the absorption of the *D*-line simultaneously observed. There was no widening of the absorption line such as would have resulted if the dispersed light had been able to raise the sodium atom to a higher energy level. E. B. LUDLAM.

Optical spectra of different atoms of the same electronic structure. II. Aluminium-like and copper-like atoms. D. R. HARTREE (Proc. Camb. Phil. Soc., 1926, **23**, 304—326; cf. A., 1925, ii, 2).—The calculation of the relations between corresponding terms of different atoms of the same electronic structure has been extended and more general formulæ have been derived. Values of the polarisability of the Al^+ and Si^{++} ions are calculated from terms of Al I and Si II, respectively, corresponding with non-penetrating orbits, and are shown to be very much greater than the values of the polarisability of the neon-like ions Al^{+++} and Si^{++++}. The quantum

defect of a penetrating orbit can be expressed as the sum of the contributions from the electrons in groups of core orbits of different principal quantum number. For corresponding terms of different atoms of the same structure, the reciprocal of the quantum defect tends asymptotically to be linear in C, the core charge. Somewhat similar relations hold for the variation of quantum defect within a sequence. Comparison with values deduced from observed spectra show fair agreement, even although the value of C is only small.

E. B. LUDLAM.

Intensity measurements in the iron spectrum. J. B. VAN MILAAN (Z. Physik, 1926, **38**, 427—436).—Tables are given of the relative intensities of the lines from 6136 to 6411 and from 5208 to 5506, also from 3680 to 3800 Å. for two different strengths of current for the arc and for the spark, which show very considerable differences. The observations for the multiplets $f'-d^2$, $p'-d^2$, $\bar{f}-d^2$ were in good agreement with the summation rule; those for $\bar{d}-d$ and $\bar{f}'-f$ showed a divergence. E. B. LUDLAM.

Interferometer measurements of the pressure-shift of lines in the arc spectrum of nickel. B. T. BARNES (Astrophys. J., 1926, **63**, 127—132).—The wave-lengths of 72 lines in the nickel spectrum when emitted by an arc operated at a pressure of 760 mm. are compared with those for 60 mm. Most of the lines had a pressure-shift of less than 0·005 Å. per atm.; a greater shift in some cases is attributed to an unsymmetrical broadening of the lines.

A. A. ELDRIDGE.

Comparison of the red cadmium line in the vacuum arc and in the discharge tube. F. L. BROWN (J. Opt. Soc. Amer., 1926, **13**, 183—192; cf. A., 1923, ii, 2).—The wave-length of the red cadmium line emitted by the vacuum arc has been compared with that of the same line emitted by the discharge tube, using a Fabry–Perot interferometer. They differ by less than 0·001 Å. The vacuum arc can be used as a safe source for all but the most precise work, and probably even then if the current density is not too great and the pressure is kept below 10 mm.

A. B. MANNING.

Structure of cadmium and zinc resonance lines. R. W. WOOD (Phil. Mag., 1926, [vii], **2**, 611—612).—The fine structure of the $1S-2p_2$ and $1S-2P$ lines of cadmium and zinc, analogous to the mercury lines 2536 and 1849 Å. previously examined (A., 1925, ii, 1015), has been determined. The cadmium line at 2288 Å. is double with a wave-length separation of 0·021 Å. The cadmium line at 3261 Å. consists of a strong and easily reversed line accompanied by a faint companion on the shorter wave-length side; the wave-length separation is 0·019 Å. The zinc line at 2138·6 Å. was found to be double and that at 3075·9 single. A. E. MITCHELL.

Fine structure of certain lines and energy levels of cadmium. W. A. MCNAIR (Phil. Mag., 1926, [vii], **2**, 613—621; cf. preceding abstract).—The Lummer-Gehrcke plate method of Wood (A., 1925, ii, 1015) has been applied to the examination of the fine structures of a number of cadmium lines and the observations have been applied to the arrangement of the fine structure of the electron orbits of cadmium. One such arrangement is similar to that suggested by Joos (A., 1925, ii, 612), except that the separations assigned to the p levels are slightly different and that the $2p_2$ level is more complex.

A. E. MITCHELL.

Effect of electric field on the spectral lines of zinc and cadmium. Y. FUJIOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 45—53).—The Stark effect for zinc and cadmium has been examined by the ordinary Lo Surdo method, and many combination lines, such as *pp*, *pb*, *pe*, and *pf*, have been observed up to $2p-7q$. The results are similar to those obtained by the new method of Schüler (this vol., 215). The lines of diffuse series are displaced towards the less refrangible side in the electric field. Many anomalous lines appearing in the electric field have been observed and approximate measurements made of the intensities of these relative to the intensities of the lines of the diffuse series. Several new energy levels have been determined.

M. S. BURR.

Intensity distribution in the fine-structure of the cadmium triplet $2p_i-2s$. J. L. SNOEK and T. BOUMA (Z. Physik, 1926, **38**, 368—369).—The intensity of the satellites has been measured, using a vacuum cadmium arc, which made an exposure of several hours necessary with the high dispersion used. The separation of the lines is about half that of the corresponding mercury lines, but the distribution of intensities is much the same. No satellites have yet been discovered for zinc.

E. B. LUDLAM.

Arc spectrum of europium. Measurements between 3500 and 3100 Å. under normal pressure. S. PINA DE RUBIES (Compt. rend., 1926, **183**, 385—387).—Examination of the arc spectra, under normal pressure, of pure preparations of europium and of europium–gadolinium and europium–samarium mixtures has disclosed all the lines described previously by Exner and Haschek and by Urbain. The six lines between 3204·37 and 3443·81 Å., attributed by Eder to europium, were not observed. Seventy-nine lines between 3485·8 and 3105·2 Å. were obtained and measured. These have not been described previously and are identified with the spectrum of europium. A. E. MITCHELL.

Arc spectrum of lead. N. K. SUR (Phil. Mag., 1926, [vii], **2**, 633—642).—The heavy-arc method has been applied to a reinvestigation of the spectrum of lead with a view to obtain the higher members of the Rydberg sequence in the series spectrum of lead. Several members of the series $2s-mp_{1,2}$ and $2x-mp_{1,2}$ have been obtained. The results indicate that the arc spectrum of lead contains negative terms similar to those described by Russell and Saunders (A., 1925, ii, 911) in the arc spectrum of calcium. Two combination lines at 7330·12 and 4618·21 Å., being intercombinations of the $^3p_1-{}^1D_2$ and $^3p_1-{}^1S_0$ terms, respectively, have been obtained. A. E. MITCHELL.

Theory of the absorption of X-rays. R. A. HOUSTOUN (Phil. Mag., 1926, [vii], **2**, 512—520).—Mathematical. The author's previous deductions (A., 1920, ii, 462) that one electron is concerned in the K-absorption and more than one in the L-absorption are elaborated. A mechanism is suggested whereby within the region of the K-absorption all but one of the electrons of an atom are absorbing energy from the incident radiation and scattering it to lose it by resonance radiation, whilst the remaining electron absorbs energy from a narrow region situated somewhere between the head of the band and infinite frequency. Most of this latter energy is transmitted to another hypothetical system. A. E. MITCHELL.

Scattered X-rays. The J-phenomenon. IV. C. G. BARKLA and S. R. KHASTGIR (Phil. Mag., 1926, [vii], **2**, 642—656; cf. A., 1925, ii, 456; this vol., 217).—It is shown that whilst the secondary differs from the primary radiation when its absorbability is examined in certain substances, it is precisely like the primary when its absorbability is measured in other materials. Experimental evidence shows that there is no change of wave-length of X-radiation either in the process of re-emission or in the subsequent transmission through matter. No gradual variation of absorbability of a scattered radiation with the angle of scattering, as required by Compton's quantum theory of X-ray scattering, was found. Where any differences were found, these were characteristic of "J-discontinuities" and corresponded with the differences between two well-defined absorption levels. A. E. MITCHELL.

X-Ray levels of the elements copper (29) to lanthanum (57). D. COSTER and F. P. MULDER (Z. Physik, 1926, **38**, 264—279).—New measurements have been made of the absorption edges and emission lines in the L region of the elements from rubidium (37) to cadmium (48), from which the energy levels can be calculated with greater accuracy than hitherto. The most trustworthy results for the elements from copper to lanthanum are tabulated and curves given. In conjunction with data from the optical spectra, the sub-grouping of the electrons is discussed.
E. B. LUDLAM.

X-Ray spectra and chemical combination. E. BÄCKLIN (Z. Physik, 1926, **38**, 215—226; cf. A., 1925, ii, 914).—The effect on an atom of combination with other atoms is to displace the K level nearer to the nucleus and the K lines in the spectrum are displaced towards shorter wave-lengths. There is difficulty arising from overlapping of the lines when the compound is decomposed by the electronic bombardment, as both the free element and the combined element give rise to lines. Measurements have been made on the so-called spark lines, $K\alpha_3$ and $K\alpha_4$ (which bear the same relation to $K\alpha_1\alpha_2$ as do spark lines to arc lines in optical spectra). Barium sulphate and sulphur are compared and silica with silicon; the latter has the advantage that none of the element is liberated; in both cases the displacement is easily measurable. With silicon, a strong $K\beta_1$ line was obtained and a weaker $K\beta_x$; with silica, no $K\beta_1$ line appeared, but $K\beta_x$ was present. As the four M electrons have gone to the oxygen atom, this may account for the absence of β_1, but leaves β_x unexplained.
E. B. LUDLAM.

Absorption of X-rays in crystalline compounds. R. J. HAVIGHURST (Proc. Nat. Acad. Sci., 1926, **12**, 477—479).—Since an empirical formula due to A. H. Compton (Bull. Nat. Res. Council, 1920, [4]) represents within about 5% the X-ray absorption of all elements of atomic number greater than 5 as a function of the atomic number N and the at. wt. A of the absorber, an approximate expression for the absorption by a compound may be obtained by substituting ΣN and ΣA for N and A, respectively, the summations being taken over each atom in the molecule. In the case of polar compounds where electrons pass from one ion to the other, N is the nuclear charge on the atom, and not the actual number of electrons which reside in the ion. The measured linear absorption coefficients for sodium chloride, sodium fluoride, calcium fluoride, and calcium carbonate for radiation of wave-length 0·71 Å. are in satisfactory agreement with those calculated from the extended Compton formula. The agreement fails for lithium fluoride. The atomic absorption of lithium ($N=3$) is probably not accurately represented by the simple atomic absorption formula and hence the lack of agreement is not surprising.
J. S. CARTER.

Zeeman effect for the spectrum of fluorine. G. H. CARRAGAN (Astrophys. J., 1926, **63**, 145—159).—The Zeeman patterns of 20 of the brighter lines of fluorine between 6239·63 and 7573·32 Å. have been determined, whence a first-order quartet system is indicated. The term combinations of the principal and diffuse series have been located, and those of other lines proposed. The possible existence of the fluorine ion and of higher order spectra is suggested.
A. A. ELDRIDGE.

Stark effect of the second order for hydrogen and the Rydberg correction for the spectra of helium and Li^+. I. WALLER (Z. Physik, 1926, **38**, 635—646).—Schrödinger's equation is developed by means of parabolic co-ordinates and the Stark effect of the second order calculated for hydrogen-like atoms. Equations are obtained which give successive approximations to the energy values. Good agreement is obtained for the helium atom and the ionised lithium atom. E. B. LUDLAM.

Schrödinger's quantum theory and the Stark effect. P. S. EPSTEIN (Nature, 1926, **118**, 444—445).—Schrödinger's theory of atomic oscillations is satisfactorily applied to the Stark effect in hydrogen.
A. A. ELDRIDGE.

Second order Stark effect. J. S. FOSTER (Astrophys. J., 1926, **63**, 191—195).—The observed average second order Stark effect for six perpendicular components of H_δ in a field of 65 kilovolts/cm. is 0·40 Å., and for the central perpendicular component of H_ϵ 0·79 Å., in agreement with values calculated from Epstein's formula. The displacement of the central perpendicular component of the helium group 4009 Å. is 0·35 Å. in a field of 60 kilovolts/cm. Although there is some evidence of a possible Döppler

effect, none was observed for neutral helium lines from a mixture of hydrogen and helium in a field of 50 kilovolts/cm. A. A. ELDRIDGE.

Compton effect and the reflexion of *X*-rays by crystals. E. J. WILLIAMS (Phil. Mag., 1926, [vii], 2, 657—674).—The laws applicable to the reflexion, by a crystal, of modified radiation scattered by its own electrons are derived by considering an electron lattice moving with a velocity which would give as a Döppler effect the wave-length change required by the quantum theory of scattering. The results so obtained differ appreciably from those of Bragg, and since the reflected radiation obeys Bragg's law, it is concluded that either no modified radiation is scattered in the directions concerned, or modified radiation is scattered but not regularly reflected. The bearing of the Compton effect on the theory of the intensity of reflexion by crystals is considered in the light of the second alternative, and the recalculated "F curves" are compared with the classical and observed curves. The recalculated curves agree much more closely with observations on the intensity of reflexion than do the classical ones, which should be the case, since they are little influenced by contributions from the outer electrons, as these electrons scatter very little unmodified radiation. The correction for the Compton effect, being a function of $\sin \beta/\lambda$, resembles the other factors entering into the theory. The capacity of a crystal to reflect modified and unmodified radiation is discussed.

A. E. MITCHELL.

Radiation produced by the passage of electricity through gases. (SIR) J. J. THOMSON (Phil. Mag., 1926, [vii], 2, 674—701).—Experiments on the character of the radiation produced when electric currents are passed through gases at low pressures are described. The method is based on a determination of the rate of emission of electrons due to the photo-electric effect when a disc of metal is placed in the path of the radiation and the emission is retarded by an electric field tending to inhibit the escape of electrons. The radiation produced by the passage of cathode and positive rays through hydrogen, oxygen, helium, and argon at different pressures is discussed. It is found that the frequencies of by far the greater part of the radiation are comparable with those corresponding with quanta of the order of the ionising and resonance potentials of the gas. Radiations due to cathode rays are mixed with others of a higher frequency. In general, the radiation is a mixture of radiation comparable with that of the ionising radiation and another of higher frequency. In a few cases it is homogeneous. The electrodeless ring discharge is found to be a ready source of this type of radiation, and various experiments for demonstrating its existence and examining its properties are described. A. E. MITCHELL.

Emission of electrons and positive ions at the m. p. of metals. A. WEHNELT and S. SEILIGER (Z. Physik, 1926, 38, 443—464).—In the liquid as contrasted with the solid state, both for negative and positive emission, the work of escape is smaller and the number emitted at the m. p. is greater. By passage into the fluid state the number of free electrons in the metal is diminished in approximately the same ratio as the resistance increases. The metals used were copper and silver. E. B. LUDLAM.

Series and ionisation potentials in the iron spectrum. O. LAPORTE (Proc. Nat. Acad. Sci., 1926, 12, 496—503; cf. Walters, A., 1924, ii, 285; Laporte, *ibid.*, 364; 1925, ii, 4; Hund, *ibid.*, 912).—A more detailed discussion in which the action of Pauli's equivalence principle (A., 1925, ii, 339) is demonstrated. The lowest term in the iron arc spectrum is a ^5D term. J. S. CARTER.

Excitation potentials of the spectra of argon II and neon II. F. L. MOHLER (Science, 1926, 63, 405).—Argon exhibits sharp increases in photo-ionisation at $32{\cdot}2 \pm 0{\cdot}2$, $34{\cdot}8 \pm 0{\cdot}5$, and $39{\cdot}6 \pm 0{\cdot}5$ volts, corresponding respectively with a spark excitation potential, the work required to remove two electrons, each from a 3_2 orbit, and, probably, the work required to remove one 3_1 electron. Neon shows critical potentials at $48{\cdot}0 \pm 1$ and $54{\cdot}9 \pm 1$ volts; the latter measures the work required to remove two 2_2 electrons, and the former probably that required to remove one electron and displace another to a 3 quantum orbit of energy 26·5 volts.

A. A. ELDRIDGE.

Application of Pauli's method of co-ordination to atoms having four magnetic parts. G. BREIT (Physical Rev., 1926, [ii], 28, 334—340).—The origin of spectral terms of an arc spectrum obtained by adding a highly excited electron to a certain term of the spark may be understood in terms of an application of the principle of mechanical transformability made by Pauli. A. A. ELDRIDGE.

Thermionic and adsorption characteristics of cæsium on tungsten and oxidised tungsten. J. A. BECKER (Physical Rev., 1926, [ii], 28, 341—361).—The electron emission from a tungsten or an oxidised tungsten filament carrying adsorbed cæsium is maximal for a monatomic layer of the alkali metal, which has its atomic rather than its ionic diameter. The positive ion emission was also studied. Practically all the adsorbed cæsium is removed by drawing away positive ions at 1040° Abs.; it appears that below 650° Abs. every atom that strikes the filament adheres until the optimum activity is reached. Cæsium on oxidised tungsten is apparently partly ionised, for the number of atoms forming the monatomic layer is 10% greater than on tungsten alone; it is held more firmly by the oxidised metal. The cæsium can evaporate either as atoms or as ions; the atomic rate depends only on the temperature and on the fraction of the surface covered, rapidly increasing with the latter for a given temperature. On the other hand, the isothermal ion evaporation rate increases only up to a point at which 1% of the surface is covered, thereafter decreasing as the fraction becomes larger. The results indicate that the work necessary to remove a positive ion can be appreciably decreased by applying large negative potential gradients. It is suggested that the new method for determining quantitatively how the concentration of adsorbed atoms is affected by surface temperature, surface potential gradient, and rate of arrival of

atoms may be applied in the elucidation of the nature of the forces which cause one atom to stick to another. A. A. ELDRIDGE.

Scattering of electrons in ionised gases. F. M. PENNING (Nature, 1926, **118**, 301)—Contrary to the observations of Langmuir (this vol., 3) oscillations were observed in mercury-vapour discharges with a hot cathode. It seems possible that the observed scattering of primary electrons is always accompanied and caused by these oscillations. A. A. ELDRIDGE.

Scattering of electrons in helium. E. G. DYMOND (Nature, 1926, **118**, 336—337).—A study of the angular distribution of scattering of electrons, which have suffered inelastic encounters and have lost 20 volts energy, in helium; results are given for initial velocities of 50—400 volts. A. A. ELDRIDGE.

Transmission of low-velocity electrons through thin metallic foils. T. KURTCHATOV and K. SINELNIKOV (Physical Rev., 1926, [ii], **28**, 367—371).—Hartig's observations (A., 1925, ii, 921) on the permeability of aluminium foil to electrons having a velocity of at least 2 volts are confirmed when the foils exhibit no holes in transmitted light, but not with foils showing no holes on being tested in water. A. A. ELDRIDGE.

Secondary electron emission from tungsten, copper, and gold. R. L. PETRY (Physical Rev., 1926, [ii], **28**, 362—366).—When a stream of electrons from a hot filament, accelerated by a field of 0—1500 volts, struck a plate of tungsten, copper, or gold, the maximum values for the number of secondary electrons emitted per primary electron striking the plate were 1·45 (700 volts), 1·32 (240 volts), and 1·14 (330 volts), respectively. Critical primary potentials were observed as follows: tungsten, 11·0, 17·1, 25·2, 29·3, 40·5, 46·0, 89·5, and 271·5 volts; copper, 7·8, 12·6, 16·8, 19·5, 23·8, 39·0, 56·9, and 73·5 volts; gold, 15·5, 21·0, 23·2, 31·5, and 43·7 volts. A. A. ELDRIDGE.

Mean free path of electrons in mercury vapour. L. R. MAXWELL (Proc. Nat. Acad. Sci., 1926, **12**, 509—514).—The mean free path of slow electrons in mercury vapour has been examined over the range 0·5—3000 volts. The mean free path increases with the accelerating potential, there being, however, changes in the direction of the curve at 4·9 and 6·7 volts and a slight minimum value at about 40 volts. J. S. CARTER.

Energy of high-velocity electrons. M. W. WHITE (Physical Rev., 1926, [ii], **28**, 247—255).—Up to 25,000 volts, all the energy supplied to a Coolidge tube is ultimately transformed into heat; any source or sinks of energy which may exist have an effect of less than 0·2%. No radiations involving an absorption of energy at the cathode could be detected. Hence all of the energy input into an *X*-ray tube goes into the moving electrons and their fields, and only a negligible part of the current in a Coolidge tube is furnished by positive ions reaching the cathode. A. A. ELDRIDGE.

Determination of effective cross-section towards slow electrons. M. RUSCH (Ann. Physik, 1926, [iv], **80**, 707—727).—A new method has been developed for determining the effective cross-section of gas particles towards slow electrons in a longitudinal magnetic field. For argon, the effective cross-section has been plotted against values of $\sqrt{}$volt, in the range 3·5—29 volts for the electron velocity. The curve resembles closely that of Ramsauer (A., 1923, ii, 529) for the transverse field, although the cross-section is always a little greater in the earlier work. R. A. MORTON.

Work of escape of electrons from oxide cathodes. H. ROTHE (Z. Physik, 1926, **38**, 410).—A reply to Katsch (*ibid.*, 407), who described cases of three-electrode valves in which a grid current was obtained with a negative potential on the grid. The beginning of a grid current is due to the contact difference of potential between the cathode and the grid. The oxide cathode slowly disintegrates and some of it deposits on the grid, thereby reducing the contact difference of potential. E. B. LUDLAM.

Dissociation of nitrogen by electron impact. V. KONDRATJEV (Z. Physik, 1926, **38**, 346—352).—Nitrogen was submitted to electron bombardment and the velocity of the electrons determined at which, in addition to the band spectrum of nitrogen, the atomic lines first appeared. The necessary voltage was found to be 32 ± 2. The nitrogen molecule can break down in one elementary action into excited atoms, $N_2 \longrightarrow N'+N'$ or $N_2 \longrightarrow N'+N^+ + \ominus$. E. B. LUDLAM.

High-voltage cathode rays outside the generating tube. W. D. COOLIDGE (Science, 1925, **62**, 441—442).—Cathode rays, obtained through an aluminium window from a vacuum tube operated at 200,000 volts and several milliampères, had a range of 46 cm. in air, causing luminosity. Calcite crystals are caused to fluoresce in the orange, and remain luminous for several hours after exposure. The high-voltage electrons affect gases in a manner similar to radium emanation; acetylene yields large quantities of a yellow substance, castor oil solidifies, and an aqueous solution of sucrose becomes acid. The effect on organised tissues is very pronounced. A. A. ELDRIDGE.

Method of demonstration of phenomena in discharge tubes. (FRL.) A. KATSCH (Z. tech. Physik, 1925, **6**, 595—598; from Chem. Zentr., 1926, I, 1600).—Excitation phenomena resulting from electron collision at very low pressures (10^{-4}—10^{-5} mm.) are used as indicators of electron movements in evacuated discharge tubes. The nature of the phenomena has been investigated over a wide range of potential and it is concluded that there are three distinct methods of excitation, viz., by electrons, by positive ions, and by negative ions. J. S. CARTER.

Mobility of acetylene ions in air. H. A. ERIKSON (Physical Rev., 1926, [ii], **28**, 372—377).—As in air, carbon dioxide, hydrogen, and argon, α-rays from polonium produce in acetylene only one negative

ion having the same mobility in air as those formed in the other gases. Like the initial positive ion of hydrogen, the positive ion of acetylene has a mobility slightly less than that of the negative ion, but, up to an age of 1 sec., is not converted into a more stable ion of smaller mobility. When acetylene is admitted into ionised air or nitrogen it takes up the charge of the final positive ions by means of an electron exchange. A. A. ELDRIDGE.

Ions of inert gases as catalysts. S. C. LIND and D. C. BARDWELL (Science, 1926, **63**, 310—311).—The velocity of polymerisation of acetylene, cyanogen, or hydrogen cyanide, mixed with xenon or krypton and irradiated with α-particles, is of the same order as with helium, neon, and argon, although the ionisation potentials of xenon and krypton are lower than those of the reactants. Hence it is indicated that the effect is due to clustering about both kinds of ions as reaction centres, although exchange of charge may also take place. This view is supported by the fact that some of the xenon is removed by occlusion in the polymeride. A. A. ELDRIDGE.

Magnetic properties of atoms. J. KUNZ, J. B. TAYLOR, and W. H. RODEBUSH (Science, 1926, **63**, 550—551).—Gerlach and Stern's results (Z. Physik, 1921, **8**, 110) for the deflexion of a beam of atomic rays in a powerful, heterogeneous magnetic field were confirmed for silver; similar results were obtained for sodium and potassium. The calculated magnetic moment is within 10% of the value of the Bohr magneton. A. A. ELDRIDGE.

Infra-red absorption of brucite and some sulphates. Isotopic effect. E. K. PLYLER (Physical Rev., 1926, [ii], **28**, 284—290).—Maximal absorption for brucite, $Mg(OH)_2$, is at 2·48 μ; small maxima occur at 2·40, 2·30, and 2·14 μ. The first three values correspond with Mg^{24}, Mg^{25}, and Mg^{26}, respectively; the small band at 2·14 μ corresponds in position with Mg^{28}, but no such isotope has been observed by other investigators. Reflexion spectra of nickel sulphate exhibit maxima at 9·15 and 9·5 μ, probably due to Ni^{58} and Ni^{60}; with potassium sulphate, maxima appear at 9·1 and 9·4 μ, representing $K^{39}{}_2SO_4$ and $K^{39}K^{41}SO_4$. The complexity of the bands of barium, strontium, and magnesium sulphates cannot definitely be ascribed to an isotopic effect. A. A. ELDRIDGE.

Homogeneous disintegration and half-period of mesothorium-2. O. HAHN and O. ERBACHER (Physikal. Z., 1926, **27**, 531—533).—Eka-cæsium (87) does not exist in amount greater than $1/10^7$ in preparations of mesothorium-2. The half-period of mesothorium-2 is found to be 6·13 hrs., which is 3% greater than the value of Widdowson and Russell (A., 1925, ii, 463). R. A. MORTON.

Anomalous scattering of α-particles. W. HARDMEIER (Physikal. Z., 1926, **27**, 574—576).—Earlier work (this vol., 450) is more rigidly considered. The polarisability of the nucleus of aluminium is $0{\cdot}5\times10^{-36}$, a value smaller than that found before. R. A. MORTON.

Number of particles in β-ray spectra. II. Thorium-*B* and thorium-*C*+*D*. R. W. GURNEY (Proc. Roy. Soc., 1926, **A**, **112**, 380—390; cf. this vol., 5).—The determination of the number of β-particles emitted with different velocities in β-ray spectra is extended to thorium-*B* and thorium-*C*+*D*. The total number of particles in the continuous thorium-*C*+*D* spectrum between Hρ 4040 and 10,080 is in agreement with the view that they contain nuclear electrons. A law of "β-ray disintegration" is suggested, viz., no γ-rays of high energy can be emitted by those radioactive substances which expel their nuclear electrons with low energies. The probability that a γ-ray of 150,000 volts energy emitted by thorium-*B* is converted into a β-ray instead of escaping from the atom is at least 1 in 4 in the *K* level. For the γ-ray of 40,500 volts emitted by thorium-*D*, the probability of conversion in the *L* level is more than 1 in 5. S. K. TWEEDY.

Pleochroic haloes in biotite. Probable independent origin of the actinium series. S. IIMORI and J. YOSHIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1926, **5**, 11—23).—The pleochroic haloes in a number of Japanese biotites have been examined. A biotite from Ishigure contains a new group of haloes, designated as *Z*-haloes, which can be ascribed neither to the uranium nor to the thorium series. They may be subdivided into Z_1, Z_2, and Z_3, but all possess a common ring, Z_3, of mean radius 18·2 μ. This approximates to the value to be expected for radium-*F*, radiothorium, or protoactinium, but the fact that the Z_3 haloes may occur without the accompaniment of uranium or thorium rings suggests that they are due to protoactinium. On this assumption, it appears that the independent origin of the actinium series is probable. The *Z*-haloes sometimes include very small inner rings of radius 10·0 μ and 5·9 μ, or a small bleached crest, corresponding with α-radiators of half-life periods of 10^{12} and 10^{23} years, respectively, which is in agreement with Piccard and Stahel's view that two α-radiators precede protoactinium (A., 1922, ii, 185). M. S. BURR.

Electrolysis of radium-*D* and -*E*. J. P. MCHUTCHINSON (J. Physical Chem., 1926, **30**, 1112—1115; cf. von Hevesy, A., 1913, ii, 174; Curie, this vol., 5).—Radium-*D* or -*E* could not be extracted from nitric acid solution under the electrolytic conditions required respectively for their isotopes. Traces of lead or bismuth make extraction possible, however, but the active matter obtained on any one electrode is due to adsorption as well as to electrolytic deposition. L. S. THEOBALD.

Method of separating radium and barium. I. BASHILOFF.—See B., 1926, 742.

Extracting radium from radium-barium salts and the like. H. FLECK.—See B., 1926, 743.

Absorption by scattering of hydrogen positive rays by passage through hydrogen. R. CONRAD (Z. Physik, 1926, **38**, 465—474; cf. this vol., 106).—The experimental results are in approximate agreement with the formula earlier deduced, when, in addition to the scattering produced by the nuclei

of the two atoms and the electrons, the repeated scattering and discharge are taken into account.
E. B. LUDLAM.

Selective radiation pressure and the accelerated motion of Ca^+ vapour in eruptive prominences. R. K. SUR (Astrophys. J., 1926, **63**, 111—121).

Law of radiation. G. GIANFRANCESCHI (Nature, 1926, **118**, 302).

Orbits and radiation of hydrogen electrons. T. ENGSET (Ann. Physik, 1926, [iv], **80**, 823—828).—Mathematical (cf. Schrödinger, *ibid.*, **79**, 361).

Quantum theory of vibration-rotation bands. J. R. OPPENHEIMER (Proc. Camb. Phil. Soc., 1926, **23**, 327—335).—The energies and frequencies of states of the diatomic molecule are calculated on the new quantum mechanics. The terms of the rotational energy are $A(m^2-\frac{1}{4})$, where $m=\pm\frac{1}{2}, \frac{3}{2}, \frac{5}{2}\ldots$; the weights of the corresponding states are $2m$. The frequencies differ from the classical ones by an amount too small for experimental detection. The intensities are valid only for the fundamental branch. The central line vanishes; the positive branch is only slightly stronger than the negative. E. B. LUDLAM.

Quantum theory of tri- and poly-atomic molecules. F. LUTGEMEIER (Z. Physik, 1926, **38**, 251—263).—The rotational energy of molecules having three different moments of inertia is calculated on the older quantum mechanics. If two of the moments of inertia are nearly equal, two formulæ are obtained according as the third is greater or less than the other two. Where there are no two moments of inertia equal, the spectra will be complicated, but one or other of the two formulæ will give the first quantum value.
E. B. LUDLAM.

Kaufmann's experiment and the spinning electron. L. C. JACKSON (Nature, 1926, **118**, 263).—If the force, $1/c(\mu[vX])$ (where μ is the magnetic moment of the spinning electron, v is the velocity, and X the magnetic field), introduced by Wentzel, has a real existence, Kaufmann's experiment shows that the free electron cannot possess any spin comparable with that required by Goudsmit and Uhlenbeck's theory. A. A. ELDRIDGE.

Dynamical model for complex atoms. J. C. SLATER (Physical Rev., 1926, [ii], **28**, 291—317).—As a model for a complex atom, the author employs the conception of a number of electrons, each moving in a central orbit, and exerting torques on one another dependent only on the angle between their angular momentum vectors, and not on their phase in their respective orbits. For two electrons and a nucleus, this model leads to a multiply periodic system which can be solved completely, whereas that in which the electrons instantaneously influence each other reduces to the astronomical three-body problem. The dynamical equations are solved and the quantum conditions applied; these agree with the quantum conditions previously set up empirically, and yield new quantum numbers relating to the orientation of electrons. The formula for the energy in terms of the quantum numbers leads to an explanation of inverted multiplets, of the fact that relativity doublets follow the same formula as alkali doublets, but are inverted, and of the fact that doublets and triplets both fit on the same "relativity" doublet curve.
A. A. ELDRIDGE.

Gyromagnetic electrons and a classical theory of atomic structure and radiation. L. V. KING (Science, 1926, **63**, 504).—A mathematical consideration of the fields due to a spinning electron moving with uniform velocity, taking into account the deformation of the electron boundary into an ellipsoid. Planck's constant is a fundamental characteristic of a rotating electron. A. A. ELDRIDGE.

Nitrogen afterglow spectra. R. C. JOHNSON and H. G. JENKINS (Phil. Mag., 1926, [vii], **2**, 621—632).—The spectrum is best produced by the presence of only a little nitrogen in a large quantity of oxygen. The most prominent point is the continuous spectrum above 4300 Å., and the absence of the mercury line at 2536, which places an upper limit of 4·86 volts to the energy of the afterglow molecule. No variation of the intensity of the β- and γ-groups was found in the presence of helium and argon. This is not in agreement with the observations of Rayleigh (A., 1923, ii, 45). The cyanogen tail bands obtained when the gas tube was contaminated with a small amount of carbon have been examined. A. E. MITCHELL.

Absorption spectra of some gases and vapours in the Schumann region. S. W. LEIFSON (Astrophys. J., 1926, **63**, 73—89).—A study of the absorption in the Schumann region of oxygen, nitrogen, nitrous oxide, nitric oxide, nitrogen peroxide, carbon monoxide, carbon dioxide, ammonia, methane, water, carbon tetrachloride, and ethyl alcohol, the continuous spectrum of hydrogen in the region 2000—1600 Å. and the secondary spectrum of hydrogen in the region 1600—1250 Å. serving as a background. Fluorite transmits the hydrogen line 1215·67 Å. Formulæ are given for the heads of the bands in terms of frequency for oxygen, carbon monoxide, carbon dioxide, and ethyl alcohol. The approximate value $11{\cdot}2\times10^{-4}$ g.cm.^{2} is obtained from the double bands for the moment of inertia of the nitric oxide molecule. A. A. ELDRIDGE.

Absorption spectrum of hydrogen iodide in the ultra-violet. K. F. BONHOEFFER and W. STEINER (Z. physikal. Chem., 1926, **122**, 287—292).—The absorption spectrum of hydrogen iodide in the spectral region between 2300 and 3000 Å. has been examined and is found to be continuous, the absorption increasing with decreasing wave-length. It is therefore probable that the primary photochemical decomposition of the iodide involves a dissociation of the molecule into uncharged atoms, not into ions (cf. Stern and Volmer, A., 1920, ii, 461).
R. CUTHILL.

Carbon monoxide bands. D. C. DUNCAN (Science, 1926, **63**, 382—383).—Three band systems previously designated the second negative and fifth and seventh positive bands of nitrogen (this vol., 549) actually belong to carbon, and are probably due to carbon monoxide. Support is afforded to the view that the structure of the carbon monoxide

molecule is very similar to that of the nitrogen molecule. Since a difference of 2% would be expected for the vibrational shifts of corresponding systems, the differences in the forces in the two molecules apparently compensate for the difference in mass. A. A. ELDRIDGE.

More refrangible band system of cyanogen as developed in active nitrogen. W. JEVONS (Proc. Roy. Soc., 1926, **A**, **112**, 407—441).—The modifications of the 3590 Å. ($n''-n'=-1$) group of cyanogen bands and of some of the "tail" bands, as developed in the afterglow of active nitrogen in comparison with the arc, are discussed. Data for the (1, 0) and (2, 1) bands of this group are identified in Kayser and Runge's arc list (Abh. Akad. Wiss. Berlin, 1889). The modifications in the 4216 and 3883 groups and the interpretations of them given by Birge and by Mulliken are discussed (cf. Strutt and Fowler, A., 1912, ii, 214; Mulliken, *ibid.*, 1925, ii, 1020). Like these groups, the 3590 group is shortened in the low wave-length direction, but unlike these groups, it is prolonged in the high wave-length direction in the afterglow as compared with the arc, and also consists of headless bands. Grating measures of the 3590 afterglow group are recorded and compared with the arc data for the same region. Each source develops some lines which the other does not. S. K. TWEEDY.

Emission of light by the decomposition of chloroazoimide. K. GLEU (Z. Physik, 1926, **38**, 176—201).—Chloroazoimide was prepared by mixing solutions of sodium hypochlorite and sodium azide and slowly adding sulphuric acid. The gas was led through a capillary tube into a wider tube heated at 400°, and kept at a pressure of 2 mm. The decomposition then took place without explosion, producing a red glow and exciting fluorescence in the glass. The spectrum shows a new band system in the red, consisting of four groups of bands. It is suggested that this is due to a molecule containing both nitrogen and chlorine. In the ultra-violet, the spectrum shows the continuous bands with maxima at 3060 and 2570 Å. of the emission spectrum of chlorine. This spectrum is not emitted in the decomposition of chlorine dioxide. The addition of hydrogen produces an intense white glow, which is identical in the visible region with the α-band of ammonia; a new band is produced in the ultra-violet with maxima at 3742 and 3752 Å., consisting of a few well-separated lines and ending at 3240 and 3610 Å., respectively. They are ascribed to a molecule containing both nitrogen and hydrogen. No nitrogen bands are observed. E. B. LUDLAM.

Validity of Beer's law in dilute solutions of electrolytes. H. VON HALBAN and J. EISENBRAND (Z. physikal. Chem., 1926, **122**, 337—348).—The very large apparent deviations from Beer's law, in the region 248·2—365·5 μμ, reported by Suhrmann and Huppert (A., 1925, ii, 773) to be exhibited by dilute solutions of potassium nitrate in water and of salicylic acid in alcohol, are due to an unsuitable method of investigation. Ebert's experimental results for potassium nitrate in water (A., 1924, ii, 824) are corroborated, and hence the applicability of Beer's law. A comparatively small deviation from Beer's law occurs with alcoholic solutions of salicylic acid, the extinction coefficients decreasing with increasing dilution (10—20% per tenfold dilution). The light absorption data of Winther (A., 1923, ii, 519) and of Henri ("Études de Photochimie," Paris, 1919) for salicylic acid in alcohol are confirmed, in contradistinction to those of Suhrmann and Huppert. L. F. GILBERT.

Absorption spectra of quinones. Relations of quinones to α-diketones. L. LIGHT (Z. physikal. Chem., 1926, **122**, 414—454).—The absorption spectra of *p*-benzoquinone in alcohol and ether, of toluquinone in hexane and alcohol, and of *p*-xyloquinone in hexane, alcohol, and ether have been investigated over the range 5000—2000 μμ, approximately. Similarities and differences between these absorption spectra are discussed with special reference to chemical constitution. The absorption spectra of vaporised *p*-benzoquinone and diacetyl have also been investigated and are compared with that of glyoxal (cf. Lüthy, A., 1924, ii, 80). Each of these latter spectra can be expressed by the equation $1/\lambda=N+n\alpha+p\beta+q\gamma$. L. F. GILBERT.

Fluorescence, phosphorescence, chemiluminescence, and the activation of molecules. N. R. DHAR (Z. anorg. Chem., 1926, **155**, 303—310).—It is suggested that fluorescence is due to molecules which have been activated by absorbed radiation returning to their normal state (cf. A., 1924, ii, 746). The effect is destroyed by the presence of other molecules which take the energy from the active molecules. Phosphorescence is essentially similar to fluorescence, but the life of the active molecules seems to be in some way lengthened. In chemiluminescence, *e.g.*, the slow oxidation of phosphorus, the molecules are activated by the ions formed in the reaction. R. CUTHILL.

Band fluorescence of potassium and sodium. P. PRINGSHEIM (Z. Physik, 1926, **38**, 161—175).—The metals were purified with great care, heated at about 300° in a glass bulb, and illuminated with light from a powerful carbon arc. In addition to the red bands of potassium and the bluish-green and orange bands of sodium, yellow bands were observed for a mixture of sodium and potassium which can also be obtained as absorption bands. These bands cannot be due to the presence of hydrogen or organic impurities and must be ascribed to molecules Na_2, K_2, and NaK. E. B. LUDLAM.

Excitement of fluorescence by short-wave ultra-violet light. O. OLDENBERG (Z. Physik, 1926, **38**, 370—377).—Light in the ultra-Schumann region was employed, necessitating the production of the light in the tube containing the gas of which the fluorescence was being studied. A spark between aluminium or copper electrodes was produced in front of a narrow aperture in a block of copper connected to a copper tube; this was enclosed in a tube through which the gas was streaming. For hydrogen, the line spectrum of the atom was emitted; for nitrogen, the bands of the neutral and ionised molecules. E. B. LUDLAM.

Phosphorescent sulphides of zinc. A. A. GUNTZ (Ann. Chim., 1926, [x], **6**, 5—55; cf. this vol., 558, 885).—The intensity I of the phosphorescence of zinc sulphide containing a trace of copper and various proportions of cadmium sulphide diminishes with time t according to Becquerel's exponential law $I^m/(t+c)=K$, where m depends on the composition of the material and on the temperature, but is always greater than 0·5 at the ordinary temperature. A rise of temperature or an increase in the concentration of the phosphorogen (copper) causes the intensity (and the value of m) to increase, but an optimum point is observed with respect to each of these variable factors. The optimum temperatures for blende and wurtzite are different. From photometric observations of the intensity of phosphorescence the energy involved is calculated to be a fraction (0·42—0·11) of a quantum per atom of phosphorogen at the ordinary temperature and one or two quanta at the optimum temperature. The yield of energy as light varies between 60 and 77%. The magnetic susceptibility of the various mixtures used has been determined, but no relation is apparent between this and the phosphorescence, nor does the susceptibility vary during the luminescence.

G. M. BENNETT.

Phosphorescence excitation by means of moderately rapid cathode rays. R. STADLER (Ann. Physik, 1926, [iv], **80**, 741—778).

Heat of dissociation of non-polar molecules. R. T. BIRGE and H. SPONER (Physical Rev., 1926, [ii], **28**, 259—283).—The limiting value of the vibrational energy of a diatomic molecule is given by $E_n=h\int_{n_0}^{n}\omega^n dn$, where ω^n is the frequency of vibration as a function of the vibrational quantum number n, and n_0 is the value of n for $\omega^n=0$. For non-polar molecules n_0 is finite, and extrapolation of the linear ω^n–n curves to $\omega^n=0$ gives values of E_n ($\pm$0·5 volt). Since the heat of dissociation of a diatomic molecule is the energy necessary to separate the normal molecule into two stable atoms, allowance must be made for any resulting excitation. The following values are tabulated: O_2 7·02 volts (162,000 cal.); O_2^+ 6·5 volts (150,000 cal.); N_2 11·9 volts (274,000 cal.); N_2^+ 9·1 volts (210,000 cal.); CO 11·2 volts (258,000 cal.); CO^+ 9·8 volts (226,000 cal.); NO 7·9 volts (182,000 cal.). The possibility of adiabatic dissociation of a molecule by light absorption, and the difference in behaviour of oxygen and nitrogen in positive-ray analysis are discussed. A. A. ELDRIDGE.

Ionisation potential of methane. G. GLOCKLER (J. Amer. Chem. Soc., 1926, **48**, 2021—2026).—Consideration of certain physical properties leads to the assumption that methane has a rare-gas structure, occupying a position intermediate between argon and krypton, whence its ionisation potential is predicted by Eve's rule (A., 1922, ii, 364) to be 13·7 volts. The value obtained experimentally by Lenard's method was 14·4—15·2 volts, special precautions being taken to avoid errors due to the effect of mercury vapour and to the possible thermal decomposition of the gas by the hot filament. S. K. TWEEDY.

Photo-ionisation experiment with hydrogen. F. L. MOHLER (Proc. Nat. Acad. Sci., 1926, **12**, 494—496).—By the method employed with monatomic gases (this vol., 877), it is found that hydrogen emits no radiation capable of ionising the normal molecule, a result in harmony with spectroscopic evidence. The excitation potentials and the ionisation potential of H_2^+ are less than 15·9 volts.

J. S. CARTER.

Influence of absorbed gases on the magnitude of the photo-electric effect. A. PREDVODITELEV and G. JOFFE (Z. Physik, 1926, **38**, 280—288).—The influence of adsorbed air on the photo-electric current from coconut charcoal has been determined, and the effect of temperature examined. With increasing quantity of gas, the current rises, reaches a maximum, at which it remains for a while with further increase of gas, afterwards diminishing. Equations are derived from considerations of the electrical moment of the medium and of the gas which represent the results of the experiments satisfactorily. E. B. LUDLAM.

Dielectric constant of diatomic dipole-gases on the new quantum mechanics. R. DE L. KRONIG (Proc. Nat. Acad. Sci., 1926, **12**, 488—493).—Mathematical. A treatment of the dielectric constant of a diatomic dipole-gas, based on the methods of Heisenberg's quantum mechanics (Z. Physik, 1925, **33**, 879), leads to an expression which under appropriate temperature conditions is identical with that of Debye, derived on the classical theory. The expression for the transition probabilities of absorption in the pure rotation spectrum is given. J. S. CARTER.

Temperature-sensitivity of the dielectric constant for methane, methyl chloride, methylene dichloride, chloroform, and carbon tetrachloride vapours. R. SÄNGER (Physikal. Z., 1926, **27**, 556—563).—Debye's theory for the temperature-sensitivity of the dielectric constant has been successfully applied to vapours. The symmetrical skeleton of methane is strongly distorted when methyl chloride is formed, and as successive hydrogen atoms are displaced the asymmetry increases, until with complete chlorination to the tetrachloride there is a return to symmetry of the molecule. The values of the electrical dipolar moments of methyl chloride, methylene dichloride, and chloroform are $1·9_7$, $1·5_9$, and $0·9_5\times10^{-18}$ c.g.s.u., respectively. R. A. MORTON.

Dielectric constant of diatomic dipolar gases according to "wave" mechanics. C. MANNEBACK (Physikal. Z., 1926, **27**, 563—569).—Theoretical. The Schrödinger–Born and the Heisenberg–Born mechanics both lead to the result that the dielectric constant of an ideal diatomic gas with rigid molecules, in which the resulting electron impulse moment is nil (accounting for the non-existence of paramagnetism in the normal state of the molecule), approaches the value indicated at high temperatures by the classical theory of Langevin and Debye. At the ordinary temperature the deviations are small.

R. A. MORTON.

Fundamental constants of nature. H. COLLINS (Chem. News, 1926, **133**, 161—162).—A theoretical

summary of the author's papers on the relative volumes of the elements. A. R. POWELL.

Gyration of light by multiplet lines. C. G. DARWIN (Proc. Roy. Soc., 1926, **A**, **112**, 314—336).—A theoretical investigation of the dispersive effect of the rotation of polarised light by a vapour possessing a multiplet spectrum (cf. this vol., 216). Frenkel's treatment is considered to be in error because the intensity changes of the Zeeman lines were not calculated (Z. Physik, 1926, **36**, 215; cf. this vol., 554). S. K. TWEEDY.

Theory of optically active isotropic media. V. BURSIAN and A. TIMOREV (Z. Physik, 1926, **38**, 475—484).—Born's theory based on a purely general model of a molecule needs expansion for the actual optically active isotropic substance. In addition to the periodic electric polarisation, a mean periodic magnetic moment must be considered. Consequently a different result for the numerical value for the rotation is obtained, and Maxwell's equations satisfy the principle of energy. E. B. LUDLAM.

Rotatory dispersion of the esters of lactic acid. II. Isomeric butyl esters. C. E. WOOD, J. E. SUCH, and F. SCARF (J.C.S., 1926, 1928—1938).—Comparison of the optical rotation of *n*-butyl *l*-lactate with its isomerides shows that *iso*butyl *l*-lactate exhibits an increased rotation, whilst the tertiary and inactive secondary esters exhibit a considerable decrease. The presence of two asymmetric carbon atoms of the same sign in the molecule causes an enhanced rotation, whereas a decrease takes place when the asymmetric centres are of opposite sign. *d-sec.*-Butyl *d*-lactate shows anomalous rotatory dispersion. C. J. STILL.

Anomalous dispersion of excited gases. R. LADENBURG, H. KOPFERMANN, and (FRL.) A. CARST (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1926, 255—273).—Exact dispersion measurements have been made in the neighbourhood of series lines of electrically excited helium, neon, mercury vapour, and hydrogen. Anomalous dispersion was observed in hydrogen only for currents above 100 milliampères, but in the others for a fraction of a milliampère. It was most evident in the *s*—*p* lines of neon lying in the yellowish-red, and in the lines 5876 and 6678 of helium and 5461 Å. of mercury. The dependence of anomalous dispersion on current strength, pressure, and temperature has been studied. The relative value A of the probability of transformation of the excited states for certain combinations has been determined, and also the ρ-value, and calculation has been made of the number of atoms in the *s*-states of neon and of the absolute value of A. M. S. BURR.

Electric double refraction in colloids. Y. BJÖRNSTÅHL (Phil. Mag., 1926, [vii], **2**, 701—732).—Measurements of the electric double refraction in mercury, gold, and sulphur hydrosols are described. The Kerr effect in all these sols is negative, whilst for pure water it is positive. In the case of gold sols, at least, the phase difference approaches saturation with increasing intensity of the electric field. It is concluded that the approach to saturation is accompanied by an approach to completion of the orientation of the particles in the electric field. A. E. MITCHELL.

Spectro-chemistry of compounds containing nitrogen. II. K. VON AUWERS and W. ERNST (Z. physikal. Chem., 1926, **122**, 217—249; cf. A., 1925, ii, 847).—Densities and refractivities are recorded for pyrazoles, *iso*oxazoles, oxazoles, thiazoles, *iso*thiazoles, and glyoxalines. With all the unsaturated heterocyclic compounds so far examined, the closing of the ring involves a reduction in the refractivity and dispersive power to such an extent that the usual optical effect of double linkings does not appear. Such optical depression may be reduced or even converted into exaltation by substituents. The pronounced optical sensitivity of nitrogen makes the analysis of the available data extremely difficult, but in a few cases at least, *e.g.*, the pyrazoles, certain relations between structure and optical properties emerge. R. CUTHILL.

Birefringence of crystalline carbonates, nitrates, and sulphates. C. V. RAMAN (Nature, 1926, **118**, 264—265).—The observation that the light scattered by dust-free nitric acid is nearly unpolarised, whilst that from concentrated or aqueous sulphuric acid is nearly completely polarised, supports Bragg's explanation (A., 1924, ii, 373; 1925, ii, 92) of the strong birefringence exhibited by the crystalline carbonates and nitrates. A. A. ELDRIDGE.

Rotation of molecules. D. M. DENNISON (Physical Rev., 1926, [ii], **28**, 318—333).—Mathematical. The application of Heisenberg's new theory of quantum mechanics to the system of a particle moving in a plane at a fixed distance from a centre is reconsidered from the point of view of a system involving a restraint, and is extended to a particle moving in space at a fixed distance from a centre, and to the motion of molecules having an axis of symmetry. A. A. ELDRIDGE.

Atomic volumes of carbon and hydrogen. W. F. SHORT (Nature, 1926, **118**, 445).—Ingold's value (115·3°) for the angle between the carbon to carbon valencies in a polymethylene chain (J.C.S., 1921, **119**, 305) is criticised; the value 116° 34′ is deduced, the ratio of the atomic volumes of carbon and hydrogen being taken as 4 : 1. A. A. ELDRIDGE.

Atomic numbers and the properties of ions in the crystal lattice. III. The metallic state. A. F. SCOTT (J. Physical Chem., 1926, **30**, 1009—1030; cf. this vol., 662).—The relationship connecting the distance between ions in the crystal lattice of a metal and the chemical forces of the element is considered in an attempt to correlate more closely the qualitative relationships existing between the chemical and physical properties of the elements. It is concluded that: (*a*) the lattice distance varies linearly with the constraint, k, acting on the valency electron, which is a measure of the forces of chemical affinity; (*b*) the relation between k and f, the constraint acting on the outer group of electrons of an ion (this vol., 662), is also linear and possibly represents a condition necessary for the existence of a crystal lattice; (*c*) the effect of changes in the nuclear charge on f

is uniform for different series of isoelectronic ions. Evidence is also advanced for the view that the valency electrons in a crystal are not "free" in the classical sense, but remain as integral components of individual atoms and, further, the determining factors in group properties lie in the characteristics of ions as well as in the number of valency electrons.

L. S. THEOBALD.

Electronic structure of the elements based on their chemical properties. H. LUX (Z. angew. Chem., 1926, **39**, 953—955).—From a consideration of the stability of the oxides of the elements, it is shown that in groups II—VIII of the periodic system two valency electrons must have elliptical n_1 orbits and the number having more or less circular n_2 orbits increases from 0 to 6. As the atomic number increases, the charge on the nucleus also increases and causes the n_1 orbits to become more elliptical and the valency electrons on these orbits to become more firmly bound; hence the stability of the highest oxides of these elements is reduced and the oxide corresponding with a valency reduction of 2 is the most stable. This is particularly marked in group III; boric anhydride and alumina are very stable, indium has an unstable monoxide and a fairly stable trioxide, and thallium a very stable monoxide and an unstable trioxide. These and other chemical considerations substantiate Stoner's grouping of the electrons, arrived at by purely physical methods (cf. A., 1925, ii, 85).

A. R. POWELL.

Crystal structure and chemical constitution of basic beryllium acetate and its homologues. G. T. MORGAN and W. T. ASTBURY (Proc. Roy. Soc., 1926, **A**, **112**, 441—448).—The crystal structures of the basic acetate, *iso*butyrate, *n*-butyrate, and pivalate of beryllium were investigated by *X*-ray methods (cf. Morgan and Bragg, *ibid.*, 1923, **A**, **104**, 437). The acetate crystals belong to the space-group T_h^4. The pivalate forms monoclinic crystals (m. p. 163°; d 1·05) of bipyramidal habit, having a nearly orthorhombic face-centred cell containing 8 molecules and of dimensions: a=19·3, b=12·4, c=35·4 Å., β=91° 21′. The space-group is either C_s^4 or C_{2h}^6, probably the former. The acetate and pivalate have similar structures; the differences can be attributed to the replacement of the ·Me group by the ·CMe_3 group, which probably cannot be arranged in a dyad axis, so that the four trigonal axes present in the acetate are not apparent in the pivalate. A complete change in crystal type occurs on passing to the *iso*butyrate, which has a triclinic pinakoidal unit. The *n*-butyrate crystals were unsuitable for complete *X*-ray investigation.

S. K. TWEEDY.

Relative intensities of reflexion of *X*-rays from the principal atomic planes of powdered sodium chloride. L. HARRIS, S. J. BATES, and D. A. MACINNES (Physical Rev., 1926, [ii], **28**, 235—239).—Measurements of the relative intensities of reflexion of the α-doublet of characteristic molybdenum *X*-rays (*a*) filtered, and (*b*) reflected from a calcite crystal, from powdered sodium chloride give results in agreement with those of Bragg, James, and Bosanquet (A., 1921, ii, 477) as corrected for "extinction."

A. A. ELDRIDGE.

Crystal structure of olivine. W. L. BRAGG and G. B. BROWN (Z. Krist., 1926, **63**, 538—556).—An olivine having the composition $9MgSiO_4,Fe_2SiO_4$ has been examined by the spectrometer and rotation methods. There are 4 molecules to the cell, space-group V_h^{16}, a=4·755, b=10·21, c=5·985 Å. The arrangement of the atoms resembles that of chrysoberyl. Co-ordinates are given for the magnesium, silicon, and oxygen atoms. The last-named stand very nearly in the close-packed hexagonal arrangement. Each silicon atom is surrounded tetrahedrally by four oxygen atoms, between which there is a minimum distance of 2·3—2·7 Å.

W. A. CASPARI.

Parameters in crystal structure. [Structure of] mercurous halides. R. J. HAVIGHURST (J. Amer. Chem. Soc., 1926, **48**, 2113—2125).—The formulæ hitherto proposed for calculating the intensities of *X*-ray reflexion for a crystal powder are shown to be unsatisfactory owing to the uncertain value of the structure factor, which is usually calculated on the invalid assumption that the atomic structure factors of the component atoms vary similarly with the angle of reflexion. Another method of determining crystal parameters is described based on the fact that the distribution density of diffracting power ("electron density") may be represented by a Fourier series (Allison and Duane, A., 1925, ii, 930), the coefficients of which may be evaluated from the measured reflexion intensities. The method is illustrated by an application to the mercurous halides for which u=0·116 and v=0·347, the unit cell containing 2 molecules and having mercury atoms at (0, 0, u; 0, 0, $\bar{u}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}+u$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-u$), and halogen atoms at (0, 0, v; 0, 0, $\bar{v}$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}+v$; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}-v$).

S. K. TWEEDY.

Crystal structure of bivalent chlorides. G. BRUNI and A. FERRARI (Atti R. Accad. Lincei, 1926, [vi], **4**, 10—13).—Laue photographs for magnesium, manganous, and cadmium chlorides show that these have a rhombohedral structure with axial ratios 2·45, 2·34, and 2·20, respectively (cf. this vol., 236). Zinc chloride, examined by the Debye method, has probably a rhombohedral cell of 2 molecules, axial ratio 2·36, a=5·27 Å., $d_{calc.}$ 3·10, or a hexagonal cell, a_1=3·77, c_1=8·90 Å.

E. W. WIGNALL.

[Crystal] structure of manganous oxide. C. FONTANA (Gazzetta, 1926, **56**, 396—397).—The determinations of Levi (A., 1924, ii, 862) are repeated, using a chromium instead of a copper anticathode, with the improved results: for λ_α=2·287, a=4·409 Å. and $d_{calc.}$=5·429; for λ_β=2·080, α=4·407 Å. and $d_{calc.}$=5·436.

E. W. WIGNALL.

Change of crystal structure of some salts when crystallised from silicic acid gel. Structure of silicic acid gel. H. A. FELLS and J. B. FIRTH (Proc. Roy. Soc., 1926, **A**, **112**, 468—474).—The separation of sodium chloride, bromide, iodide, and nitrate crystals from silicic acid gels occurs usually in the form of blades with a straight fibrous habit. The fibres are flexible and somewhat elastic. *X*-Ray examination of the sodium chloride crystals showed them to be of cubic structure. Transverse and longitudinal cleavages are present; the former

are inclusions, probably bubbles, and, being parallel to the cube, indicate that the needles are elongated parallel to the cubic axis. The longitudinal cleavages are negative crystals. Sodium bromide crystallised in six-sided prisms elongated parallel to the principal axis and showing a perfect basal cleavage. Aniline and toluene hydrochlorides yielded distorted plates, but no distortion occurred in the case of sodium tartrate. The results are considered to support a capillary structure for silicic acid gels, the pores being centres of crystal growth, which is controlled by the continuous accumulation of salt at the pore.

S. K. TWEEDY.

Crystal structure of ruthenium and osmium. G. R. LEVI and R. HAARDT (Gazzetta, 1926, **56**, 369—375; cf. Hull, A., 1922, ii, 624).—*X*-Ray photographs, photomicrometer curves, and tabulated data are given for powders of ruthenium and of osmium (cf. this vol., 693). For the close-packed hexagonal lattice a=2·680, c=4·261 Å., axial ratio 1·59, for ruthenium, and a=2·714, c=4·316 Å., axial ratio 1·59, for osmium are found, giving $d_{calc.}$ 12·71 and 22·98, respectively, somewhat higher than observed values. The structure is the same whether or not the metals are cooled slowly after the initial heating at 1050°. E. W. WIGNALL.

Lattice structure of calcium chromate. K. HERRMANN, M. HOSENFELD, and N. SCHÖNFELDT (Wiss. Veröff. Siemens-Konz., 1926, **5**, 119—127).—The lattice structure of calcium chromate, forming rhombic bipyramidal crystals, has been determined. The crystal unit contains 4 molecules, a=7·45, b=10·3, c=5·88 Å. The most probable space-group is B_h^{13}, and symmetry C_i. The parameters of the molecules are ($\frac{1}{4}$, $\frac{1}{4}$, 0; $\frac{3}{4}$, $\frac{1}{4}$, 0; $\frac{1}{4}$, $\frac{3}{4}$, 0; $\frac{3}{4}$, $\frac{3}{4}$, 0) or ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$; $\frac{3}{4}$, $\frac{1}{4}$, $\frac{1}{2}$; $\frac{1}{4}$, $\frac{3}{4}$, $\frac{1}{2}$; $\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{2}$).

C. J. SMITHELLS.

Crystal structure of cobaltous oxide and hydroxide. G. NATTA and A. REINA (Atti R. Accad. Lincei, 1926, [vi], **4**, 48—54).—Cobaltous oxide is of the sodium chloride type with 4 molecules to the cell; a=4·22 Å., from which the diameter of the Co^{++} ion is 2·92 Å., $d_{calc.}$ 6·62, agreeing well with the value found for the sample used. Cobaltous hydroxide has a uniaxial rhombohedral structure (cf. De Schulten, A., 1889, 1114), the unit cell of one molecule, of the brucite type, having co-ordinates Co (0, 0, 0), O ($\frac{2}{3}$, $\frac{1}{3}$, u), ($\frac{1}{3}$, $\frac{2}{3}$, $\bar{u}$), where u is $\frac{1}{4}$—$\frac{1}{3}$, and dimensions a=3·19, c=4·66 Å. Hydroxides of cobalt and nickel precipitated together give lines intermediate between those of the pure substances, a proof that they are isomorphic. E. W. WIGNALL.

X-Ray examination of metallic hydrides. Copper hydride. A. QUILICO (Atti R. Accad. Lincei, 1926, [vi], **4**, 57—62; cf. Müller and Bradley, this vol., 889).—*X*-Ray photograms of preparations by various methods fail to indicate the existence of copper hydrides. The action of hydrogen on heated copper or cupric oxide, and that of zinc on an acid copper sulphate solution, gives products consisting of copper with a small quantity of occluded hydrogen. The reduction of copper sulphate by hypophosphorous acid gives below 40° a black substance consisting of amorphous copper with varying amounts of occluded hydrogen; at about 70°, mainly cuprous oxide containing occluded hydrogen; and at the b. p., copper either alone or mixed with cuprous oxide.

E. W. WIGNALL.

Crystal structure of tiemannite and coloradoite. W. F. DE JONG (Z. Krist., 1926, **63**, 466—472).—From *X*-ray rotation photographs, with special reference to intensities, it is concluded that these minerals crystallise like sphalerite in space-group T_d^2. For tiemannite d_{100}=6·04 Å., whence d=8·41 and distance Hg—Se=2·62 Å. For coloradoite d_{100}=6·43 Å, whence d=8·20 and distance Hg—Te=2·78 Å.

W. A. CASPARI.

Crystal structure of telluric acid. L. M. KIRKPATRICK and L. PAULING (Z. Krist., 1926, **63**, 502—506).—The cubic modification of $Te(OH)_6$, crystallising in octahedra, has been examined by the spectrometer and Laue methods. The lattice is found to be face-centred, with d_{100}=15·48 Å. The Laue photograph results indicate O_h^3 as space-group.

W. A. CASPARI.

Micro-structure of mercury. W. ROSENHAIN and A. J. MURPHY (Nature, 1926, **118**, 261).—A photograph showing the typical micro-structure of solid mercury is reproduced. A. A. ELDRIDGE.

Morphology of graphite. J. BRUNNER and H. HAMMERSCHMID (Z. anorg. Chem., 1926, **155**, 255—256).—In incomplete combustion of laminated graphite numerous regular hexagons are seen with the microscope, indicating an uptake of oxygen according to a certain orientation. In graphite, the carbon atoms lie in planes, and in each plane are arranged in regular hexagons; the planes lie so that the middle of a hexagon side coincides with the angle of the next. That this structure explains the phenomena observed when graphite is burnt is proved by microscopic comparison of partly burnt crystalline and amorphous graphite. In the latter case, no orientation is observed. M. CARLTON.

Structure and isotrimorphism of the tervalent metallic acetylacetones. W. T. ASTBURY (Proc. Roy. Soc., 1926, **A**, **112**, 448—467).—*X*-Ray investigation of ten metallic acetylacetones shows that the α-acetylacetones are monoclinic-prismatic crystals of space-group C_{2h}^5, β-acetylacetones are rhombic-pyramidal crystals of space-group C_{2v}^7, both types containing 4 molecules per unit cell, and γ-acetylacetones are rhombic-pyramidal crystals of space-group C_{2v}^9 with 4 groups of 4 molecules in each cell; none of the three forms is pseudo-hexagonal. The nature of the isotrimorphism exhibited by the crystals is explained from the results, which also confirm the assumptions that the univalent acetylacetone radical in these compounds is a chelate grouping functioning in the co-ordinated complex as a two-fold associated unit, and that 3 such groups are arranged symmetrically around the central tervalent atom (cf. Morgan and Moss, J.C.S., 1914, **105**, 189).

S. K. TWEEDY.

[**X-Ray analyses. II.**] V. M. GOLDSCHMIDT (Z. physikal. Chem., 1926, **122**, 250—253).—A criticism of Günther and Wilcke's analysis of a

gadolinite (this vol., 663) on the ground that in analysis by *X*-ray spectroscopy the possibility of a line of a particular element being reinforced by the coincidence with it of a line of another element must be taken into account. R. CUTHILL.

[*X*-Ray analyses. II.] P. GÜNTHER and G. WILCKE (Z. physikal. Chem., 1926, **122**, 254—256).—A reply to Goldschmidt (cf. preceding abstract). R. CUTHILL.

Parallelism between the phenomena of magnetostriction and magnetic hysteresis in nickel. B. WWEDENSKI and J. SIMANOV (Z. Physik, 1926, **38**, 202—214).—A nickel wire of 0·5 mm. diameter was suspended from a lever, passed through the vertical core of an electromagnet, and stretched by a weight. The striction curves as a function of the applied tensile stress follow the same course as the hysteresis curves, and it is concluded that they are related. There is no simple parallelism between magnetostriction and magnetisation, remanence, or coercitive force. The hysteresis curves as a function of the strength of field have a quite different course from those of striction. E. B. LUDLAM.

Distortion of iron crystals. G. I. TAYLOR and C. F. ELAM (Proc. Roy. Soc., 1926, **A**, **112**, 337—361).—Experiments on the stretching and compression of single iron crystals are described (cf. Taylor and Farren, *ibid.*, **A**, **111**, 529). Unlike other metals, the iron particles adhere along a certain crystallographic direction, so that the resulting distortion resembles that of a collection of rods sliding over one another in groups of irregular cross-section. The slip lines apparent on the crystal surface are the traces of these groups in the surface. When the distortion is a uniform shear, the groups stick together in the form of plates of irregular thickness, which are more or less parallel to the plane of slip and have no immediate directional relationship with the crystal axes. This theory requires that the slip lines in a crystal section parallel to the direction of slip should be all straight; experiment confirmed this prediction. S. K. TWEEDY.

Pure zinc at normal and elevated temperatures. J. R. FREEMAN, jun., F. SILLERS, jun., and P. BRANDT (U.S. Bur. Standards Sci. Paper 522, 1926, **20**, 661—695).—The properties of pure cast zinc (99·997%) were studied from the ordinary temperature to the m. p. No evidence of any allotropic modifications was found (cf. Bingham, B., 1920, 660A). The following values were obtained for cast metal: coefficient of linear expansion from 20° to 100° 0·0000395, Brinell hardness 31, decreasing to 6·5 at 200°, tensile strength 4000 lb./sq. in., d 7·131. *X*-Ray measurements showed no change in structure between 20° and the m. p. The length of the side of the elementary prism is 2·65 Å., $d_{calc.}$ 7·19. Strain-free cast zinc does not recrystallise on annealing up to 390°. Three types of fracture were obtained in tensile tests depending on the temperature: 20—100° brittle, 100—220° oblique, 220—350° wedge. These are explained with reference to stages in recrystallisation and the development of a preferred orientation in the stressed specimens. C. J. SMITHELLS.

Behaviour of single crystals of aluminium under reversed torsional stresses. H. J. GOUGH, S. J. WRIGHT, and D. HANSON (Inst. Metals, July, 1926, advance copy, 16 pp.; cf. this vol., 666).—Single crystals of aluminium are subjected to alternating torsional stressing. The resulting distortion under this complex type of straining action is observed using slip-band measurements, and is related to the atomic spacing by means of *X*-ray analysis. The observed system of slip bands is shown to be in agreement with the simple law that slip is confined at any point of the surface of the crystal to one of the octahedral planes, and in the direction of the most highly stressed principal lines of atoms. The progressive hardening during a long endurance test is studied, and the phenomena attending the last stages of the test are isolated from those of the earlier stages. It is shown that no slip occurs in the stages immediately preceding fracture. Some quantitative data on hardening are deduced from ball indentation tests on cross-sections of the specimens. C. J. SMITHELLS.

Deformation of tungsten crystals. C. J. SMITHELLS, H. P. ROOKSBY, and W. R. PITKIN (Inst. Metals, July, 1926, advance copy, 9 pp.).—When metals are rolled or drawn, the crystal fragments tend to take up a definite orientation with respect to the direction of working. It is shown that the same effect is produced during the swaging of tungsten rods. The micro-structure and *X*-ray diffraction pattern at various stages in the swaging of tungsten rods have been examined with a view to understand the mechanism by which this " preferred " orientation is attained. When large crystals are deformed, they are first broken up into fragments with random orientation. It is shown that the percentage reduction necessary to develop a given degree of preferred orientation is less the finer the original grain size. The results are discussed in connexion with Goucher's work on the deformation of tungsten single crystals (A., 1924, ii, 818). It is suggested that the size of the crystal fragments, rather than the amount of work done, determines their ability to assume the preferred orientation. C. J. SMITHELLS.

Determination of the mol. wt. of fatty acids. M. TRAUTZ and W. MOSCHEL (Z. anorg. Chem., 1926, **155**, 13—20).—Determinations of the mol. wt. of the five lowest fatty acids by the Beckmann cryoscopic method in benzene and nitrobenzene solution give values varying from two to three times the normal value, no definite constant being obtained. Vapour-density measurements were of no value with formic acid owing to its decomposition, but with the next four acids almost exactly dimeric equivalents were obtained and dimeric heats of 13—18 cal. The step-rule was not followed, but there were indications of it in cryoscopic measurements with nitrobenzene. M. CARLTON.

Electrical conductivity of liquid cyanogen bromide. G. GLOCKLER (Proc. Nat. Acad. Sci., 1926, **12**, 522—523).—According to the theory of " pseudo-atoms " put forward by Grimm (A., 1925, ii, 1123), the cyanogen radical resembles sodium, and

hence fused cyanogen halides should conduct electricity. This is found to be the case, the specific conductance of liquid cyanogen bromide at 55° being 0·02 mho/cm. cube. Observations on the electrolysis in a cell with platinum electrodes are recorded.

J. S. CARTER.

Dual theory of metallic conduction. E. H. HALL (Physical Rev., 1926, [ii], **28**, 392—417).—The theory is considered in relation to the Peltier effect within metallic crystals, the Volta effect, Richardson's formula for thermionic emission, and the " equation " connecting the Peltier and Volta effects. A theory of heat conduction is derived, and the effect of high pressure on the characteristic constants of metals is considered. Generally, compression of a metal reduces the latent heat of the ionisation process within it, and increases the ratio of free-electron conductivity to total electric conductivity. The evidence supports the suggestion that the free electrons may pass through, and not necessarily between, the atoms in their progress through a metal. Possibly, in the superconductive state, the distinction between " free " and " associated " electrons disappears.

A. A. ELDRIDGE.

Temperature relations of photoelectric emission and thermionic emission of electrons. E. H. HALL (Proc. Nat. Acad. Sci., 1926, **12**, 486—488; cf. preceding abstract).—The total work done against resisting forces in the photo-electric emission of electrons is practically independent of temperature. This is not the case with thermionic emission.

J. S. CARTER.

Electrical and photo-electric properties of thin films of rubidium on glass. H. E. IVES and A. L. JOHNSRUD (Astrophys. J., 1925, **62**, 309—319).—An invisible film of rubidium, spontaneously deposited on a glass surface in an exhausted cell, is an electrical conductor (for a plate 19×40 mm. the resistance was $1·3\times10^8$ ohms) and is photo-electrically active. In the dark, the resistance is ohmic, but on illumination it is decreased on account of the added current formed by the liberated photo-electrons under a potential gradient.

A. A. ELDRIDGE.

Electrical polarity of molecules. C. V. RAMAN and K. S. KRISHNAN (Nature, 1926, **118**, 302).—Electrically polar molecules generally exhibit a Kerr effect which is very large in relation to their optical anisotropy, indicating that the orientative action of the field on the molecule is in such cases chiefly due to the permanent electric doublet present in it. The permanent electric moment can be calculated for molecules having an axis of optical symmetry to which the electric doublet is parallel or is inclined at a known angle; thus for hydrogen chloride the moment is 1·06 or $1·04\times10^{-18}$ e.s.u., according as the orientative couple or the induced doublet is not, or is, taken into account.

A. A. ELDRIDGE.

Thermomagnetic and galvanomagnetic effects in arsenic. N. C. LITTLE (Physical Rev., 1926, [ii], **28**, 418—422).—The following coefficients (in absolute e.m.u. at 20°) are recorded: specific resistance, $4·60\times10^4$; thermal conductivity, $3·68\times10^6$; Peltier heat against lead, $3·80\times10^5$; Thomson heat, $3·33\times10^3$; Hall coefficient, $4·52\times10^{-2}$; Nernst coefficient, $2·25\times10^{-3}$; Ettingshausen coefficient, $1·75\times10^{-7}$; Righi-Leduc coefficient, $4·15\times10^{-7}$. The results are compared with Bridgman's corresponding values for antimony and bismuth. The temperature cofficient of resistance is 0·00435 per 1° and the thermal *E.M.F.* against copper is $+(7·91t+0·051t^2)\times10^{-6}$ volt between 0° and 170°. None of the coefficients varies with the strength of the magnetic field. When the plate of arsenic was subjected to a temperature gradient of 10° per cm., a field of 8000 gauss caused a fall in temperature of 0·4°. The value of the coefficient, provisionally defined by the equation: temperature change = coefficient × (temperature gradient)^2 × (field strength)^2, is for arsenic $-6·25\times10^{-10}$ at 20°.

A. A. ELDRIDGE.

Magnetic analysis of hydroxides. (MLLE.) S. VEIL (Rev. Scient., 1926, **64**, 8—10; from Chem. Zentr., 1926, I, 2220).—The magnetic properties of ferric hydroxide are largely dependent on the method of preparation and the oxide obtained on calcination is usually much less magnetic than the original hydroxide. If the precipitated hydroxide is heated with water in sealed vessels at high temperatures, a brick-red, less-hydrated, strongly magnetic product is obtained, which does not lose its magnetic properties on ignition. The product is soluble only in hot concentrated hydrochloric acid. Reprecipitation with ammonia and repetition of the heating process cause a further increase in magnetic properties. Continued repetition leads to a product which is about thirty times as magnetic as the original hydroxide. The reverse is true of chromium hydroxide, the magnetic properties of which appear to fall to a lower limiting value on repeated precipitation from hot solutions. The magnetic character of cupric hydroxide is independent of temperature and of the conditions of precipitation. Nickelous hydroxide from cold solutions is about six times as magnetic as the corresponding oxide. On treatment with hot water and reprecipitation, the hydroxide becomes less magnetic, whilst the magnetic properties of the corresponding oxides reach a maximum and then decrease. Nickelic hydroxide behaves similarly. Nickelous hydroxide in contact with solutions of hydrogen peroxide becomes continually less magnetic as the peroxide decomposition proceeds. The magnetic properties of the corresponding oxides pass through a maximum value.

J. S. CARTER.

Polishing of surfaces. J. M. MACAULAY (Nature, 1926, **118**, 339).—It is suggested that in the process of polishing, surface layers of molecules are really melted by the communication to them of heat vibrations.

A. A. ELDRIDGE.

Specific heats of silver and diamond in the region of high temperatures. A. MAGNUS and A. HODLER (Ann. Physik, 1926, [iv], **80**, 808—822).—The mean specific heats of silver and of diamond have been measured between the ordinary temperature and a temperature extending from 500° to 900°. On the basis of the results the true atomic heat of silver is satisfactorily expressed by a formula employing three constants. The more complicated results for

diamond require an expression containing at least five constants. If C_p (diamond) is reduced to C_v and the values are compared with those calculated from Debye's theory (A., 1912, ii, 1134), when the characteristic temperature is taken as 1909° satisfactory agreement is obtained. It was found that Born's elasticity constants could not be evaluated trustworthily. R. A. MORTON.

Lattice dynamics of melting. W. BRAUNBEK (Z. Physik, 1926, **38**, 549—572).—It is assumed that the crystal model consists of two partial lattices and that thermal agitation consists in their mutual vibration. The potential energy of tho lattice has a threshold value which the two halves must overcome in their mutual displacement; by the elimination of this value, the following thermal relationships are obtained in satisfactory agreement with experimental data: the proportionality between the latent heat of fusion and the absolute m. p., the divergence of the atomic heat from $3R$ at high temperatures, the relation between the m. p. and the variation in the temperature coefficient of the atomic heat at high temperatures, the connexion between m. p. and infra-red specific vibration frequency. A relationship is also found between the m. p. and the lattice constant. E. B. LUDLAM.

Normal densities of gases. (MISS) M. S. BLANCHARD and S. F. PICKERING (U.S. Bur. Standards, Sci. Papers 529, 1926, **20**, 141—177).—A review of the literature relating to the densities of forty-eight different gases. A table gives the most probable value for the weight of a normal litre of each gas under standard conditions, and the deviation from the ideal value is plotted against the b. p. In general, the deviation diminishes with b. p., but there are some marked exceptions. M. S. BURR.

Preparation and determination of the weight of a normal litre of hydrogen iodide. E. MOLES and R. MIRAVALLES (Anal. Fís. Quím., 1926, **24**, 356—399; cf. this vol., 340).—Hydrogen iodide was prepared by the following methods: (1) direct synthesis over platinised asbestos at 300° and solution of the resultant hydrogen iodide in water; (2) hydrolysis of the phosphorus iodide obtained by the action of a suspension of iodine in water on red phosphorus; (3) reduction of iodine with hydrogen sulphide; (4) action of metaphosphoric acid on sodium iodide or on a mixture of sodium iodide and ammonium iodide. The hydrogen iodide solution was freed from water by allowing the solution to drop on excess of phosphoric oxide, and after further drying, was condensed and distilled. The last is considered the best method. The density results obtained with the first and third methods are in good agreement, but the results with the second method are in disagreement with the results by other methods. The value obtained, as the mean of twenty measurements, for the weight of a normal litre of hydrogen iodide is 5·78882. The corresponding figure for the gas obtained by the second method is 5·7976. From measurements made at pressures lower than atmospheric pressure the coefficient of compressibility of hydrogen iodide is given as 0·000113 per mm. G. W. ROBINSON.

Absolute density and coefficient of expansion of silicon tetrachloride. P. L. ROBINSON and H. C. SMITH (Nature, 1926, **118**, 303).—Previously published values of the absolute density and coefficient of expansion of silicon tetrachloride (cf. this vol., 771), when corrected for the expansion of the "durosil" glass, become $1{\cdot}481461 \pm 0{\cdot}000020$ and $0{\cdot}0014048 \pm 0{\cdot}0000022$, respectively. The value of the at. wt. of silicon is not affected. A. A. ELDRIDGE.

Dependence of the density of a liquid on the temperature. A. BATSCHINSKI and K. SCHAPOSCHNIKOV (Z. Physik, 1926, **38**, 573—574).—Polemical (cf. Predvoditelev, this vol., 669). The claim of Predvoditelev to have deduced Saslavsky's formula from the van der Waals equation of state is not justified. E. B. LUDLAM.

Density measurements at high temperatures. VIII. Density and expansion of white and grey pig iron in the liquid and solid states. F. SAUERWALD and E. WIDAWSKI (Z. anorg. Chem., 1926, **155**, 1—12).—Changes in the specific volume of white iron up to the m. p. and above are normal and correspond with known structural changes. The contraction between 900° and 1000° noted in previous experiments with grey iron was confirmed dilatometrically, whereby it was possible to determine the amount of contraction due to pearlite solution. The specific volumes of molten grey and white iron agree to within 1%, the value of dv_s/dt for grey iron being $0{\cdot}31 \times 10^{-4}$ and for white iron $0{\cdot}30 \times 10^{-4}$. The hypothesis was confirmed that the contraction of solid grey iron was due to solution of graphite and also that cementite is formed when grey iron is melted. No change in the volume of molten iron at constant temperature could be detected. M. CARLTON.

Halochromy. III. Densities of some molecular compounds. S. SKRAUP and M. EISEMANN (Annalen, 1926, **449**, 1—14; cf. A., 1923, i, 667).—Of 33 molecular compounds only 6 showed contraction, *i.e.*, a molecular volume smaller than additive, whilst 16 showed dilatation, and 11 were approximately additive. This characteristic does not run parallel with the "stability constant, G" (Dimroth, A., 1925, ii, 36), but the most stable complexes show dilatation, and the metastable show contraction. Compounds of trinitro-benzene, -toluene, and -xylene with amines and indole show appreciable dilatation, whilst in the compounds with hydrocarbons the molecular volume is simply additive. On the other hand, compounds of picric acid with both classes equally show a small or no dilatation. The preparation of the following molecular compounds is detailed: trinitrobenzene–indole; *trinitrotoluene–anthracene*, m. p. 162°; trinitrotoluene–indole, m. p. 121°; trinitrotoluene–α-naphthol, m. p. 125°; *trinitroxylene–indole*, m. p. 126°. C. HOLLINS.

Vapour pressure of ethane near the normal b. p. A. G. LOOMIS and J. E. WALTERS (J. Amer. Chem. Soc., 1926, **48**, 2051—2055).—The vapour pressure of ethane between 0·0245 and 2·1441 atm. is given by: $\log_{10} p(\text{atm.}) = -(780{\cdot}24/T) + 4{\cdot}2563 - 0{\cdot}000103T - 9{\cdot}3 \times 10^{-10}(T-238)^4$, from which the

normal b. p. is 184·46(7)° Abs. and the molar heat of evaporation at the b. p. 3642·4 cal.

S. K. TWEEDY.

Vapour pressures and specific volumes of saturated ethane vapour. F. PORTER (J. Amer. Chem. Soc., 1926, **48**, 2055—2058; cf. preceding abstract).—The vapour pressures of saturated ethane vapour between 203·49 and 288·26° Abs. are given by $\log_{10} p(\text{atm.}) = -(780{\cdot}24/T) + 4{\cdot}2563 - 0{\cdot}000103T + 1{\cdot}4 \times 10^{-11}(T-238)^5$; the observed specific volumes of the vapour and the (calculated) latent heats of evaporation of the liquid are tabulated for some intermediate temperatures. The normal density of ethane at 25° is 0·0012383. S. K. TWEEDY.

High vapour pressures of nitrogen. F. PORTER and J. H. PERRY (J. Amer. Chem. Soc., 1926, **48**, 2059—2060).—The vapour pressures of nitrogen between 90·12 and 121·47° Abs. are given by the equation: $\log_{10} p(\text{atm.}) = -(302{\cdot}34/T) + 3{\cdot}94127 - 0{\cdot}00274T + 1{\cdot}116 \times 10^{-6}(T-100{\cdot}5)^3$, which, when extrapolated to low pressures, agrees fairly well with the data of von Siemens (A., 1913, ii, 1023).

S. K. TWEEDY.

Isotherms of helium, hydrogen, and neon below −200°. L. HOLBORN and J. OTTO (Z. Physik, 1926, **38**, 359—367).—Determinations of the isotherms of the three gases were made at −208° up to 100 atm. and for helium also at −252·8° and −258·0°. The correction of the gas thermometer to the thermodynamic scale is calculated.

E. B. LUDLAM.

Internal pressure and coefficient of expansion. W. HERZ (Z. anorg. Chem., 1926, **155**, 323—326).—The internal pressures of a number of liquids have been calculated from their densities and critical data, and are found to decrease with increasing temperature, whilst at the same time the expansion coefficients increase in such a way that the product of the two quantities is approximately constant, independently of the temperature. R. CUTHILL.

Entropy of amorphous substances. F. SIMON and F. LANGE (Z. Physik, 1926, **38**, 227—236).—The problem of the entropy of crystalline and amorphous substances at absolute zero is discussed. Measurements of the specific heats of fused silica and super-cooled glycerol have been made at temperatures as low as 10° Abs. It is obvious from the curves for glycerol that extrapolation to absolute zero from the temperature of liquid air would lead to quite untrustworthy conclusions; from 10° Abs. downwards the specific heat is so small that the experimental error is large. It is calculated that for silica the amorphous form has an entropy 0·9±0·3 cal./degree per mol. greater than that of the crystalline; for glycerol the difference is 4·6±0·3.

E. B. LUDLAM.

Viscosities and densities of anhydrous methyl alcohol and of solutions of some halides of sodium and potassium in this solvent. F. K. EWART and H. R. RAIKES (J.C.S., 1926, 1907—1912).—Pure methyl alcohol was prepared by the method of Hartley and Raikes (A., 1925, i, 498). The effect of small quantities of both water and acetone on the viscosity was determined, and this property used for testing the dryness of the material. The values obtained for the pure alcohol were d_4^{25} 0·78641 and viscosity 0·00545 c.g.s.u., which agree closely with accepted values. The influence of concentration on the density and viscosity of solutions of potassium iodide, potassium bromide, potassium chloride, sodium iodide, and sodium bromide in methyl alcohol was determined. The results display no irregularities.

C. J. SMITHELLS.

Dielectric constants of binary mixtures. J. W. WILLIAMS and I. J. KRCHMA (J. Amer. Chem. Soc., 1926, **48**, 1888—1896).—The dielectric constants of the pure liquids and of mixtures of benzene and toluene, chlorobenzene and bromobenzene, and carbon tetrachloride and benzene were measured at 25° by an improved resonance method. Evidence is quoted in support of the value found for chlorobenzene, 5·610, which is about half the accepted value (Veley, Phil. Mag., 1906, [vi], **11**, 73). The results for the first-named mixture do not agree with those of Grützmacher (A., 1925, ii, 263). Each system is discussed from the point of view of departure from the ideal solution. S. K. TWEEDY.

Surface tension and vapour pressure of binary mixtures. N. A. YAJNIK, R. K. SHARMA, and M. C. BHARADWAJ (J. Indian Chem. Soc., 1926, **3**, 63—72).—The variation of surface tension with composition has been examined at three temperatures. For the mixtures benzene–ethylene dichloride, ethylene dibromide–propylene dibromide, bromobenzene–toluene, and chlorobenzene–toluene the variation is linear. The observed values for the mixtures acetic acid–pyridine, chloroform–acetone, and methyl alcohol–ethyl iodide are greater than those calculated from a simple mixture law, whilst the converse is the case for ethyl acetate–carbon tetrachloride, ethyl acetate–ethyl iodide, ethyl iodide–carbon tetrachloride, and acetone–carbon disulphide. The conclusions reached are similar to those of Worley (J.C.S., 1914, **105**, 273). G. M. BENNETT.

Total and partial vapour pressures of aqueous ammonia solutions. T. A. WILSON (Univ. Ill. Eng. Exp. Sta. Bull., 1925, [146], 1—47).

CHEMICAL ABSTRACTS.

Nitric acid. III. Partial pressures of aqueous nitric acid solutions at 12·5° and 30°. Partial pressure of hydrochloric acid at 12·5°. A. KLEMENC and A. NAGEL (Z. anorg. Chem., 1926, **155**, 257—268).—The partial pressure of nitric acid in its aqueous solutions at 12·5° and 30° was determined by a dynamic method in which a measured amount of nitrogen was led through the aqueous solution. The nitric acid carried over by the gas was determined by absorption in standard alkali and the total increase in weight of the absorption apparatus gave the aqueous vapour pressure. Comparison experiments were made with aqueous solutions of hydrochloric acid and the results are tabulated. Hydrochloric acid has a much greater partial pressure at higher concentrations than nitric acid, but in dilute solution the reverse is the case.

Of the hydrates of nitric acid the vapour-pressure

curve shows only a dihydrate at about 14*N*; there is, however, some evidence for a monohydrate at 18*N*. M. CARLTON.

Critical solution temperature of acraldehyde and water. A. BOUTARIC and S. CORBET (Compt. rend., 1926, **183**, 42—44).—Mixtures of acraldehyde (stabilised with 0·004 of its weight of quinol) and water were heated in sealed tubes until completely mixed, and were then allowed to cool until opalescence just occurred. The effect of acraldehyde resin on the critical temperature suggests that this has a high mol. wt. Confirmation of this view is obtained from cryoscopic measurements with acraldehyde resin in acetic acid, which give a mol. wt. of about 545, in rough agreement with the formula $(CH_2{:}CH{\cdot}CHO)_{10}$. L. F. GILBERT.

Thermal anomalies of certain solid solutions. P. CHEVENARD (Inst. Metals, Sept., 1926. Advance copy).—Certain feebly magnetic solid solutions show transformations similar to those of ferromagnetic substances in that they occur without change of phase or of the space lattice. They exist over a large range of temperature and give rise to anomalies in various physical properties. It is shown that such transformations occur in α-copper–aluminium, nickel–chromium, and copper–nickel solid solutions. Their effects on the dilatation of the first two groups of alloys and on the resistivity of the last have been studied in detail. C. J. SMITHELLS.

Method for investigating binary systems. IV. The "thaw-melt" diagram as a micro-method. H. RHEINBOLDT and M. KIRCHEISEN (J. pr. Chem., 1926, [ii], **113**, 348—354; cf. this vol., 908).—A method is described for the investigation of the m. p. of binary mixtures, requiring about 15 mg. of each component, and illustrated by results obtained for the systems *d*- and *l*-carvoximes, α-naphthol–β-naphthylamine, and β-naphthylamine–*s*-trinitrobenzene. F. G. WILLSON.

Heterogeneous systems of biological interest. I. Distribution of saline compounds between immiscible solvents. J. HOLLÓ and D. DEUTSCH (Biochem. Z., 1926, **173**, 298—309).—Various indicators were shaken up with a two-phase mixture of ether and water and the amount and extent of dissociation of the indicators determined in each phase. With basic dyes (methylene-blue, fuchsin, Nile-blue sulphate, Bismarck-brown) in alkaline solution both phases are almost equally coloured, whereas in acid solution the ether phase is not coloured. Acid dyes (methyl-red, phenol-red, *m*-nitrophenol) are distributed almost equally in acid solution, whereas in alkaline solution they are present almost exclusively in the water phase. When other anions are added in acid solution to the system and are placed in order of their effect on the distribution of the dyes, the Hofmeister series is obtained. P. W. CLUTTERBUCK.

Absorption of gases by charcoal. I. R. A. SMITH (Proc. Roy. Soc., 1926, **A**, **112**, 296—303).—Extracts from a paper, now important historically, which was summarised in Proc. Roy. Soc., 1863, **12**, 424. S. K. TWEEDY.

Adsorptive power of charcoals. M. SURUN (Compt. rend., 1926, **183**, 44—46).—The adsorptive power was measured by shaking known volumes of various 0·01*N*-solutions (mercuric chloride, chloral, citric acid, phenol, resorcinol, antipyrine, and pyramidone) for 30 min. with the charcoal under examination, and systematically increasing the quantity of charcoal until, after filtration, none of the solute could be detected by tests of known sensitivity. L. F. GILBERT.

Adsorption. IX. Adsorption of gases by wood charcoal at low pressures. A. MAGNUS and L. CAHN (Z. anorg. Chem., 1926, **155**, 205—219).—The adsorption of ammonia and carbon dioxide at pressures down to below 0·001 mm. at different temperatures by wood charcoal which had been variously treated as regards degree of gas extraction was investigated. The results with ammonia are not very definite, but on the whole confirm and extend Titov's measurements. The power of adsorption of carbon dioxide by charcoal between 0° and 300° diminishes constantly with the increase in amount of gas absorbed. The more strongly heated the charcoal before adsorption the stronger is its adsorptive power, especially for small quantities of gas, and the greater is the deviation from proportionality between the volume adsorbed and the gas pressure, especially at low pressures. Large deviations from Henry's law are met with, although carbon dioxide at 300° and at pressures of 0·001 mm. behaves as if it were a perfect gas. The greater deviations from Henry's law depend more on the nature of the adsorption medium than on the properties of the adsorbed gas. M. CARLTON.

Adsorption. X. Wood charcoal as adsorption medium for gases. A. MAGNUS (Z. anorg. Chem., 1926, **155**, 220—224; cf. preceding abstract).—Equations are deduced to show that increase of the adsorption potential by roughening the surface is to be expected only if the cavities formed are comparable in their dimensions with the molecular diameter of the adsorbed gas. Formation of such small holes can be produced only by chemical disintegration in the charcoal surfaces. Whereas strong heating may bring this about, a lower temperature will liberate only adsorbed gases or vapours from a somewhat smooth surface. Thus for less strongly heated charcoal Henry's law is nearly fulfilled, whilst stronger heating leads to greater deviations in the ratio of gas adsorbed to gas pressure.

Adsorption in strongly outgassed charcoal in which the places of highest adsorption potential are already filled gives a better approximation to Henry's law than adsorption in the initial stages. This is explained by the equalisation of the charcoal surface as regards its adsorption potential when the finer pores are occupied. M. CARLTON.

Adsorption of gases by platinum-black. A. F. BENTON (J. Amer. Chem. Soc., 1926, **48**, 1850—1861).—The adsorption of hydrogen, oxygen, and carbon monoxide at 1 atm. pressure by the same specimen of platinum-black was measured at 25° by a method designed to eliminate the errors of previous work. The 25° isotherm for hydrogen was also

determined. Hydrogen and carbon monoxide are adsorbed to equal extents; the adsorption of oxygen is little more than half as great, but it is inferred that at somewhat higher temperatures the amounts of hydrogen and carbon monoxide adsorbed would be unchanged, whereas the amount of oxygen would increase. The results with the two former gases support the hypothesis of unimolecular adsorbed films. S. K. TWEEDY.

Adsorption of gases by glass walls. II. Ammonia. M. CRESPI and E. MOLES (Anal. Fis. Quím., 1926, **24**, 210—221).—The adsorption of ammonia by the walls of glass vessels at different pressures was measured by means of an apparatus which is described in detail. The results obtained may be expressed by the equation $A=k\times10^{-6}\,.\,p^{1/4}$, where A is the weight of ammonia adsorbed per cm.^{2} and k is a constant (0·071 for blown glass and 0·045 for drawn glass). The weight of ammonia adsorbed by flasks of different capacity is calculated. G. W. ROBINSON.

Adsorption of acids, bases, and salts by freshly-precipitated silicic acid. M. R. MEHROTA and N. R. DHAR (Z. anorg. Chem., 1926, **155**, 298—302).—Inorganic bases are very readily adsorbed by silicic acid, and tend to cause peptisation, whereas with organic and inorganic acids the reverse is the case. It is therefore probable that peptisation is conditioned by the affinity between the colloid and the peptising agent. R. CUTHILL.

Absorption of ammonia by chromic, ferric, and aluminium oxides. N. NIKITIN (Z. anorg. Chem., 1926, **155**, 358—360).—The above oxides when prepared by ignition of the precipitated hydroxides possess at the ordinary temperature a considerable absorptive power for ammonia, which increases in the order given. With ferric oxide, this is much reduced by increasing the temperature of ignition of the hydroxide, but with the other oxides this is not so. Calcium oxide is much less active than any of the above. R. CUTHILL.

Adsorption mechanisms. M. L. HUGGINS and J. FIELD (Science, 1926, **63**, 454—455).—An attempt to classify types of adsorption by reference to the commonest sources of affinity: (*a*) an unpaired electron in the valency shell of an atom, *e.g.*, probably amorphous carbon and the fresh surfaces of some metals; (*b*) a positive atomic kernel not surrounded by electron-pairs; (*c*) a lone electron-pair in the valency shell of a negative atom; (*d*) double and triple linkings, three- or four-membered rings, etc., in which one or more of the linking electron-pairs is not near the line joining the centres of the two atoms it unites. Adsorption of the types *ab*, *ad*, *ac*, *bc*, *dd*, *bd*, and *cd* is considered; *bd* is "polar," whilst *dd* is probably "apolar." A. A. ELDRIDGE.

Interpretation of adsorption isotherms and isosteres. A. S. COOLIDGE (J. Amer. Chem. Soc., 1926, **48**, 1795—1814).—The discontinuity in adsorption isotherms at saturation pressure is not adequately explained by the capillary-condensation theory (McGavack and Patrick, A., 1920, ii, 417) or by the appearance of a new phase, but is not contrary to Pólányi's adhesion theory (A., 1916, ii, 474). The conditions are discussed under which forces which are continuous functions of distance can give rise to potentials which are discontinuous functions of the volume of adsorbed gas, and the author considers that the observed discontinuities are not incompatible with the hypothesis that the observed vapour is in the liquid state. The Clausius-Clapeyron equation applies to adsorption within a few per cent., the discrepancy being attributed to the presence of air in the vapour. The heat of adsorption in unsaturated systems is mainly the work performed by the attraction of the adsorbent plus the latent heat of condensation of the vapour; in saturated systems, the heat may be the work of compression (cf. Harkins and Ewing, A., 1922, ii, 123, 197). The evidence for and against the existence of a high pressure due to adsorption suggests that the liquid does not obey the ordinary equations of state and that adsorption may be considered as a special case of solution (Homfray, A., 1910, ii, 771, 1041). S. K. TWEEDY.

Structure of thin films. VIII. Expanded films. IX. Dibasic substances. N. K. ADAM and G. JESSOP (Proc. Roy. Soc., 1926, **A**, **112**, 362—375, 376—380; cf. this vol., 348, 468).—VIII. The "expanded" state of surface films and the relation of such films to condensed and gaseous films have been examined. When a definite surface vapour pressure exists between the expanded and the gaseous film such that the transition between the two is discontinuous, the former is regarded as "liquid." The present results on the expanded state of films of some organic compounds containing one and more chains in the molecule indicate the existence of "vapour" expanded films in the case of esters and methyl ketones. These are expanded films which neither behave as liquid films nor show the phenomena of surface evaporation; they pass without discontinuity into gaseous films as the surface pressure is decreased. There is a definite limit to the area occupied by liquid expanded films at no compression; this is about 48 Å.^{2}/mol. in the case of fatty and bromo-acids and 21 Å.^{2}/mol. in that of methyl ketones. It is independent of the length of the chain and of the nature of its head. The long chains in liquid expanded films may assume the form of helices with vertical axes in a close-packed arrangement. Hysteresis, due to the slowness of the molecules in assuming their final packings, probably occurs, even with a simple fatty acid. It becomes apparent with hydrolecithin in the condensed state, which takes some minutes to reach its final pressure in the films. Acid potassium permanganate solution affects ethylenic linkings in the middle of the chain so as to make the films gaseous.

IX. Films of the acids $[CH_2]_n(CO_2H)_2$ where $n=16$, 20, 24, 32, of the diethyl esters where $n=10$, 11, 16, 20, 32, and of the monoethyl ester with $n=16$ were investigated. They are all unimolecular and of the gaseous and condensed types. The films of the esters in which $n=10$ or 11 represent the closest approach to the perfectly gaseous state yet found with insoluble films. The transition from the condensed to the gaseous films is of the same nature as that from the condensed to the expanded films

described in previous papers (cf. A., 1925, ii, 195, 658); in all cases, the condensed films expand to films of the " vapour " type. S. K. TWEEDY.

Distribution and orientation of molecules. I. LANGMUIR (Third Colloid Symposium Monograph, 1925, 48—75).—As a first approximation, the field of force about a group or radical in a large organic molecule is independent of the rest of the molecule. From the Boltzmann equation it is calculated that the probability that in the surface layer the hydroxyl group is immersed in the liquid phase is 300—100,000 : 1. The evaporation of pure substances, the vapour pressures of binary mixtures, the mutual solubilities of liquids, and the orientation of molecules in liquids and interfaces are considered mathematically. The author considers that in expanded films only the heads of the molecules behave as a two-dimensional gas. Such molecules of palmitic acid as are free must lie flat on the surface; the substance therefore does not expand beyond a certain definite area. CHEMICAL ABSTRACTS.

Thermal synthesis of colloids. II. Colloidal selenium. A. GUTBIER [with R. KÖHLER] (Z. anorg. Chem., 1926, **155**, 199—204; cf. this vol., 574).—Superheated selenium vapour was passed into water free from air. Only under the most favourable conditions were the colloidal solutions obtained clear yellowish-red, or deep red in colour; usually they were rose-coloured and at first of a blue tint and cloudy. All showed the Tyndall phenomenon and the Brownian movement. Under the cardioid ultra-microscope the yellowish-red solution is the most highly dispersed, but in all solutions there is evidence of the polydisperse character of the sols. The blue sols are exceedingly stable and may be kept in closed vessels for months at the ordinary temperature.

Non-dialysed solutions decompose after a few days, and in these selenious acid may be detected, but no other compounds; there is no trace of this in the yellowish-red preparation. Dialysed sols may be frozen to an almost colourless ice; these slowly thaw at the ordinary temperature, but quickly decompose.

Coagulation by electrolytes sets in readily with chlorides. Under the influence of a *P.D.* of 110—220 volts, the selenium particles migrate to the anode, the system containing 0·003—0·01% of selenium. The presence of protective colloids leads occasionally to the formation of the yellowish-red variety. The amount of colloid is only slightly increased; the stability is the same as with water. M. CARLTON.

Reactions taking place in the preparation of colloidal copper by Bredig's method. V. PODROUŽEK (Chem. Listy, 1926, **20**, 403—406).—When an arc is struck between two copper electrodes under water, cupric hydroxide appears to be first formed on the electrodes. Under the action of the heat of the arc, dehydration takes place and cupric oxide is the final product of the action. The ratio $Cu(OH)_2$: CuO decreases with the time the arc is in operation and increases with the alkalinity of the medium. A small quantity of hydrogen peroxide is formed during the process, and this produces a small quantity of copper peroxide, which, however, soon decomposes into cupric hydroxide or oxide.

A. R. POWELL.

Number of electrical quanta on colloid particles. W. KISTIAKOVSKI (Kolloid-Z., 1926, **39**, 329).—An error in a previous paper (this vol., 679) is corrected. N. H. HARTSHORNE.

Shear modulus and relaxation of sols. E. HATSCHEK and R. S. JANE (Kolloid-Z., 1926, **39**, 300—313).—Measurements have been made by Schwedoff's method of the shear modulus of a number of sols of gelatin, ammonium oleate, mercuric sulphosalicylate, cotton-yellow, and benzopurpurin. With the exception of the very labile ammonium oleate, the moduli increase with age. With rising temperature they fall rapidly, and at 40—45° the shear elasticity is scarcely measurable. In some cases, the time in which the tension required to maintain a certain deformation falls to the e^{th} part of its initial value was determined. From the relaxation times and the moduli, the viscosity coefficients were calculated, and found to be of the order of magnitude of 10^2—10^4 absolute units. Some observations were also made on the decrease of torsion in the wire with time. An equation is derived, giving the viscosity as a function of the time and the small difference in the angle of torsion, and from this equation the viscosity coefficient can be calculated at extremely small shear gradients of the order of magnitude 10^{-4}—10^{-6} sec.$^{-1}$ The values so obtained show moderate agreement with those calculated from the Maxwell formula. The elasticity of a sol is strongly dependent on its previous history. Thus, benzopurpurin sols of 0·2, 0·3, and 1%, prepared in the cold, show no elasticity and low viscosity; heated to boiling, on the other hand, they show a high shear modulus and viscosity. L. L. BIRCUMSHAW.

Consistency measurements of solutions of rubber in benzene. W. H. HERSCHEL and R. BULKLEY (Kolloid-Z., 1926, **39**, 291—300).—Various equations for the streaming of a plastic material through a capillary tube are considered, and it is found that the expression $d^4/L \,.\, (P-k)^n/q=I$ (where I is an empirical constant, d the capillary diameter, L the effective length, P the total effective pressure, k the initial pressure, and q the velocity of streaming) is the most suitable for a solution of raw rubber in benzene up to a concentration of 1·2%. This equation yields applicable values for all practical streaming velocities, and avoids the necessity of using very high pressures. A simple experimental method can be used, and the errors caused by the uncertainty in the application of the kinetic energy correction are avoided. By using the logarithmic streaming-pressure diagram, better agreement can be obtained for capillaries of different dimensions than by the determination of shear modulus, rigidity, or mobility. The material constants n and I can be obtained from the logarithmic curve, and both increase with the concentration. In comparison with the shear modulus and mobility, both these constants have the advantage that they influence the streaming in the same direction. The initial pressure k vanishes with large capillary tubes and low concentrations, or is too small to be deter-

mined. When measurable, its value increases with decrease of the capillary diameter.

L. L. BIRCUMSHAW.

Stability of colloidal solutions. V. Effect of similarly charged ions as a factor in electrolyte antagonism in the coagulation of sols and the mechanism of stabilisation. K. C. SEN (J. Indian Chem. Soc., 1926, **3**, 81—90; cf. this vol., 122).—The antagonistic effect of potassium oxalate, tartrate, or citrate and of sodium oxalate in the coagulation of sols of copper ferrocyanide by potassium or sodium chloride has been examined. The oxalate or tartrate has a stabilising effect, and the consequent antagonistic action is greater if the coagulating salt does not contain a common ion with the stabiliser, this being attributed to the depressing effect of the common ion on the ionisation of the stabiliser. The mechanism of stabilisation in presence of two electrolytes is discussed. G. M. BENNETT.

Stability of suspensoids under influence of electrolyte mixtures. H. R. KRUYT and P. C. VAN DER WILLIGEN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 484—491).—The concentrations of various salt mixtures have been determined which induce coagulation of sols of arsenious and mercuric sulphides and of selenium. The addition of lithium chloride, potassium ferrocyanide, and to a less extent of potassium chloride makes the concentration of magnesium chloride necessary for coagulation much larger than would be the case in their absence—an effect classified as antagonistic action. Cataphoretic velocities for these sols afford independent evidence of the increased charge on the particles. Potassium hydroxide does not cause antagonistic action in gold, platinum, and silver sols, but has rather a sensitising effect with both magnesium and barium chlorides. The charge on the metal particles cannot be due to adsorbed hydroxyl ions, but probably involves a double layer built up by complex compounds of the metals which are unstable in the presence of alkalis. G. M. BENNETT.

Anomalous flocculation of clay. N. M. COMBER (Nature, 1926, **118**, 412).—Polemical (cf. Joseph and Oakley, this vol., 576). The significance of the results is entirely dependent on what is meant by a "highly purified clay," *i.e.*, on the complete removal of adventitious and absorbed calcium.

A. A. ELDRIDGE.

Adsorption. VI. Influence of the hydrolysis of sols and precipitating electrolytes on the coagulation of colloids. S. GOSH and N. R. DHAR (Kolloid-Z., 1926, **39**, 346—361).—Hydrolysable sols such as arsenic and antimony trisulphides, Prussian-blue, copper ferrocyanide, mastic, gamboge, and dammar resin, if coagulated with a mixture of an acid and a salt, require a much smaller quantity of the salt than the calculated value. The addition of acids, by preventing hydrolysis, makes the sols unstable, for the weak acids produced by hydrolysis have a markedly stabilising effect. Hydrochloric acid is a much better coagulator for mastic, gamboge, and dammar resin sols than is potassium chloride at an equivalent concentration. With arsenic and antimony trisulphides and Prussian-blue, the difference between hydrochloric acid and potassium chloride is not so great, because these sols are not so strongly hydrolysed. If hydrolysable sols are coagulated with hydrolysable salts such as potassium hydrogen carbonate, potassium acetate, and potassium nitrite, greater quantities of them are required than of potassium chloride, since the hydroxyl ions formed increase the hydrolysis and the stability of the sols. The abnormal behaviour of these sols on dilution, viz., that they require a greater quantity of electrolyte for coagulation than when concentrated, cannot be explained solely by the adsorption of similarly charged ions; the greater degree of hydrolysis must be taken into account. Thus the results show that the more hydrolysable the sol the greater the abnormality, whilst if acids are used and the hydrolysis is thus suppressed, the coagulation values tend to become normal.

The strong coagulative power of hydroxyl ions for hydroxide sols depends more on the fact that they destroy the stabilising electrolytes present than on their high migration velocity. N. H. HARTSHORNE.

Adsorption of similarly charged ions as stability factor in the dilution of sols, the acclimatisation, and the antagonistic action of electrolytes on the coagulation of colloids. K. C. SEN (Kolloid-Z., 1926, **39**, 324—328; cf. A., 1925, ii, 664, 665).—Data relating to the coagulation of various sols and emulsions are quoted in support of the author's theory that the phenomena of acclimatisation and of stabilisation by dilution or by a mixture of electrolytes, are related, and are to be explained by the adsorption of similarly charged ions. In the action of electrolytes on a suspension, a non-solvated emulsoid, or a solvated emulsoid there will always be abnormal behaviour on dilution, marked acclimatisation, and antagonistic electrolytic action if similarly charged ions are adsorbed in greater quantities. L. L. BIRCUMSHAW.

Anomalous precipitation series. H. MAYANAGI (Kolloid-Z., 1926, **39**, 319—322).—By the addition of increasing quantities of strongly adsorbable ions of high valency to a sol, four zones are to be distinguished: the lower non-precipitation zone, the lower precipitation zone, the upper non-precipitation zone, and the upper precipitation zone. The ionic concentrations at the three boundary points, where precipitation just begins or ceases, are designated as the first, second, and third swelling values. A consideration of the mechanism causing the lowering of *P.D.* of the colloid particles on addition of electrolytes shows that the relation between the colloid concentration and the electrolyte concentration necessary for precipitation can be predicted from the adsorbability of the electrolyte concerned. In the first precipitation zone the concentrations should be proportional, whereas in the second the salt concentration should be constant and independent of the colloid concentration. The author's views are supported experimentally by observations of the three swelling values in the case of mastic sol (coagulator, ferric chloride), gold sol (coagulator, ferric chloride), ferric hydroxide sol

(coagulator, potassium ferrocyanide), and albumin sol (coagulator, ferric chloride). L. L. BIRCUMSHAW.

Rapid and slow coagulation of polydisperse systems. P. TUORILA (Koll. Chem. Beihefte, 1926, 22, 191—344).—From von Smoluchowski's theory (cf. A., 1917, ii, 297) it is shown that the rate of "rapid" coagulation of monodisperse systems is comparatively slow if the initial number of particles is small, but if this number is large, the rate is high, and after a time is independent of the original number of particles. The coagulation curves of all monodisperse systems ultimately approach each other, and the number of particles tends to a value which does not depend on the original number of particles. Müller's theory (this vol., 242) leads to the conclusion that after a short time the rapid coagulation of systems containing two sizes of particles closely resembles that of monodisperse systems unless the initial number of larger particles lies between 10^7 and 10^{10} and the number of smaller particles is as great or greater, in which case the two systems behave differently. Even then the difference is appreciable only if the radius of the larger particles is at least 20 times that of the smaller particles. After a time, the coagulation curves of both types of system approximate to each other and the number of particles reaches a value which is independent of the dispersity of the system.

The above deductions have been confirmed by experiments with gold sols. In the slow coagulation of polydisperse systems, the amicrons coagulate much more slowly than the submicrons, whilst for monodisperse submicroscopic gold sols the rate of coagulation after a time becomes rather less than is calculated from von Smoluchowski's theory. The coagulative power for gold sols of the chlorides of lithium, sodium, potassium, rubidium, cæsium, and hydrogen increases in this order. In respect of rapid coagulation, monodisperse suspensions of clay and kaolin behave like gold sols, but polydisperse suspensions coagulate more rapidly than the theory indicates, probably owing to the influence of stirring and sedimentation. A direct ultra-microscopic method of observing the continuous decrease in the number of particles during coagulation is described. R. CUTHILL.

Influence of lyophilic colloids on the precipitation of insoluble salts. Gelatin and silver chromate. I and II. T. R. BOLAM and (MISS) M. R. MACKENZIE (Trans. Faraday Soc., 1926, 22, 151—161, 162—177).—See this vol., 678.

Formula for the electrolytic swelling value of gold sol and iron hydroxide sol. K. HAKOZAKI (Kolloid-Z., 1926, 39, 316—319; cf. Tsuji, this vol., 795).—Investigations have been made with gold and ferric hydroxide sols to discover if Tsuji's formula (*loc. cit.*) for the swelling value of the coagulation concentration of electrolytes for mastic sol is also applicable to other hydrophobic colloids. The concentration of sodium chloride at which precipitation of gold sol began in 24 hrs. was found to be independent of the colloid concentration. The swelling value of sodium chloride at different hydrogen-ion concentrations was then determined, using acetate buffer and phosphate buffer. By introducing into Tsuji's formula the values so obtained for the sodium-ion concentration (including that of the buffer) and the hydrogen-ion concentration, which must be combined for the precipitation of the gold sol, the value $10^{-5\cdot3}$ is obtained for K. The experimental results are in good agreement with those calculated from the formula. Similar experiments with ferric hydroxide sol, using acetate buffer, yielded the value $10^{-9\cdot3}$ for K. The observed values agree moderately well with those calculated. L. L. BIRCUMSHAW.

Reactions of colloidal gold with proteins. R. WERNICKE and F. MODERN (Rev. Soc. Argentina Biol., 1926, 2, 143—156).—Electrically dialysed serum-albumin from the horse precipitates gold sols obtained by reduction with formaldehyde or dextrose and purified by prolonged electrodialysis. The precipitating action is less marked with undialysed sols. When appropriate amounts of electrolytes are added, the precipitating action is changed to a protective action. G. W. ROBINSON.

Colloid chemistry of urine. F.-V. VON HAHN (Kolloid-Z., 1926, 39, 329).—A brief reply to Bechhold (this vol., 902). N. H. HARTSHORNE.

Ebullioscopic determination of the equilibrium constant relative to the formation of complexes with mercuric cyanide. F. BOURION and E. ROUYER (Compt. rend., 1926, 183, 390—392).—Ebullioscopic examination has shown that at 100° mercuric cyanide does not combine to a great extent with alkali halides in aqueous solutions. When the ordinary method of mixtures is used to interpret the results, these indicate that in solutions containing 1 mol./litre of each constituent potassium bromide–mercuric cyanide mixtures are combined to the extent of 40·5%, whilst in potassium chloride–mercuric cyanide mixtures only 30% combined. When calculated on the basis of the b.-p. elevations per unit weight of water, the results indicate that only 27% of the potassium bromide–mercuric cyanide mixture is combined. The observations lead to no conclusions regarding the rule to apply for the calculation of the equilibrium constant from the b.-p. elevations of the single salts. A. E. MITCHELL.

Empirical viscosity formula. M. KUNITZ (J. Gen. Physiol., 1926, 9, 715—725).—The expression $\eta=(1+0\cdot5\varphi)/(1-\varphi)^4$, where η is the relative viscosity of the suspension and φ the fraction of the total volume occupied by the dispersed substance, represents very closely the relation between the volume of the solute and the viscosity of the solution. The formula was found to hold for solutions of sugars, glycogen, caseinogen, and rubber up to 50% concentration. In the case of sugar solutions and sulphur suspensions, the volume of the solute calculated from viscosity values agrees with the actual volume of the substance in the dry state; for solutions of rubber in benzene, the values of φ calculated from viscosity measurements fit the equation for the osmotic pressure. W. ROBSON.

Viscosities of solutions in ethyl and methyl alcohols. H. GOLDSCHMIDT and H. AARFLOT (Z. physikal. Chem., 1926, 122, 371—382).—The viscosity changes caused by the addition of water to solutions

of electrolytes in methyl and ethyl alcohols and the neutralisation of acids dissolved in these solvents by bases of different strengths have been investigated. Measurements of the viscosities of mixtures of the two alcohols and of the densities of the various solutions have also been made. The results obtained are correlated with existing conductivity data.

L. F. GILBERT.

Viscosities of aqueous solutions of organic substances and the polymerisation of water. H. M. CHADWELL (J. Amer. Chem. Soc., 1926, **48**, 1912—1925).—The densities and viscosities at 25° of solutions of some organic substances in water and of water in methyl and ethyl acetates and in benzene are recorded. Although the organic constituents are all less viscous than water, the solutions have a viscosity higher than that of water. The viscosity decrease due to depolymerisation of water is thus more than balanced by other effects causing a viscosity increase; the volume of the solute molecules is probably the most important factor in this respect. The effect may also be due to the volume contraction accompanying solution, since the contraction and the viscosity increase run parallel. For normal solutes, the larger the molecular volume the larger is the relative viscosity. S. K. TWEEDY.

Viscosities of univalent salts of the higher fatty acids in aqueous solution. K. S. MALIK (Kolloid-Z., 1926, **39**, 322—324; cf. Yajnik and Malik, A., 1925, ii, 779).—The viscosities of aqueous solutions of sodium stearate and sodium palmitate at 60°, 70°, and 80° and at various concentrations have been employed to test whether or not the viscosities of colloidal electrolytes follow any of the known equations connecting viscosity and concentration. The observed values of η_s/η_0 are considerably higher than those calculated from Einstein's formula, but the logarithmic formula of Arrhenius is applicable to aqueous solutions of the salts in question. Calculation of the Arrhenius constant shows that it deviates strongly from the value 0·01086 given by Arrhenius and increases with increasing concentration of the salt. L. L. BIRCUMSHAW.

Theory of concentrated solutions. I. Theory of hydration. II. Thermodynamics of binary mixtures. W. HEITLER (Ann. Physik, 1926, [iv], **80**, 629—671).—I. The assumption of complete dissociation of moderately concentrated solutions of strong electrolytes and the recognition of inter-ionic attractions have been admitted to require solvation or hydration in one form or another before they can provide agreement with experience. The molecules of solvent and solute are regarded as arranged on a space lattice. Such deviations from the laws obtaining in dilute solutions as can be traced to solvation arise from certain positions in the sphere of influence of a solute molecule being forbidden to solute, but not to solvent molecules. The solvent molecules held fast in this way undergo no permanent change which would differentiate them from the rest of the medium. Interchanges of solvent molecules are permitted only with other solvent molecules and not with the solute. The forces operating between solute and solvent exert no direct influence on the medium, their effect being confined to distortion of the space lattice.

II. The assumption of oriented molecules is carried over to a quite distinct investigation of the potential energy between two molecules, and of the statistical conditions under which molecules of the same or of different kinds occur in close proximity one to another. A simple set of expressions is advanced which accounts in a fairly complete manner for the behaviour of a mixture, *e.g.*, its vapour pressure and miscibility. The heat of mixing is the important quantity for the theoretical reasoning, and the experimental data agree in respect of sign and order of magnitude with the results deduced.

A note is appended on the velocity of sound in mixtures as a basis for the determination of characteristic frequency in relation to the specific heat.

R. A. MORTON.

Milner and Debye theories of strong electrolytes. G. SCATCHARD (Phil. Mag., 1926, [vii], **2**, 577—586).—It is claimed, contrary to the conclusions of Pike and Nonhebel and of Nonhebel and Hartley (A., 1925, ii, 1061), that Debye's theory of strong electrolytes offers a better representation of observed facts than does Milner's. It is shown that, when the complete Debye equation is applied to an electrolytic cell comprising a methyl alcohol solution of hydrochloric acid, the *E.M.F.* values obtained are more constant and show less deviation from the experimental values over a much wider range of concentration than those given by Milner's formula.

A. E. MITCHELL.

Milner and Debye theories of strong electrolytes. G. NONHEBEL and H. HARTLEY (Phil. Mag., 1926, [vii], **2**, 586—587; cf. preceding abstract).—The authors disagree with Scatchard in the choice of the constant E_0 in the equation $E=E_0-0{\cdot}1183 \log cf$ and claim that the value assumed is incompatible with that obtained by a simple extrapolation without resource to any theory. An extract from a communication from Milner indicates that the numerical differences obtained in the application of the two theories are attributable to greater approximations in the Milner as compared with the Debye formula.

A. E. MITCHELL.

Inter-ionic attraction theory of ionised solutes. VI. Ionisation and ionisation constants of moderately ionised acids. M. S. SHERRILL and A. A. NOYES (J. Amer. Chem. Soc., 1926, **48**, 1861—1873).—The ionisation constants of moderately ionised acids are calculated from the relation $\alpha=\Lambda/\Lambda_\infty$, where Λ_∞ is corrected for the mobility decrease of the ions due to their higher concentration. This decrease is calculated as a function of ionic strength (Lewis and Randall, A., 1921, ii, 427). The method is used to calculate the first ionisation constants of orthophosphoric acid (0·0083 at 18°) and sulphurous acid (0·012 at 25°), and the second ionisation constant of sulphuric acid (0·0115 at 25°). S. K. TWEEDY.

Recognition and separation of mono- and polybasic acids. E. WEITZ (Leopoldina, 1926, **2**, 160—165).—The solubility in water of the ammonium salts of monobasic organic and inorganic acids increases in

presence of ammonia, whereas the solubility of the ammonium salts of polybasic acids diminishes (cf. Gaus, A., 1901, ii, 7). The increase is probably due to the formation of ammonia–ammonium salt complexes; the decrease is probably a salting-out effect which occurs when no complexes are formed. Graphical representation of the results indicates that ammonium persulphate and perchlorate both form solutions with ammonia which are completely miscible with water. The polymerised hydrofluoric, iodic, and periodic acids behave as polybasic acids; dithionic and persulphuric acids behave as monobasic acids. The two last-named acids can probably be regarded as "doubly monobasic," $(HSO_3)_2$ and $(HSO_4)_2$, there being two separate nuclei in the molecule, each containing an acid hydrogen atom. Only two dibasic organic acids behave thus, viz., *iso*phthalic and benzene-*m*-disulphonic acids. It is considered that the reciprocal influence of the carboxyl groups in *iso*phthalic acid is much smaller than in the normally-behaving phthalic and terephthalic acids, so that their rôles are separately conserved and the acid reacts as doubly monobasic. The order of increase of solubility in ammonia solution of some ammonium salts of monobasic and doubly monobasic acids places the latter in a series identical with Hantzsch's series for the strength of acids (A., 1923, ii, 475), which is compatible with the view that the solubility increase is due to complex formation. Mixtures of ammonium salts of monobasic acids with a similar salt of a polybasic acid may often be separated by passing ammonia into the aqueous solution of the mixture, when the latter salt is precipitated. S. K. Tweedy.

Electrolytic dissociation of dibasic acids. III. Determination of the second dissociation constant from solubility experiments. E. Larsson (Z. anorg. Chem., 1926, **155**, 247—254).—A method is described for calculating the second dissociation constant of dibasic acids from the solubility of a sparingly soluble monobasic acid in the solution of a neutral salt of the dibasic acid. The applicability of the method to oxalic, succinic, fumaric, *l*-malic, and *d*-tartaric acids is shown; the results are in good agreement with those obtained electrometrically. M. Carlton.

Foundation of the expressions $r_{(n)}$ and $r_{(p)}$. A. F. Richter (Biochem. Z., 1926, **174**, 271—275; cf. Giribaldo, *ibid.*, 1925, **163**, 8; A., 1925, ii, 325).—Theoretical. E. C. Smith.

Equilibrium point in the reaction between iodic and hydrobromic acids. A. Schwicker and G. Schay (Z. physikal. Chem., 1926, **122**, 482—484).—The mass law constant corresponding with the equilibrium $2IO_3' + 10Br' + 12H^{\cdot} \rightleftarrows I_2 + 5Br_2 + 6H_2O$, as determined from analyses of the equilibrium products of mixtures of solutions of iodic and hydrobromic acids, is, approximately, $1{\cdot}6 \times 10^{-22}$ at 25°. L. F. Gilbert.

Electrolyte-free water-soluble proteins. VI. Acid glutins and the Donnan equilibrium. W. Pauli and H. Wit (Biochem. Z., 1926, **174**, 308—332).—Measurement of the conductivity and hydrogen-ion concentration of solutions of glutin in hydrochloric acid solutions shows that with increasing concentration of the acid, the activity and conductivity of glutin hydrochloride increase to a maximum in 0·01—0·03*N*-hydrochloric acid. Similar results are obtained with sulphuric acid. At the maximum point, the apparent normality of the glutin hydrochloride also diminishes, which would indicate that hydrogen ions previously attached to the protein are again liberated by further addition of acid. The anomaly indicates the inapplicability of the Debye–Hückel formula to this system. The effect of doubling the glutin concentration is to increase the maximal normality 100%, but the maximal activity and conductivity increase only 97%. At constant temperature and hydrogen-ion concentration the charge on the glutin particle appears to be independent of the glutin concentration, and at the point of optimal activity of the hydrochloride and of the sulphate the charge carried is of the same magnitude. The viscosity curves follow those of conductivity very closely, the maxima being, however, at a slightly higher p_H. The difference is probably due to the greater degree of hydrolysis resulting from the higher temperature at which the viscosity measurements were made. E. C. Smith.

Volatility and dissociation of borax. H. V. A. Briscoe and P. L. Robinson (Nature, 1926, **118**, 374),—The volatility of borax is well established (cf. Kolthoff, this vol., 813). Moreover, a silica muffle used for the fusion of borax acquired an interior enamel produced by interaction with the volatilised material (cf. A., 1925, ii, 619). A. A. Eldridge.

Dissociation pressures and the transition point of sodium sulphate decahydrate. M. Matsui, E. Nanai, S. Ito, and S. Fukushima (J. Soc. Chem. Ind. Japan, 1926, **29**, 161—167).—The dissociation pressures of sodium sulphate decahydrate (mixed with the anhydrous salt) were measured dynamically by Partington's method (J.C.S., 1911, **99**, 467). The curve of log p against $1/T$ was fairly concordant with that of Baxter and Lansing (A., 1920, ii, 286). The dew-point method of Cumming (J.C.S., 1909, **95**, 1772) was also used. The transition point, established from the intersection of the two curves so obtained, was 32·6°, in agreement with Cohen's result (Z. physikal. Chem., 1897, **14**, 53). The transition point was also estimated by the tensimeter (32·33°) and the dilatometer (32·436°), respectively. K. Kashima.

Decomposition of the double ammonium fluorides of the elements of the titanium group. S. Hartmann (Z. anorg. Chem., 1926, **155**, 355—357).—The thermal dissociation in a current of nitrogen of the double compounds of the fluorides of hafnium, titanium, and zirconium with ammonium fluoride has been examined. The hafnium compound decomposes rather more readily than the zirconium compound (cf. Wolter, A., 1908, ii, 701), whilst the titanium salt occupies an intermediate position. The solubility of the last named in 0·125*N*-hydrofluoric acid is 1·344 g.-mol./litre. Scandium ammonium fluoride commences to decompose at 125°. R. Cuthill.

Heat of vaporisation and surface tension. W. HERZ (Z. anorg. Chem., 1926, **155**, 348—350).—The empirical relation $\log L = a + b \log \gamma$, where L is the heat of vaporisation, γ is the surface tension, and a and b are constants, is valid for water and certain organic liquids over considerable temperature ranges. Near the critical point irregularities occur.

R. CUTHILL.

Association of liquids and a relation between the capillary constant and the heat of vaporisation. N. DE KOLOSOVSKI (Z. anorg. Chem., 1926, **155**, 351—354).—Combination of the relation between the molecular elevation of the b. p. and the b. p. previously deduced (this vol., 791) from van 't Hoff's expression for the molecular elevation and Kistiakovski's rule (A., 1913, ii, 837) leads to the conclusion that the ratio between the heat of vaporisation of a liquid and its capillary constant is independent of the temperature, and for non-associated liquids has the value 18. This is confirmed by an examination of available data, liquids known to be associated giving values for the constant as high as 36.

R. CUTHILL.

Free energy of hydration of ions. T. J. WEBB (Proc. Nat. Acad. Sci., 1926, **12**, 524—529).—Previous calculations of the heat of hydration of gaseous ions (Born, A., 1920, ii, 527; Latimer, this vol., 684) assume that the ions are spherical and that the heat of hydration is equal to the energy obtained from discharging the spheres in a vacuum and subsequently charging them in water. Consideration of the principles involved leads to the conclusions that: (*a*) the above energy change is a free energy change; (*b*) the dielectric constant of a molecular medium is not constant in the immediate vicinity of an ion (Sack, this vol., 456); (*c*) the effective ionic radius is that of the cavity surrounding the ion, in which there are no solvent molecules; (*d*) there is an energy change due to the compression of the solvent in the vicinity of the ion. Starting from these premises, the effective radii and the free energies of hydration of a number of ions have been calculated, details of the calculations, which are rather complex, being promised later. The following numbers represent the free energies of hydration (Cal./mole) of the ions of sodium, bromine, hydrogen, and zinc, respectively, the figures in parentheses being the corresponding effective radii in Å.: 99·0, (1·505); 66·2, (2·38); 250, (<0·5); 525, (1·04). The effective radii are in general about 0·5 Å. higher than those given by Wasastjerna (A., 1923, ii, 593) and Bragg (Proc. Roy. Inst., 1925, **24**, III, 614) for the radii of ions in crystals. The electron affinities of the halogens have been calculated.

J. S. CARTER.

Residual affinity and co-ordination. II. Thermal measurements on derivatives of cupric iodide. G. T. MORGAN, S. R. CARTER, and W. F. HARRISON (J.C.S., 1926, 2027—2030).—The heat of formation of *ethanolbisethylenediamminocupric iodide*, $[Cu,2en,Et{\cdot}OH]I_2$, m. p. 235° (decomp.), has been found to be +55·28 cal., whilst the heats of formation of the mono- and di-hydrated bisethylenediamminocupric iodides (cf. this vol., 1027) are +53·78 and 55·55 cal., respectively. The heat of formation of the monoalcoholate from cuprous iodide, iodine, and aqueous ethylenediamine is +22·12 cal.

C. J. STILL.

Heats of mixing of water with acetic acid and *iso*propyl alcohol. C. SANDONNINI (Atti R. Accad. Lincei, 1926, [vi], **4**, 63—68).—The heat evolved on mixing water with acetic acid at 15—18° rises to a maximum of 48 cal. per 100 g. of mixture at 14% acetic acid and falls through zero above 34% to a minimum of −192 cal. at 79%. The specific heats and heats of mixing for water–*iso*propyl alcohol mixtures have been determined. The former are always higher than those calculated by the mixture rule, and the latter have a maximum of 871 cal. per 100 g. of mixture at 25% alcohol, falling to a minimum of −32·5 cal. at 95%.

E. W. WIGNALL.

Moving-boundary method for determining transference numbers. V. Constant current apparatus. D. A. MACINNES, I. A. COWPERTHWAITE, and K. C. BLANCHARD (J. Amer. Chem. Soc., 1926, **48**, 1909—1912; cf. A., 1925, ii, 542).—An automatic device is described which maintains a constant current through a moving-boundary transport apparatus, the resistance in which increases steadily during a determination. The transport number of the cation in 0·1*N*-potassium nitrate solution at 25° is 0·5122 (cf. Denison and Steele, A., 1906, ii, 68).

S. K. TWEEDY.

Theory of electrolytic ions. XXXIII. Transport numbers of anions of chlorides of sodium, potassium, and lithium and of potassium bromide and iodide. R. LORENZ and J. WESTENBERGER (Z. anorg. Chem., 1926, **155**, 273—280; cf. this vol., 910).—From Lorenz's theory of transport numbers it is shown that if the transport number of the anion of an electrolyte is plotted against the cube root of the concentration, the resulting graph will be in general, not a straight line, but a hyperbolic curve. This is shown to be true by an examination of published data for the above salts.

R. CUTHILL.

Oxidation-reduction. IX. Potentiometric and spectrophotometric study of *meri*quinones of the *p*-phenylenediamine and benzidine series. W. M. CLARK, B. COHEN, and H. D. GIBBS (U.S. Pub. Health Ser., 1926, Suppl. 54, 1—61).—Potentiometric measurements have been conducted on solutions containing *meri*quinones (partly oxidised products), the normal potentials being calculated by means of a relation developed on the assumption that a *meri*quinone consists of equal parts of oxidant and reductant. The curves connecting electrode potential with p_H of solution show points of inflexion corresponding with the first and second ionic dissociations of reductants, the dissociation constants being evaluated for both oxidants and reductants. Calculations of the concentrations of *meri*quinone are found to be roughly in accord with spectrophotometric and colorimetric methods of determination. The instability of the systems in question causes great experimental difficulties.

C. H. D. CLARK.

Oxidation-reduction. X. Reduction potentials in cell suspensions. R. K. CANNAN, B. COHEN, and W. M. CLARK (U.S. Pub. Health Ser., 1926, Suppl. 55, 1—34).—Measurements of the electrode reduction potentials of suspensions of rat liver, dried yeast and tissue, and of growing bacterial cultures indicate that these may be advantageously employed in place of reversible indicators in the study of biological reactions. The unimolecular reduction of methylene-blue by yeast-cell suspensions is decreased by washing the cells. Possibly on account of the influence of hydrogen donators within the cells, the reduction of methylene-blue by boiled, washed yeast-cells is accelerated by glutathione.

P.D. measurements made with bacterial cultures using platinum electrodes are somewhat uncertain. In considering the problem of oxygen catalysts in biochemistry, it appears that account should be taken of a characteristic oxidation-reduction potential of aërated suspensions of different cultures in the region marked by the indophenol indicators.

The cell suspensions, in the absence of oxygen, develop increasing negative potential, and a small quantity of active material appears to be continuously produced from a large reserve. The behaviour of cell-enzymes in presence of oxidants such as methylene-blue is discussed in the light of electronic theories.

C. H. D. CLARK.

Increase in potential when some reducing agents are added to certain oxidants. W. S. HENDRIXSON (Proc. Iowa Acad. Sci., 1924, **31**, 319—323).—When added to dilute solutions of oxidants in sulphuric acid, ferrous iron seems to cause a rise in the potential of electrodes by accelerating the rate at which they take up their full charges. In all but extremely dilute solutions, the electrodes reach saturation after several hours, and normal falls of potential are then produced by the addition of ferrous sulphate. Other similar instances are cited.

CHEMICAL ABSTRACTS.

Location of the *E.M.F.* in a photo-active cell containing a fluorescent electrolyte. C. C. MURDOCK (Proc. Nat. Acad. Sci., 1926, **12**, 504—508).—Goldmann (Ann. Physik, 1908, [iv], **27**, 449) has reported that it is necessary to illuminate the actual boundary between electrode and solution in order to obtain an *E.M.F.* from the arrangement, Pt|fluorescent solution|Pt. Grumbach, on the other hand (A., 1923, ii, 108; 1925, ii, 549), has pointed out that by working with very dilute solutions (Goldmann used concentrated alcoholic solutions of dyes) an effect may be obtained merely by illuminating a portion of the solution. He concludes that the total *E.M.F.* when the electrode is illuminated is due in part to an effect in which the electrode is not directly concerned. In the present investigation, measurements have been made using Goldmann's type of semi-transparent film-electrodes on glass and a 3% solution of rhodamine-B in absolute alcohol, under such conditions that the solution flows along the surface on which the electrode is deposited and may be illuminated through, or on either side of, the electrode. An effect is observed even when the only light falling on the electrode is that due to scattering and fluorescence in the neighbouring illuminated solution; the maximum effect is observed when the electrode is completely bathed in light. The results indicate that the photo-active *E.M.F.* in the Goldmann cell is partly due to some action of light on the electrolyte in which the electrode plays no active part. There is, however, a residual *E.M.F.* for the production of which illumination of the electrode appears to be necessary.

J. S. CARTER.

Determination of the velocity constant of a unimolecular reaction. E. A. GUGGENHEIM (Phil. Mag., 1926, [vii], **2**, 538—543).—It is shown that if $v_1 \ldots v_i \ldots v_n$ are n readings taken at times $t_1 \ldots t_i \ldots t_n$ and $v_1' \ldots v_i' \ldots v_n'$ those for times $t_1+\tau \ldots t_i+\tau \ldots t_n+\tau$, then the gradient of the straight line obtained by plotting $\log_{10}(v_i'-v)$ against t will be $-k \log_{10} e$, where k is the velocity constant. This method of determining k is considered to be more accurate than the usual one depending on an extrapolated value of v_∞, since each measurement is employed once only.

A. E. MITCHELL.

[Radiation] theory of the velocity of chemical reactions. J. K. SYRKIN (Z. anorg. Chem., 1926, **155**, 317—322).—It is shown that the application of the quantum theory to the theory of the velocity of chemical reactions necessitates the assumption that the cross-section of the light quanta is proportional to the square of the wave-length, which conflicts with the results of light absorption measurements. Further, the decomposition of sulphuryl chloride (Smith, A., 1925, ii, 876) takes place at a higher speed than is accounted for by the radiation theory.

R. CUTHILL.

Interaction (coaction) of molecules in termolecular reactions. H. J. PRINS (Chem. Weekblad, 1926, **23**, 389—393).—The conditions under which termolecular reactions may occur are considered, and it is concluded that such reactions will occur most readily where one or more pairs of molecules are able to form intermediate aggregates in virtue of their electronic configurations. S. I. LEVY.

Expression of equations of chemical actions as functions of time. S. G. BOTELLA (Anal. Fís. Quím., 1926, **24**, 400—412).—The equations showing the relationship between the quantity of substance changed and the time in homogeneous unilateral reactions may be transformed into direct functions of the time. For example, the ordinary equation $dx/dt=k(a-x)$ becomes $x=a(1-e^{-kt})$. The equations obtained in different cases are discussed. In the case of multimolecular reactions, solutions are possible only when the reacting substances are initially present in equal concentration. From the author's analysis, it would appear that the hypothesis of Damianovitch (Anal. Asoc. Quím. Argentina, 1913, **1**, 289) that there are alternate maxima and minima in the reaction velocity–time curve for bimolecular and higher reactions is untenable. G. W. ROBINSON.

Kinetics of the reaction between iodic and hydriodic acids. E. ABEL and F. STADLER (Z. physikal. Chem., 1926, **122**, 49—80).—The above reaction has been investigated at 25°, since Dushman's

work (A., 1904, ii, 718) appears to be marred by numerous errors. The complicating effect of the triiodide equilibrium is eliminated by keeping the solution saturated with iodine, or else removing it as it is formed with benzene, and in this way the reaction is found to be quinquemolecular. In sulphuric acid solutions, the velocity constant decreases with increasing concentration of acid, or on addition of potassium sulphate, whilst in solutions containing acetic acid–acetate mixtures change in the concentration has very little effect. This effect can be accounted for in a satisfactory manner by applying Brönsted's theory of reaction velocity, but not by means of the classical theory of electrolytic dissociation. The experimental results have also been worked out in terms of Debye's theory of strong electrolytes.

R. CUTHILL.

Decomposition of formaldehyde by heat. S. S. MEDVEDEV and E. A. ROBINSON (Trans. Karpov Inst. Chem., 1925, No. 4, 117—125).—The effect of temperature, duration of heating, and concentration of formaldehyde in gaseous mixtures on the speed of decomposition of formaldehyde ($H{\cdot}CHO=CO+H_2+$ 22,300 cal.) was determined by passing dry carbon dioxide first through a U-tube containing trioxymethylene at various temperatures from 60° to 150°, and then through an electrically heated glass tube. Undecomposed formaldehyde was absorbed by water and determined iodometrically. For a formaldehyde concentration of 39·7% and time of heating 29 sec., the amounts of decomposition were: 450°, 10·21; 500°, 38·6; 550°, 44·7; 600°, 87·5; 650°, 94·9; 700°, 97·6%. The quantity of formaldehyde decomposed thus increases proportionally to the rise of temperature; it also increases proportionally to the time of heating. The original concentration of formaldehyde in the gaseous mixture, however, has no influence on the rate of decomposition; apparently the reaction takes place only at the surface of contact of the formaldehyde with the glass tube. The catalytic effect is apparently peculiar to glass, since the increase of surface by introducing asbestos or aluminium phosphate does not perceptibly increase the decomposition.

CHEMICAL ABSTRACTS.

Reaction velocity of chloral hydrate and permanganate. A. BUZAGH (Mat. Term. Ertesito, 1923, **40**, 134—143).—Between 30° and 40°, no chloroform is formed, and the progress of the reaction can be followed by determining the decrease in concentration of the permanganate. The reaction is bimolecular. The velocity constants are: 0°, 0·00116; 8·5°, 0·00254; 25°, 0·0112; 40°, 0·0474; 60°, 0·289.

CHEMICAL ABSTRACTS.

Velocity of hydrolysis of acid anhydrides in aqueous solutions of electrolytes and non-electrolytes. R. SZABÓ (Z. physikal. Chem., 1926, **122**, 405—413).—The velocity of hydrolysis of acetic and succinic anhydrides in presence of various acids, salts, and non-electrolytes in iso-osmotic solution was determined by means of an optical (refractive index) method at 14° and 18°. The viscosities of the solutions were also determined. In the presence of salts the velocity coefficient is roughly inversely proportional to the viscosity. The hydrolysis of acetic and succinic anhydrides is catalysed by hydrogen and acetate ions, and by hydrogen and succinate ions, respectively. The influences of the non-electrolytes employed are specific.

L. F. GILBERT.

Velocity of hydrolysis of the simplest formals. A. SKRABAL and H. H. EGER (Z. physikal. Chem., 1926, **122**, 349—356).—The velocities of the acid (hydrogen chloride) hydrolysis of the formals of ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *iso*butyl, and *sec.*-butyl alcohols in dilute aqueous solutions have been measured at 25°. A connexion between chemical constitution and velocity coefficient is apparent which is similar to that obtaining for the acid saponification of the esters.

L. F. GILBERT.

Velocity of hydrolysis of mixed acyl acetals. A. SKRABAL and I. SAWIUK (Z. physikal. Chem., 1926, **122**, 357—370).—The velocities of the acid and alkaline hydrolysis of the diacetate, dipropionate, and acetate–propionate of ethylidene glycol have been measured. The velocity coefficients of the last-named compound are approximately the arithmetic means of those of the other compounds (cf. A., 1924, ii, 666). The factors underlying the velocity of hydrolysis of acetals, generally, are analysed, and systematic numerical relations between the influences of the chemical groups concerned are deduced.

L. F. GILBERT.

Kinetics of the change of halogenalkylamines into heterocyclic compounds. IV. H. FREUNDLICH and H. KROEPELIN (Z. physikal. Chem., 1926, **122**, 39—48; cf. A., 1914, ii, 448; 1922, ii, 489).—The affinity constant of bromoethylamine is found by conductivity measurements to be 3×10^{-7} at 20°. There is in neutral aqueous solution no true equilibrium between this substance and dimethyleneimine hydrobromide owing to side reactions of the latter. The velocity constants for the closing of the chain have been determined for γ-bromopropylamine, and for ζ-chloro- and ζ-bromo-hexylamine. Of the monobromoalkylamines with 2—6 carbon atoms and having the bromine atom at the opposite end of the chain to the amino-group, δ-bromobutylamine has the greatest constant, and γ-bromobutylamine the least. The closing of the chain of bromoethylamine in alkaline aqueous solutions of methyl alcohol has also been investigated. This reaction is of the first order, the velocity constant, k, decreasing with increasing concentration of methyl alcohol, although there is no simple relation between the two magnitudes except for alcohol concentrations below 25%, when $\log_e k$ is a linear function of the alcohol concentration in g.-mol. %.

R. CUTHILL.

Calcination rates of limestone. W. A. GILKEY. —See B., 1926, 707.

Rate of solution of aluminium. M. CENTNERSZWER and W. ZABLOCKI (Z. physikal. Chem., 1926, **122**, 455—481).—The rate of solution of aluminium in dilute hydrochloric acid has been determined from measurements of the amount of hydrogen evolved. An induction period, during which the rate of solution increases, is followed by normal solution. It is considered that metallic aluminium is covered with a passive film which is continuously

transformed to active metal (in the presence of acid), and of thickness, as determined from the surface area and the volume of hydrogen evolved during the induction period, 30—84 μ. The (normal) velocity coefficient is increased by increasing the concentration of hydrochloric acid; this is explained on the hypothesis that the reaction occurs between aluminium atoms and non-ionised molecules of acid. Other data presented as confirming this hypothesis are: (*a*) The addition of chlorides increases and the addition of sulphates and nitrates decreases the velocity of solution (in consequence of the decrease and increase, respectively, of the ionisation of hydrochloric acid thereby caused); (*b*) the velocity of solution in other acids (sulphuric, hydrobromic, hydriodic) has no apparent connexion with their degrees of ionisation. The values of the temperature coefficients for the reaction between aluminium and hydrochloric acid, and the slight effect of the velocity of rotation of the aluminium samples on the rate of solution are also in accordance with the view that the reaction velocities measured are those of the reaction which takes place directly between acid and metal, and are not determined by the velocity of diffusion of the acid through an adhering liquid film. The rate of solution of aluminium in alkali increases as the concentration of the alkali decreases, and can thus be explained as a reaction between metallic aluminium and hydroxyl ions.

L. F. GILBERT.

Kinetics of carbon dioxide assimilation. J. HOLLUTA (Z. physikal. Chem., 1926, **121**, 429—438).—Theoretical. An expression for the rate of assimilation of carbon dioxide by plants is derived which agrees approximately with Warburg's results (Naturwiss., 1925, **13**, 985). Stoicheiometric equations for the assimilation processes in presence of light are advanced which accord with Einstein's law of photochemical equivalence. L. F. GILBERT.

Kinetic laws of homogeneous catalysis. E. SPITALSKY (Z. physikal. Chem., 1926, **122**, 257—286).—A development of a theory of the velocity of catalysed reactions, including enzyme reactions, starting from the assumption that the function of the catalyst is to convert the substrate into a reactive form by combining with it. The rate of the reaction as a whole is proportional to the concentration, not of the substrate, but of the intermediate compound, which is formed by a practically instantaneous reversible reaction to an extent dependent on the affinity of the catalyst for the substrate. It is then deduced by application of ordinary mass law considerations that the apparent order of such a catalysed reaction is determined by the magnitude of this affinity, and may have any value from zero upwards either integral or fractional. This apparent order bears in general no relation to the true order of the reaction as a whole, which is that of the relatively slow decomposition reaction of the intermediate compound. Change of temperature may, by altering the equilibrium concentration of the intermediate compound, change the apparent order of the reaction. Hydroxyl or hydrogen ions, if present, may influence the reaction either by entering into the composition of the intermediate compound, or by affecting the rate of its decomposition. In the former case, but not in the latter, the order of the reaction may be changed. A further complication is the possibility of the formation of more than one compound of catalyst and substrate, which differ in stability, in which case the reaction velocity may pass through one or more maximum or minimum values. If at the same time hydroxyl or hydrogen ions play a part, the phenomenon of an optimum concentration may manifest itself. When several catalysts are present together, the state of affairs is very complex, as the substrate may form compounds with two or more of the catalysts simultaneously, as well as with each of them singly. In such a case, therefore, there is usually no question of a simple addition of the effects of the individual catalysts. The above theory is supported by numerical examples. R. CUTHILL.

Catalytic action of copper ions in the evolution of hydrochloric acid [from chloride solutions evaporated with sulphuric acid]. J. BODNÁR and L. E. ROTH (Z. angew. Chem., 1926, **39**, 1101—1102).—Prolonged evaporation of a 1% solution of sodium chloride with sulphuric acid on the water-bath removes only 10—15% of the hydrochloric acid; addition of 1 mg. of copper sulphate per 100 c.c. causes, under the same conditions, a loss of more than 80% of the chlorine. This action is much more marked if the heating is carried out in a Kjeldahl flask over a small gas flame; in 3 hrs., no hydrochloric acid is lost from a mixture of 10 c.c. of 10% sodium chloride solution and 5 c.c. of concentrated sulphuric acid when copper is absent, whilst the whole of the hydrochloric acid disappears in the presence of 1 mg. of copper sulphate. A. R. POWELL.

Oxidation of oxalic acid by iodic acid. O. WARBURG (Biochem. Z., 1926, **174**, 497—499).—The effect of hydrocyanic acid on the oxidation of oxalic acid by iodic acid is not the destruction of the catalytic action of iron by the formation of un-ionised cyanide, but the destruction of the catalytic action of iodine, formed in the first stage of the reaction, by conversion into cyanogen iodide. E. C. SMITH.

Transfer of excited energy from ozone to hydrogen and nitrogen. A. C. GRUBB (Science, 1926, **63**, 460—462).—When a mixture of hydrogen and nitrogen (3 : 1 vols.) is passed over a platinum anode at which ozonised oxygen is being rapidly evolved, ammonia is produced. In the dark, the yield is decreased but slightly; no light phenomena were observed. Neither nitrate nor any decomposition product of the aqueous sulphuric acid electrolyte was found. The formation of ammonia probably results from cumulative excitation of the second kind. The ozone appears to transfer its excitation to the hydrogen. A. A. ELDRIDGE.

Decomposition of potassium chlorate in the presence of iron oxide. F. E. BROWN and W. C. O. WHITE (Proc. Iowa Acad. Sci., 1924, **31**, 291—298).—The minimum temperature (approx. 324°) for the "spontaneous decomposition" of potassium chlorate in the presence of ferric oxide does not vary between the limits $32KClO_3 : Fe_2O_3$ and $KClO_3 : 4Fe_2O_3$. The

history of the ferric oxide affects the temperature, which is lowered by water of hydration. The presence of ammonium chloride in the ferric oxide may lower the temperature to 120°. CHEMICAL ABSTRACTS.

Mechanism of poisoning of catalysts. N. BAKH (Trans. Karpov Inst. Chem., 1925, No. 4, 11—40).—An examination of the reaction $NaH_2PO_2+H_2O=NaH_2PO_3+H_2$, catalysed by palladium, to determine whether definite or infinitesimal quantities of poisons are required to destroy the activity of the catalyst. With palladium-black, the quantities of various poisons required for 1 mol. of palladous chloride were: potassium cyanide, 1·75 mol., mercuric chloride, 1 mol., thiocarbamide, 1·5 mol., quinine hydrochloride, more than 10 mols. Alkaloids generally have a relatively weak action on catalysts. The poisoning effect is due partly to chemical combination between the palladous chloride and the poison, yielding a compound which cannot be reduced by sodium hypophosphite, and partly to adsorption on the surface of the palladium-black. With colloidal palladium, the effect is one of adsorption, and again a definite number of mols. of the poison is required to saturate the surface of the palladium particles and paralyse their action.
CHEMICAL ABSTRACTS.

Catalytic action considered as a surface action. G. R. LEVI and R. HAARDT (Gazzetta, 1926, **56**, 424—429).—The first quantitative results relating catalytic action to the surface of unit mass of catalyst are obtained by the help of a new method of regulating the size of platinum particles.

The edge of particles, supposed cubic, obtained by reducing potassium chloroplatinate in acid solution at 60° with aluminium is found to have the value 5·05 μμ (cf. this vol., 365). When such preparations are heated for 12 hrs. at different temperatures from 60° to 215°, particles of edge ranging from 5·05 to 20·3 μμ can be obtained, with corresponding surface per 0·01 g. decreasing from 5588 to 1385 cm.^{2}

Using this mass of platinum to catalyse the decomposition of hydrogen peroxide solutions, it is found that the extent of the decomposition in unit time increases with increasing surface up to a limiting value; above 3000 cm.^{2}/0·01 g., increase of surface has comparatively little effect. E. W. WIGNALL.

Mechanism of the inhibition of the respiration model by hydrogen cyanide. H. BLASCHKO (Biochem. Z., 1926, **175**, 68—78).—The inhibition by hydrogen cyanide of a number of oxidations in presence of charcoal can be reversed by simple physical means. Thus inhibition of the oxidation of leucine is completely reversed by washing for a short time. Inhibition of the process of decomposition of hydrogen peroxide by palladium is also readily reversible, whereas palladium-black, poisoned by hydrogen cyanide, only regains its power to oxidise alcohol extremely slowly. The oxidation of lævulose in alkaline phosphate solution (p_H 8·3) is inhibited by hydrogen cyanide, but recovers on evacuating and warming until the solution attains p_H 4·5. P. W. CLUTTERBUCK.

Catalytic dissociation of carbon monoxide. J. CLEMINSON and H. V. A. BRISCOE (J.C.S., 1926, 2148—2154).—The reaction $2CO \rightarrow CO_2+C$ does not proceed at or below 400° when glass forms the only contact surface. The minimum temperatures of reaction with various catalysts were: carbon, 300°; magnesium oxide, 290°; aluminium oxide, 250°. The percentages of carbon monoxide decomposed in presence of alumina were: 5·35 at 250°; 8·50 at 270°; and 12·25 at 290°. S. K. TWEEDY.

Activation of the inert varieties of calcium sulphate. P. BUDNIKOV (Compt. rend., 1926, **183**, 387—388).—The influence of various catalysts on the rate of rehydration of gypsum calcined between 600° and 700° for 4 hrs. has been examined. Of the substances examined, sodium and potassium hydrogen sulphates in concentrations of 1 and 2%, respectively, were the most effective. Plasters made with their aid from material passing 4900 meshes/cm.^{2} set in 15 min. and acquired tensile strengths of 49 and 50 kg./cm.^{2}, respectively, after 21 days. The variation of tensile strength with time is not regular. In the case of sodium hydrogen sulphate, the strength reaches a maximum after 8 hrs., and the subsequent variation is attributed to recrystallisation of the plaster. A. E. MITCHELL.

Inhibiting agents in the oxidation of unsaturated organic compounds. O. M. SMITH and R. E. WOOD.—See B., 1926, 713.

Catalytic oxidation of methane. II. S. S. MEDVEDEV (Trans. Karpov Inst. Chem., 1925, No. 4, 117—125).—On oxidation of methane by atmospheric oxygen with tin phosphate or borate as catalyst the activity of the latter soon decreases, whereas hydrogen chloride originally present is gradually removed. It is now shown that in the absence of hydrogen chloride only about .2% of the methane was decomposed, whereas the addition of 4% of hydrogen chloride to the gaseous mixture caused the decomposition of 27% of methane. Small concentrations of hydrogen chloride afford formaldehyde as the principal product; larger concentrations give chiefly carbon monoxide. The best catalyst for the production of formaldehyde is a mixture of aluminium, tin, and iron phosphates at 600°; employing a mixture of methane, 58·2; oxygen, 26·1; nitrogen, 8·7; hydrogen, 6·96; hydrogen chloride, 0·13%, half of the total quantity (6·7%) of methane decomposed is converted into formaldehyde, by way of the liberation of chlorine and chlorination of the methane. The maximum oxidation of formaldehyde by excess of hydrogen chloride is reached when 90% of the methane is converted into carbon monoxide. The yield of formaldehyde is increased by operating in a series of communicating tubes. Thus, in a 2-tube system the total yield of formaldehyde was 8·8% of the amount of methane taken, 15% of the methane remaining undecomposed, but by passing the mixture through the system twice, the yield of formaldehyde was increased to 15·2%.
CHEMICAL ABSTRACTS.

Catalysis by metallised silica gel. L. H. REYERSON and K. THOMAS (Third Colloid Symposium Monograph, 1925, 99).—Silica gel, prepared by

Patrick's method, was evacuated by heating for 2 hrs. at 250°, cooled to −20°, saturated with hydrogen, and metallised with 0·1*M*-solutions of platinum, palladium, copper, gold, or nickel. Using palladium and platinum, ethylene was hydrogenated to the extent of 60·9% at 0°, 98·9% at 95°; with nickel at 180°, 50—60% of phenol was converted into *cyclo*hexanol; aniline gave ammonia and, probably, phenylamino-*cyclo*hexane. The metallised gels also catalyse oxidations. CHEMICAL ABSTRACTS.

Cathodic sputtering. A. VON HIPPEL (Ann. Physik, 1926, [iv], **80**, 672—706).—The particles of metal emitted in the process of cathode sputtering consist primarily and predominantly of uncharged atoms. The particles collide with electrons and ions in the glow discharge, and excitation follows with consequent emission of the resonance lines of the cathode metals. This forms the basis of a quantitative method for the spectroscopic measurement of vapour pressure. An independent check was provided by a method for determining the vapour pressure from the thickness of the metallic film. The somewhat elaborate conditions which must be observed in the spectroscopic work are discussed in detail. The decisive experiments were carried out with a cadmium cathode; zinc and silver were used in confirmatory work. A special absorption effect was observed in the sputtering of cadmium. R. A. MORTON.

Cathodic sputtering. II. A. GÜNTHER-SCHULZE (Z. Physik, 1926, **38**, 575—588; cf. this vol., 693).—The sputtering of silver in hydrogen has been investigated at a cathode fall of potential of 1000 volts. The quantity of silver sputtered was found to be inversely proportional to the distance apart of the electrodes and also to the pressure of hydrogen; it had been shown previously (*loc. cit.*) to be directly proportional to the fall of potential. A table of values for other metals, and for oxygen as well as hydrogen, is given. E. B. LUDLAM.

Electrolytic separations by graded potentials. A. LASSIEUR (Bull. Soc. chim., 1926, [iv], **39**, 1167—1183; cf. A., 1925, ii, 159, 711),—Zinc can be deposited from an acid solution of p_H between 4·5 and 5·0, or from a solution of the complex cyanide, provided that only sufficient potassium cyanide is added to form the complex salt. To separate tin from zinc, hydrochloric acid and hydroxylamine hydrochloride are added to the solution, and the tin is separated with an auxiliary potential of 480 millivolts; the zinc is then deposited from the neutral cyanide solution. Cadmium is separated from zinc by using an auxiliary potential of 650 millivolts and a solution of such acidity that it turns thymol-blue a cherry-red. A method is described of separating antimony, copper, lead, tin, cadmium, and zinc. R. CUTHILL.

Electrolysis of sodium chromate with a mercury cathode. I. STSCHERBAKOV and O. ESSIN.—See B., 1926, 712.

Theory of photophoresis. G. HETTNER (Z. Physik, 1926, **37**, 179—192).—Mathematical. A theory is developed in which photophoresis is regarded as a radiometer effect and its variation with pressure is calculated. The photophoretic force for molecules of the usual radius has a maximum at a pressure about equal to that of the atmosphere, and this explains the fact that change of pressure in this region of pressure makes very little difference. For higher pressures, the theory is in satisfactory agreement with experiment. Independence of the effect on the nature of the gas is also satisfactorily accounted for within certain limits. E. B. LUDLAM.

Photolysis of gaseous hydrogen iodide in the light of the quartz mercury-vapour lamp. M. TRAUTZ and B. SCHEIFELE (Z. wiss. Phot., 1926, **24**, 177—216).—In the direct light of a quartz lamp running at 350 watts and at 10—50 cm. distance, hydrogen iodide, in a quartz cell at ordinary or decreased pressure, is decomposed at a velocity which can be readily measured manometrically. The reaction proceeds to complete decomposition of the hydrogen iodide; no decomposition in the dark or re-formation of hydrogen iodide in the light was observed. The active wave-lengths lie between 300 and 220 μμ. The reaction velocity is apparently independent of temperature up to 120°, of the interposition of hydrogen, water, or 10% copper sulphate solution between the lamp and the cell, of the admixture of nitrogen with the hydrogen iodide, and of placing a palladium mirror behind the cell. The reaction velocity falls if a glass plate or an iodine filter is interposed between lamp and cell, if iodine vapour is mixed with the gas, and apparently if an excess of hydrogen is added. At first, the reaction velocity is for a time constant; it then falls to that of a unimolecular reaction (constant$=10^{-4}$ sec.$^{-1}$ for lamp at 15 cm. distance), and later falls again. These results indicate that at the start the active wave-lengths are strongly absorbed, but in the region where the unimolecular law is followed, only very weakly so. An approximate value is derived for the absorption constant. The falling off in reaction velocity towards the end of the reaction starts the sooner the higher is the initial pressure of hydrogen iodide and the lower the temperature. At 120°, it is very small. The initial reaction velocity appears to increase approximately proportionally to the initial concentration of hydrogen iodide. Exposure to the neon arc lamp or to a high candle-power Wotan lamp resulted in practically no decomposition. Simultaneous exposure to these sources and to the mercury lamp gave results no different from those obtained with the mercury lamp alone. The effect of varying the distance of the lamp from the cell was in accordance with the inverse square law. There is no appreciable absorption of the active wave-lengths by air. W. CLARK.

Photosensibility of selenium. I. A. KASARNOVSKII (Trans. Karpov Inst. Chem., 1925, No. 4, 93—97).—The potential of selenium becomes more positive on illumination; hence the difference between illuminated and non-illuminated selenium cannot be ascribed to the formation of a new allotropic modification, and the cause of the photosensibility is not a reversible photochemical reaction. CHEMICAL ABSTRACTS.

Photochemical properties of chromates and of other compounds. J. PLOTNIKOV and M. KARSCHULIN (Z. Physik, 1926, **38**, 502—510).—The fact that the authors had found a different position for the maximum absorption for chromated collodion from that found by Eder (this vol., 774) is attributed to different medium and the difference in the distribution of energy in the light from different sources. The spectrographic and photochemical absorption have been determined for potassium and ammonium chromates, iron carbonyl, iodine, potassium iodide, solutions of iodine in potassium iodide, and bromine. The photochemical absorption in each case shows a position of maximum effect, but the slope of the rise and fall varies. Mixtures of chromate and potassium iodide show the photochemical absorption of each substance separately. E. B. LUDLAM.

Decomposition of potassium manganioxalate in plane polarised, circularly polarised, and ordinary light. J. C. GHOSH and A. N. KAPPANNA (J. Indian Chem. Soc., 1926, **3**, 127—140; cf. this vol., 366).—The molecular extinction coefficients of potassium manganioxalate in aqueous solution have been measured for all visible regions of the spectrum. It absorbs light throughout, but a maximum occurs at about 4870 Å. Beer's law is obeyed for light of 5790 Å. The decomposition of the salt is a unimolecular reaction which proceeds spontaneously in the dark, the temperature coefficient of the velocity being 2·13 per 10°. White light more than trebles the velocity of decomposition, its effect having a temperature coefficient of 1·30 per 10°. Ordinary and plane polarised light are equivalent in effect, but circularly polarised light has a slightly greater efficiency. Addition of oxalic acid to the solution diminishes the velocity of the reaction. From measurements of the velocity in approximately monochromatic light (4880 Å.) it is calculated that one molecule is decomposed per quantum of energy absorbed. G. M. BENNETT.

Thiocarbamide fog and a suggested explanation of a Waterhouse reversal. S. O. RAWLING.—See B., 1926, 721.

Photographic solarisation. H. BELLIOT.—See B., 1926, 721.

Nature of optical sensitisation and desensitisation. H. H. SCHMIDT.—See B., 1926, 772.

Optical sensitisation. II. Water as sensitiser. G. KÖGEL and A. STEIGMANN.—See B., 1926, 772.

Effect of concentration of sensitiser on speed, and fog corrections. S. E. SHEPPARD.—See B., 1926, 773.

Primary action of photochemical absorption. Optical photochemical transformation of radiation. G. KÖGEL (Z. wiss. Phot., 1926, **24**, 216—218).—*o*-Nitrobenzaldehyde is very sensitive to light, whereas *o*-nitrocinnamaldehyde is insensitive, and the reactivity of the aldehyde group as oxygen acceptor is very different in the two substances. The action of the aldehyde group is not specific, either chemically or photochemically. The *o*-nitro-groups in *o*-nitrobenzaldehyde and also in *o*-nitrocinnamaldehyde are exceedingly sensitive to light in presence of pyrogallol. The influence of substituents disappears under these conditions. The fact that such an apparently inactive substance, exposed with or without acceptor, shows the same spectral absorption, indicates that the thermal, photoinactive absorption and the photochemically active absorption are alike. The light does not undergo a particular form of absorption determined by the presence of conditions favourable to a particular chemical reaction. It is possible that the light-sensitive group can be influenced favourably by some internal change (*e.g.*, loosening of linkings) brought about by the presence of an acceptor, without requiring any specifically different absorption of light. W. CLARK.

Yield of photochemical reactions with complex light in comparison with that obtained with the component lights. III. M. PADOA and N. VITA (Gazzetta, 1926, **56**, 375—388).—A more detailed account of work previously published (this vol., 584). In the bromination of cinnamic acid the amount of reaction does not at first decrease to the extent demanded by the inverse square law as the light source is removed. To the previous results are added those of an experiment in which hydriodic acid is decomposed by white light and by the same filtered through an ammoniacal copper sulphate solution. In the latter case, although only 47% of the luminous energy was available, the iodine formed was increased by 25%. E. W. WIGNALL.

Lithium chlorate. L. BERG (Z. anorg. Chem., 1926, **155**, 311—316).—Attempts to prepare the hemihydrate of the above salt described by previous authors (cf. Bruhl, A., 1913, ii, 50) have been fruitless, but a *hydrate*, $3LiClO_3,H_2O$, which loses its water when heated to about 55°, has been obtained. R. CUTHILL.

Action of organic compounds on sodium hydrogen sulphate. H. B. DUNNICLIFF and S. SINGH (J. Indian Chem. Soc., 1926, **3**, 91—100; cf. J.C.S., 1920, **117**, 649; 1923, **123**, 476).—Trisodium hydrogen disulphate, like the corresponding ammonium salt, is unaltered by prolonged extraction with alcohol or ether. Methyl, ethyl, *n*-propyl, *iso*propyl, butyl, *iso*butyl, and *iso*amyl alcohols extract sulphuric acid from sodium hydrogen sulphate with diminishing readiness, leaving ultimately a residue of trisodium hydrogen disulphate. Acetone and methyl ethyl ketone have a similar effect, but aromatic ketones are without action. Since the hydrogen sulphates of sodium and ammonium thus yield two thirds of their acidity to solvents, a termolecular formula is suggested for them, whilst the hydrogen sulphates of potassium, rubidium, and cæsium, which are not affected by solvents, are regarded as unimolecular. The relative effects of alcohol and acetone on sodium hydrogen sulphate do not appear to be connected with their relative electrical conductivities. The specific conductivities are recorded for three series of mixtures of alcohol with acetone, alcohol with ether, and acetone with ether, respectively. G. M. BENNETT.

Reaction between sodium phosphates and calcium hydroxide. H. HAYASHI and M. MATSUI (J. Soc. Chem. Ind. Japan, 1926, **29**, 175—179; cf. *ibid.*, 1925, 101).—Trisodium phosphate was agitated with calcium hydroxide for a definite time, the solution filtered, and its content of phosphoric acid determined. The amount of reaction increases with time and rise of temperature. At 70—90° and 1·5 hrs., the quantity of calcium hydroxide necessary to precipitate the total phosphoric acid is 137·5% of the theoretical. Trisodium phosphate is more active than disodium hydrogen phosphate towards calcium hydroxide; the amount of the calcium hydroxide is almost constant so long as the amount of free alkali is less than 20%. When the solution of sodium phosphates is diluted with water, the amount of the calcium hydroxide above given is sufficient up to a dilution of 150%. The action of quick, slaked, and weathered limes is in the above order. The grains of lime passing through 90—150-mesh sieves give the same result. When other salts are present, the reaction is retarded owing to increasing solubility of calcium phosphate formed. K. KASHIMA.

Separation of copper and ferrous sulphates by crystallisation. G. AGDE and H. BARKHOLT.—See B., 1926, 707.

Displacement of cæsium and of rubidium by iron. L. HACKSPILL and H. PINCK (Compt. rend., 1926, **183**, 388—389).—The previous work of Hackspill and Grandadam (A., 1925, ii, 233), where it was shown that, in a vacuum and at temperatures where the vapour pressure of the alkali metal was of the order of 1 cm., iron would readily displace sodium and potassium from most of their salts, has been extended to a number of salts of cæsium and rubidium with corresponding results. A. E. MITCHELL.

Gold from mercury. E. DUHME and A. LOTZ (Wiss. Veröff. Siemens-Konz., 1926, **5**, 128—151).—See this vol., 930.

Reported transmutation of mercury into gold. M. W. GARRETT (Proc. Roy. Soc., 1926, **A**, **112**, 391—406).—Unsuccessful experiments designed to bring about the above transformation are described (cf. Miethe and Stammreich, this vol., 367, 493).
S. K. TWEEDY.

Alleged preparation of artificial gold from mercury. A. SMITS (Z. anorg. Chem., 1926, **155**, 269—272)—A reply to Haber, Jaenicke, and Matthias (this vol., 699) giving a detailed account of the purification of lead from the last traces of mercury.
M. CARLTON.

Constitution of cement. E. JÄNECKE.—See B., 1926, 747.

Fluoborates. H. FUNK and F. BINDER (Z. anorg. Chem., 1926, **155**, 327—332)—The *fluoborates* of the following metals have been prepared by the action of the acid on the carbonate or oxide: magnesium, $Mg(BF_4)_2,7H_2O$; calcium, $Ca(BF_4)_2,5H_2O$; strontium, $Sr(BF_4)_2,4H_2O$; zinc, $Zn(BF_4)_2,6H_2O$; cadmium, $Cd(BF_4)_2,6H_2O$; mercury, $HgBF_4,HF,H_2O$. The *ferrous* salt, $Fe(BF_4)_2,6H_2O$, is obtained by the action of the acid on the metal. R. CUTHILL.

Saccharification of starch by Japanese acid clay. K. KOBAYASHI and K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1926, **29**, 95—102).—On heating starch with Japanese acid clay under pressure, the former is hydrolysed and consequently saccharified. The saccharifying action of the clay towards starch is proportional to the "acidity" of the clay as previously shown to be the case with the inversion of sucrose. An aqueous extract of the acid clay gives no acid reaction, but on contact with water, a double layer is formed on its surface. Thus the acid clay itself is not an acidic substance, but an arrangement may result on the surface of the clay as in the scheme: $H^+[OH(\text{acid clay})]^-$. The saccharifying action of Japanese acid clay seems to be due to these "bound hydrogen ions." K. KASHIMA.

Carbon suboxide. O. DIELS (Z. angew. Chem., 1926, **39**, 1025—1028).—A summary of the properties and reactions of the suboxide C_3O_2, from which the conclusions are reached that the allene formula OC:C:CO is most probable and that other oxides, C_4O_2, C_5O_2, etc., may be found capable of existence.
S. I. LEVY.

Reduction of carbon monoxide under ordinary pressure. A. JAEGER and H. WINKELMANN.—See B., 1926, 698.

Complex iodates of tin and antimony. P. RÂY and S. N. RAY (J. Indian Chem. Soc., 1926, **3**, 110—117).—Stannic chloride reacts with iodic acid in dilute nitric acid solution to produce *dihydroxytetraiodatostannic acid*, $[Sn(IO_3)_4(OH)_2]H_2$, and if the iodic acid be in large excess *stanni-iodic acid*, $[Sn(IO_3)_6]H_2$, which on ignition leaves a residue containing iodine. The *potassium*, *ammonium*, *rubidium*, *cæsium*, *sodium*, and *lithium* salts of this acid are obtained by the action of iodic acid on the corresponding chlorostannates. Addition of potassium iodate to a solution of potassium chlorostannate, however, yields a *double* compound of the composition $K_2Sn(IO_3)_6,K_2Sn(IO_3)_5OH$, and stannic chloride with an excess of sodium iodate in dilute nitric acid solution gives a precipitate of *tetrahydroxydi-iodatostannic acid*, $[Sn(IO_3)_2(OH)_4]H_2$. Antimony pentachloride and an excess of iodic acid furnish *trihydroxytri-iodatoantimonic acid*, $[Sb(IO_3)_3(OH)_3]H$.
G. M. BENNETT.

Double sulphates of the rare-earth and alkali metals. VI. (Cerous) cerium and potassium sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1926, [vi], **4**, 5—10).—In the system A–B–H_2O, where A is $Ce_2(SO_4)_3$, and B is K_2SO_4, the following crystalline *double sulphates* are obtained at 25°: $A,B,2H_2O$, stable in a solution containing 4·9—6·7% A, 0·07—0·04% B; $2A,3B,8H_2O$, obtained from solutions in which A and B have equal concentrations; $2A,9B$ and $A,5B$, stable in solutions of 1·2—5·0 and 5—9% B, respectively.
E. W. WIGNALL.

Heterogeneous lead complexes. Iodothiocyanates. A. C. VOURNAZOS (Z. anorg. Chem., 1926, **155**, 241—246; cf. this vol., 371).—The following salts have been prepared: *Sodium* and

potassium lead iodothiocyanate, $X_4[PbI_2(SCN)_4],2H_2O$; on electrolysis the complex ion yields lead iodide, sulphur, and the compound $(SCN)_2$. *Ammonium lead iodothiocyanate*, $(NH_4)_8[PbI_2(SCN)_8],2H_2O$; white needles readily decomposed by moisture. *Lead aniline iodothiocyanate*, $[PbI_2,C_6H_5\cdot NH_2,HSCN]$, yellow, exists in amorphous and prismatic forms. *Lead guanidine iodothiocyanate*, $PbI_2,CH_5N_3,HSCN$, yellow.

M. CARLTON.

Action of stannous chloride on nitrous acid. F. RASCHIG (Z. anorg. Chem., 1926, **155**, 225—240).—Reduction of nitrous acid by excess of stannous chloride gives a solution which decolorises more potassium permanganate than can be accounted for by the excess of stannous chloride determined by iodine. This is due to formation of hydroxylamine and hyponitrous acid. These together with nitrous oxide are the only products of the reduction. The course of the reaction is explained thus: $O{:}N\cdot OH+2H=O{:}NH+H_2O$, the nitroxyl then yielding nitrous oxide. Then $HO\cdot N{:}O+2H=HO\cdot NH\cdot OH$ (dihydroxyammonia, which is known to be an intermediate product), which breaks up into hyponitrous acid and on reduction gives hydroxylamine.

The ratio of amount of hydroxylamine formed to hyponitrous acid changes with the conditions of experiment. About 90% of nitrous acid is converted into nitrous oxide, and the remaining 10% into hyponitrous acid and hydroxylamine. This division, which is unaffected by external conditions, is suggested to be due to difference in constitution of nitrous acid: $H\cdot N<^{O}_{O}$ and $HO\cdot N{:}O$. The acid solution of hyponitrous acid is only slowly neutralised by sodium hydroxide and is stable in acid and alkaline solution. If, however, the acid solution be suddenly made alkaline by soda, it is at once decomposed. If the neutralisation be slowly performed, the acid is only partly decomposed. The stability of hyponitrous acid is greatest in strongly acid or strongly alkaline solution.

M. CARLTON.

Sulphurous acid and its salts. III. Behaviour of sulphurous acid towards thiosulphuric acid. F. FOERSTER and R. VOGEL (Z. anorg. Chem., 1926, **155**, 161—191).—The following equilibria arise when thiosulphate solutions are acidified: $S_2O_3''+H^{\cdot}\rightleftharpoons HS_2O_3'$; $HS_2O_3'\rightleftharpoons HSO_3'+S$; *i.e.*, $S_2O_3''+H^{\cdot}\rightleftharpoons HSO_3'+S$ (i), since (*a*) hydrogen sulphite as well as thiosulphate on acidification gives sulphur and sulphurous acid; thus hydrogen sulphite dissolves sulphur, forming thiosulphate, with increasing acidification; (*b*) changes in concentration of the substances taking part in the equilibrium move this in the direction anticipated, *e.g.*, increasing the hydrogen-ion concentration moves the equilibrium to the right, increasing the hydrogen sulphite concentration (and consequently diminishing the hydrogen-ion concentration) moves it to the left, sometimes so far that separation of sulphur ceases; (*c*) in thiosulphate solutions which are decomposed by such weak acids as acetic, formic, etc., the equilibrium constant expected from the law of mass action, $[S_2O_3'']/[H^{\cdot}][HSO_3']=k$ is about 13×10^{-2} at 11°.

That the addition of excess of sulphurous acid to thiosulphate solutions gives yellow solutions without separation of sulphur was already known. The assumption that these solutions contain free colloidal sulphur is here disproved, the colour being rather due to complex anions in which sulphur dioxide is co-ordinately linked through thiosulphate ions. The possibility of such anions existing is suggested by the existence of numerous other similar anions (cf. Ephraim, this vol., 36) and was confirmed by preparations of the yellow solid compounds $K_2S_2O_3,SO_2$ and $Rb_2S_2O_3,SO_2$, which are prepared from anhydrous thiosulphate and liquid sulphur dioxide at low temperatures and give clear yellow solutions with a little water in which the equilibrium $S_2O_3''+SO_2\rightleftharpoons[S_2O_3(SO_2)]''$ (ii) exists. Among the components of this equilibrium the following may also exist: $H^{\cdot}+HSO_3'\rightleftharpoons H_2SO_3\rightleftharpoons SO_2+H_2O$ (iii); thus by sufficiently acidifying the thiosulphate solutions, equilibrium (ii) can set in, with consequent yellow coloration of the solution. Since by appearance of (ii) the concentration of thiosulphate is diminished, the separation of sulphur in (i) may be hindered by sufficiently lowering the hydrogen-ion concentration or increasing hydrogen sulphite or sulphurous acid concentration, *i.e.*, the ratio of the concentration of sulphurous acid to that of thiosulphate must be somewhat greater than 1. According to (ii), it must be the greater the smaller is the thiosulphate concentration; such solutions are yellow and remain completely clear for some time.

Solutions (i) and (ii) are subject to slow change, during which polythionates are formed; penta- or tri-thionates are formed: $5S_2O_3''+6H^{\cdot}\longrightarrow 2S_5O_6''+3H_2O$ (iv) or $S_2O_3+4HSO_3'+2H^{\cdot}\longrightarrow 2S_3O_6''+3H_2O$ (v); also $S_5O_6''+HSO_3'\longrightarrow S_4O_6''+S_2O_3''+H^{\cdot}$ (vi); $S_4O_6''+HSO_3'\longrightarrow S_3O_6+S_2O_3''+H^{\cdot}$ (vii) give rise to the anions of all three polythionic acids on conversion of the components of (i) and (ii).

Since the trithionate anion is not stable: $S_3O_6''+H_2O\longrightarrow SO_4''+S_2O_3''+2H^{\cdot}$ and thiosulphate and hydrogen ions again enter in equilibrium (i), finally the acidified thiosulphate solution passes into sulphate, sulphur, and sulphurous acid. Moreover, in the thiosulphate solution coloured yellow by sulphur dioxide, this, and with it the yellow coloration, can completely vanish before large amounts of free sulphur are precipitated from the trithionate.

M. CARLTON.

Precipitation of metals from non-aqueous solutions. I. R. MÜLLER, A. SCHIMKE, and N. M. FARMAKIDES (Z. anorg. Chem., 1926, **155**, 333—347).—Experiments have been made on the precipitation of nickel by zinc from solutions of nickel chloride in 98% ethyl alcohol. The rate of the reaction is much greater than in aqueous solution, and very little nickel hydroxide is formed (cf. Kremann, Angelberger, Bakalarz, Röhrich, and Stöger, A., 1923, ii, 866), but the deposit of metal is chiefly in the form of a loose powder. The reaction is more nearly complete at 18° than at 77°, and the completeness also increases with increase of the ratio of metallic zinc to nickel in solution, and with increase in the surface of the zinc, *i.e.*, it is greater with the zinc in the form of

turnings than in the form of small cylinders. Examination of the turnings after the reaction has occurred shows them to consist of a nucleus of unchanged zinc, surrounded by a thin layer of zinc–nickel alloy, with a powdery external coating of nickel.

R. CUTHILL.

Palladium oxides. G. R. LEVI and C. FONTANA (Gazzetta, 1926, **56**, 388—396; cf. Levi and Tacchini, A., 1925, ii, 424).—*X*-Ray examination shows that partial oxidation of finely-divided palladium gives a mixture of the metal and palladous oxide, PdO, no suboxide Pd_2O being formed (cf. Wöhler and König, A., 1905, ii, 722). Palladous oxide has a face-centred tetragonal symmetry; for the unit cell of 4 molecules $a=4{\cdot}23$, $c=5{\cdot}20$ Å., axial ratio 1·23, $d_{calc.}$ 8·73, $d_4^{20}{}_{obs.}$ 8·70. From the hydrated peroxide, PdO_2,xH_2O, no *X*-ray spectrum was obtained.

E. W. WIGNALL.

Hydrogen from water-gas. R. M. EVANS and W. L. NEWTON.—See B., 1926, 698.

Preparation of a chromium carbonyl through the intermediary of a magnesium compound. A. JOB and A. CASSAL (Compt. rend., 1926, **183**, 392—394).—When an ethereal solution of magnesium phenyl bromide is added drop by drop to an ether–benzene suspension of chromium chloride in the presence of carbon monoxide maintained below 10°, hydrolysis results. On distilling away the ether, white crystals of chromium carbonyl, $Cr(CO)_6$, are obtained. The carbonyl is not attacked by hot or cold potassium hydroxide, hydrochloric acid, concentrated sulphuric acid, or bromine, but is attacked immediately by cold fuming nitric acid, forming chromic nitrate and evolving carbon monoxide.

A. E. MITCHELL.

Preparation of colloidal lead. W. STENSTRÖM and M. REINHARD (J. Biol. Chem., 1926, **69**, 607—612).—Repetition and extension of the work of Bell (Brit. Med. J., 1926, i, 537) shows that more concentrated and more stable lead sols can be obtained by the use of potassium chloride as a stabilising salt instead of the calcium chloride recommended by him.

C. R. HARINGTON.

Iodometric determination of chloride and the determination of chloride, bromide, and iodide in the presence of cyanide. R. BERG (Z. anal. Chem., 1926, **69**, 1—15).—For the determination of iodide alone or in the presence of chloride and bromide, the solution is treated with 5—10 c.c. of *N*-potassium cyanide solution and then with phosphoric, sulphuric, or hydrochloric acid to an acidity of 30, 15, or 5—10%, respectively. After addition of starch solution, the liquid is titrated at the rate of one drop per second with 0·1*N*-potassium bromate; the reaction is as follows: $HBrO_3+3HI+3HCN=3CNI+HBr+3H_2O$. Bromide is determined in the absence of iodide by a somewhat similar process; the solution is treated with 10 c.c. of *N*-potassium cyanide and hydrochloric acid is added until the solution contains 10—15% of free acid. The 0·1*N*-bromate solution is dropped in slowly until no further yellow colour appears, a mixture of 20 c.c. of 10% aniline hydrochloride and 10 c.c. of 0·1*N*-potassium bromide solutions is added, followed by 1 g. of potassium iodide, and the liberated iodine is titrated with thiosulphate. The aniline solution destroys the excess of bromate required to complete the reaction: $HBrO_3+2HBr+3HCN=3CNBr+3H_2O$, and the iodine liberated is a measure of the cyanogen bromide formed in the first reaction thus: $3CNBr+6HI=3I_2+3HBr+3HCN$. The reaction between chloride and bromate in the presence of cyanide takes place only in a strongly acid solution according to the equation $HBrO_3+2HCl+3HCN=2CNCl+CNBr+3H_2O$. The following is the procedure: The chloride solution (20—30 c.c.) is treated with an excess of *N*-cyanide solution (measured exactly) in a glass-stoppered flask and 1 : 1-sulphuric acid is added to 30% acidity, whereby the temperature rises to 30—35°. Without cooling, 8—10 times the requisite quantity of *N*-bromate solution is added and the flask is kept at 35—40° for 20—30 min. After cooling, the contents of the flask are poured in a thin stream into a mixture of 50—100 c.c. of 10% aniline hydrochloride solution, 10 c.c. of *N*-potassium bromide solution, and 20 c.c. of 1 : 1-sulphuric acid. The content of cyanogen chloride and bromide formed is then determined by adding potassium iodide (1% of the total volume) and titrating the liberated iodine with thiosulphate. A blank test must be carried out on the same volume of cyanide solution as that used in the analysis, as most samples of commercial cyanide contain small amounts of chloride. For the determination of the three halogens in the presence of each other the iodide is determined by the first of the above methods, and the same solution is used for the determination of the sum of the bromide and iodide by the second method, allowance being made for the bromide introduced in the first titration. In a second portion of the original solution, the sum of the three halides is determined by the third procedure.

A. R. POWELL.

Determination of small quantities of halogen compounds, especially of perchloric acid. F. KÖNIG (Z. anal. Chem., 1926, **68**, 385—387).—Perchloric acid is reduced in sulphuric acid solution by boiling with excess of titanous sulphate, the excess oxidised cautiously in the cold by means of ammonium persulphate, and the filtered solution titrated with mercuric nitrate, using sodium nitroprusside as indicator, and employing the Tyndall effect to observe the end-point. Small quantities of bromides, chlorides, cyanides, and thiocyanates may be titrated directly with mercuric nitrate if heavy metals are absent.

S. I. LEVY.

Combined determination of oxygen absorbed and albuminoid ammonia in sewages and effluents. J. W. H. JOHNSON.—See B., 1926, 726.

Analysis of sulphur dioxide in presence of excess of air. E. D. RIESS and L. E. CLARK.—See B., 1926, 706.

Decomposition of standard sodium thiosulphate solutions. E. SCHULEK (Z. anal. Chem., 1926, **68**, 387—397).—Hydrogen sulphide is nearly

always present in thiosulphate solutions, and may be determined colorimetrically by addition of sodium hydroxide and lead acetate. No suitable method was found for the detection of traces of sulphite. Tetrathionate was determined by the cyanide method, and was always present. Bacteriological examination showed the presence of some twenty different kinds of bacteria; several of these were selected, and cultures added to sterile thiosulphate solutions. Two found to be most powerful caused considerable diminutions in the values of the solutions, with relatively high development of sulphide and tetrathionate.

S. I. LEVY.

Rapid electrolytic determination of tellurium by the use of a reduced potential. J. LUKAS and A. JÍLEK (Chem. Listy, 1926, **20**, 396—403).—For the determination of tellurium in a preparation of the element, 0·3 g. is dissolved by heating with 3 c.c. of concentrated sulphuric acid. The cold solution is diluted with water and 0·5 g. of tartaric acid added, followed by ammonia until neutral to methyl-red; the solution is acidified with 3 g. of malonic acid, cooled to 18°, treated with 10 g. of ammonium sulphate, diluted to 120—150 c.c., and electrolysed with a rotating anode in a platinum dish at 2 volts. The current, originally 0·03—0·09 amp., falls to 0·004—0·007 amp. when the tellurium is completely deposited. Without shutting off the current, the deposit is washed first with water, then with alcohol, dried at 100°, and weighed; it should possess a bright, silvery lustre and be firmly adherent to the dish.

A. R. POWELL.

Electrometric titration of phosphates. S. BODFORSS (Svensk Kem. Tidskr., 1925, **37**, 296—300; from Chem. Zentr., 1926, I, 1675—1676).—The volumetric method for the determination of phosphates by titration with a solution of a uranyl salt in presence of acetic acid may be followed potentiometrically. In presence of a small amount of a quadrivalent uranium salt, the equilibrium $UO_2^{\cdot\cdot}+4H^{\cdot}-2F \rightleftarrows U^{\cdot\cdot\cdot\cdot}+2H_2O$ is set up and the potential E of the solution with respect to a platinum electrode is given by the formula $E=E_0+RT/2F \cdot \log_e [UO_2^{\cdot\cdot}][H^{\cdot}]^4/[U^{\cdot\cdot\cdot\cdot}]$. If the hydrogen-ion concentration remains constant, the potential is altered only when an excess of uranyl salt has been added. In order to obtain a sharper end-point, it is advisable to add quinol or potassium ferrocyanide. A more suitable method is to use a mercury electrode and add a known amount of mercurous sulphate, the titration being carried out at 70°. The fall in voltage at the end-point is extremely sharp. On further addition of uranyl salt, the voltage, after passing through a minimum, increases to an almost constant value. This behaviour is interpreted as resulting from the equilibrium relations involved in the formation and dissociation of a complex mercury uranyl phosphate. The accuracy is of the order 0·3—0·4%.

J. S. CARTER.

Titration of hypophosphorous acid and its salts with permanganate. I. M. KOLTHOFF (Z. anal. Chem., 1926, **69**, 36—38).—Titration of neutral or alkaline hypophosphite solutions with permanganate at 100° usually yields slightly high results owing to partial decomposition of the permanganate (cf. Köszegi, this vol., 702). The reaction between hypophosphite and permanganate in acid solution at the ordinary temperature is slow and does not go to completion unless a large excess of the oxidising agent is present. Accurate results may be obtained, however, as follows. The hypophosphite solution is acidified with half its volume of 4*N*-sulphuric acid, treated with about 2·5 times the theoretical quantity of 0·1*N*-permanganate, and set aside over-night in a stoppered flask. The excess of permanganate is then determined iodometrically. A blank test on the reagents is necessary in order to allow for any slight decomposition of permanganate. A similar procedure serves for the determination of various organic acids, alcohols, and sugars, whilst hydrazine and sulphites may be titrated similarly, using an alkaline solution for the oxidation process.

A. R. POWELL.

Effect of cellulose on arsenic determinations. T. J. WARD (Analyst, 1926, **51**, 457).—If glass wool be substituted for filter-paper and cotton wool in the purifying tube of the Gutzeit or Marsh arsenic apparatus, the life of the tube may be considerably prolonged, since the small amounts of acid present in the evolved gas cause cellulose to retain arsenic.

D. G. HEWER.

Destruction of filter-papers by alternate oxidising agents applied to quantitative analysis. R. POGGI and A. POLVERINI (Atti R. Accad. Lincei, 1926, [vi], **4**, 55—57).—Cellulose is oxidised completely by treatment alternately with nitric acid, *d* 1·5, and with hydrogen peroxide (15 vol.-%) intermediately evaporating to dryness. This enables filter-papers to be used and destroyed in the gravimetric determination of arsenic, in which they may not be burnt.

E. W. WIGNALL.

Detection and colorimetric determination of carbon monoxide. H. KAST and H. SELLE (Gas- u. Wasserfach, 1926, **69**, 812—815).—A review of the various methods that have been proposed for the detection and determination of carbon monoxide is given together with comparative data on their limits of sensitivity. Accurate quantitative results are obtained, in the absence of other combustible gases, only by the combustion method. With practice, however, the time required to produce a reaction in a solution of ammonium chloropalladite or of ammoniacal silver nitrate gives a sufficiently accurate idea of the concentration of the gas in the air. Thus, the first visible darkening is noticed in 350 sec., when 100 c.c. of air containing 0·05% of carbon monoxide are shaken with 10 c.c. of the chloropalladite solution, and in 80 sec., when shaken with 10 c.c. of the silver nitrate solution; the corresponding figures for air containing 0·4% of the gas are 50 and 20 sec., and, for air containing 1·6%, 20 and 7 sec., respectively.

A. R. POWELL.

Carbonic acid content of distilled water and its determination. I. M. KOLTHOFF (Chem. Weekblad, 1926, **23**, 381—384).—The high values found by titration for the carbonic acid concentration of distilled water are due to improperly neutralised indicators and the slowness with which distilled water

reaches equilibrium with the atmosphere. Water freshly distilled from tap water contains a large excess of carbon dioxide, which does not escape for more than a week; if washed air is drawn through the water, equilibrium is attained in 10 hrs. By calculation, the p_H after titration corresponding with the theoretical concentration of carbon dioxide, $1{\cdot}5\times10^{-5}M$, should be about 8·0; hence the indicator must be neutralised to this point before use. With these conditions, and keeping the flasks and vessels used always full of liquid, the theoretical value is confirmed by titration. This value is so small that it may be neglected for most purposes. S. I. Levy.

Determination of potassium in the presence and absence of sulphate. M. A. Hamid (Analyst, 1926, **51**, 450—453).—The cobaltinitrite method is recommended for general use in the determination of potassium, both in the presence and absence of sulphate. The precipitate was found to be dipotassium monosodium cobaltinitrite monohydrate, $K_2NaCo(NO_2)_6,H_2O$. Results by this method agree well with those by the perchloric acid method in the absence of sulphate, whilst the perchloric acid method breaks down in the presence of sulphate.

D. G. Hewer.

Gravimetric determination of sodium. E. Crepaz (Annali Chim. Appl., 1926, **16**, 219—224).—Blanchetière's method (A., 1923, ii, 579; Kling and Lassieur, Chim. et Ind., 1924, **12**, 1012) involving the precipitation of sodium magnesium uranyl acetate is too inexact for the determination of sodium, but when applied in the presence of alcohol it is of value in the detection of small quantities of sodium in the presence of potassium and magnesium.

R. Sansone.

Detection of small amounts of silver and cadmium. W. Geilmann (Z. anorg. Chem., 1926, **155**, 192—198).—Silver in ores is detected by microchemical reactions as rubidium silver gold chloride, $Rb_6Ag_2Au_3Cl_{17}$. In 0·1—0·2 g. of ore, 0·005% of silver may be recognised. Cadmium is detected by the dry method of Biewend (Berg- und Hüttenmännische Ztg., 1902, **61**, 401). In zinc ores, 0·002% of cadmium could be detected. In glasses, the limit of detection is 0·0002%. M. Carlton.

Absence of mirror formation in Vortmann's method of separating silver and lead. G. Vortmann (Analyst, 1926, **51**, 456—457; cf. this vol., 262).—To ensure the absence of a mirror, the liquid should not be heated above 70—80°, and only a slight excess of ammonia should be added after addition of tartaric acid or ammonium tartrate. D. G. Hewer.

Determination of total alkalinity in presence of alkaline earths. R. Bürstenbinder.—See B., 1926, 742.

Determination of zinc as acetate. (Miss) H. J. Ravenswaay (Chem. Weekblad, 1926, **23**, 375).—Zinc acetate on ignition gives widely varying proportions of residue, and cannot be quantitatively converted into oxide. When the substance is heated in a distilling flask, the condensate collected below 100° contains zinc. S. I. Levy.

Oxidation of manganese to permanganate. Application to the determination of manganese. A. Travers (Ann. Chim., 1926, [x], **6**, 56—86).—A more detailed account of work already published (this vol., 704).

Colorimetric determination of ferric iron and some remarks on known reactions. H. W. van Urk (Pharm. Weekblad, 1926, **63**, 1101—1107; cf. Heczko, B., 1926, 791).—In the examination of battery acid for iron, a large excess of thiocyanate should be used to compensate for the high concentration of acid. This reaction is somewhat more sensitive than the pyramidone test, and considerably more sensitive than the ferrocyanide test. The ferric thiocyanate may be extracted by means of ether or amyl alcohol, but is insoluble in other organic solvents; the colour is more intense in dry than in moist ether. Oxidation of ferrous to ferric iron is readily accomplished by boiling with potassium persulphate.

S. I. Levy.

Determination of ferro- and ferri-cyanides. W. M. Cumming and W. Good (J.C.S., 1926, 1924—1928).—Insoluble ferrocyanides may be determined by the gravimetric method previously described, provided the heavy metal is first removed, either as carbonate or sulphide (cf. Cumming, A., 1924, ii, 353). The volumetric method is modified; a measured quantity of standard benzidine dihydrochloride solution is added to a neutral solution of the ferrocyanide after removal of the heavy metal, and the filtrate titrated with standard alkali, using phenolphthalein as indicator: $3[B,2HCl]+M_4Fe(CN)_6=3B,H_4Fe(CN)_6+4MCl+2HCl$. Both methods are applicable to the determination of ferricyanides, provided a large excess of the benzidine dihydrochloride solution is used. In each case, the same sample of salt may be determined both gravimetrically and volumetrically. S. K. Tweedy.

Separation of zirconium from titanium. L. Moser (Z. anal. Chem., 1926, **68**, 468).—An acknowledgment of Schröder's correction (this vol., 705) of a statement erroneously made in an earlier paper by Moser and Lessnig (A., 1925, ii, 718).

A. R. Powell.

Microchemical detection of germanium. E. M. Chamot and H. I. Cole (Mikrochem., 1926, **4**, 97—102).—Although a large number of organic and inorganic reagents were tried, no characteristic microreaction for the detection of germanium was discovered, and only those tests which are available for the detection of silicon (complex fluorine and molybdenum compounds) are practicable for germanium. Since the fluogermanates and germanomolybdates closely resemble the corresponding compounds of several other elements, a preliminary separation is essential. The material to be tested is placed in a small crucible, moistened with concentrated hydrochloric acid, and warmed over a micro-burner. Volatile germanium chloride condenses on a cooled celluloid object-slide covering the crucible and is converted into sodium fluogermanate or rubidium germanomolybdate for microscopical examination. The former compound is obtained by warming the

distillate with sodium chloride and ammonium fluoride. On cooling, crystals begin to appear at the circumference of the drop as hexagonal plates or as skeletal six-pointed stars. Later, hexagonal prisms may appear. The crystals are feebly double-refracting, and since their refractive index is almost that of water, they are seen only with difficulty. The sensitivity is 0·1 μg. Rubidium germanomolybdate is obtained by warming with nitric acid and ammonium molybdate, evaporating to dryness twice with nitric acid, dissolving in water, and precipitating with rubidium chloride. Pale yellow octahedral or dodecahedral isotropic crystals are obtained. The sensitivity is 0·02 μg. It is obvious that fluorides must be absent from the original material tested, otherwise silicon fluoride may appear in the distillate.

J. S. CARTER.

Detection of vanadic acid by means of hydrogen peroxide. J. MEYER and A. PAWLETTA (Z. anal. Chem., 1926, **69**, 15—20).—Vanadic acid dissolves in a solution of hydrogen peroxide, giving a pale yellow solution which appears to contain vanadic acid in a colloidal form; at the same time, the hydrogen peroxide is catalytically decomposed. With sulphuric acid, the yellow solution yields an almost colourless solution containing the compound $(VO)_2(SO_4)_3$, which is oxidised by hydrogen peroxide to the reddish-brown substance $(VO_2)_2(SO_4)_3$. Further, hydrogen peroxide causes the colour to fade to yellow, but the reddish-brown colour is restored by adding more sulphuric acid. These changes are due to hydrolysis according to the scheme: $(VO_2)_2(SO_4)_3+6H_2O \rightleftharpoons 2VO_2(OH)_3+3H_2SO_4$. In concentrated sulphuric acid solution, however, hydrogen peroxide reduces vanadic acid to vanadyl sulphate. In view of these results, the most satisfactory procedure for detecting and determining vanadium by the colorimetric method is as follows: The alkaline solution obtained by fusion is treated with sufficient sulphuric acid to give a 15—20% solution of the acid and, after a short time, 3% hydrogen peroxide is added drop by drop until the colour ceases to increase in intensity. In this way, 1 part of vanadium may be detected in 160,000 parts of solution.

A. R. POWELL.

Action of potassium iodide on vanadophosphoric acid. T. HECZKO (Z. anal. Chem., 1926, **68**, 461—468).—A solution of vanadic acid in phosphoric acid reacts with potassium iodide with the liberation of iodine and reduction of the vanadium from the quinquevalent to the quadrivalent form. For every 0·1 g. of vanadic acid, 7 c.c. of 83% phosphoric acid are required for solution; after heating gently for a few minutes, the liquid is cooled, diluted with 3—4 times its volume of water, and treated with an excess of potassium iodide. The liberated iodine is titrated with 0·1*N*-thiosulphate solution. The method is adapted to the determination of very small quantities of vanadium.

A. R. POWELL.

Determination of antimony by electrolysis in hydrochloric acid solution. A. SCHLEICHER [with L. TOUSSAINT and P. H. TROQUAY] (Z. anal. Chem., 1926, **69**, 39—47).—The deposit of metallic antimony obtained by electrolysis of a solution of the chloride in 1—1·5*N*-hydrochloric acid, maintaining a cathode potential of 0·28—0·35 volt against the normal calomel electrode, always contains chlorine, the amount varying from 0·04 mg. for a deposit weighing 0·05 g. to 0·77 mg. for a deposit weighing 0·5 g. No hydrogen or antimony hydride appears to be adsorbed by the metal, but a minute trace of the hydride is evolved at the end of the electrolysis if the cathode potential is allowed to rise above 0·5 volt. When hydrazine sulphate is used as the anode depolariser, only slightly more than the theoretical quantity required to combine with the liberated chlorine, *i.e.*, 0·2 g. for 0·2 g. of antimony, is required, provided that the solution is thoroughly stirred by mechanical means. Addition of ammonium persulphate towards the end of the electrolysis is recommended to guard against loss of antimony as hydride; no reaction takes place between the hydrazine sulphate and the ammonium persulphate. Engelenburg's modification of Classen's method is recommended as a standard procedure (cf. A., 1923, ii, 260).

A. R. POWELL.

***X*-Ray spectrograph.** J. T. NORTON (J. Opt. Soc. Amer., 1926, **13**, 231—233).—An *X*-ray spectrograph of the rotating crystal type is described. It is of simple construction, is easy to set up, and gives results of considerable precision.

A. B. MANNING.

High-vacuum *X*-ray spectrometer. M. SIEGBAHN and R. THORÆUS (J. Opt. Soc. Amer., 1926, **13**, 235—242).—The details of construction and method of operation of a vacuum *X*-ray spectrometer are described. The spectrometer and *X*-ray tube are mounted together, and can be evacuated to the same low pressure. The plate holder can be turned to make any desired angle with the tube up to 35° while still maintaining the vacuum. The required range of wave-lengths, using reflexion angles not exceeding 35°, is obtained by choosing suitable crystal gratings, *e.g.*, calcite up to 3·5 Å., mica up to 11·0 Å., and palmitic acid up to 40·0 Å.

A. B. MANNING.

Direct-reading ionisation gauge. C. F. FOUND and N. B. REYNOLDS (J. Opt. Soc. Amer., 1926, **13**, 217—222; cf. A., 1924, ii, 586).—An ionisation gauge is described which can be operated directly from a 125 volt supply, and is independent of small fluctuations in the voltage. The electron current to the grid of the three-electrode tube forming the gauge is automatically maintained constant at 10 milliamps. The voltage drop across a high resistance in the plate circuit, which is proportional to the positive ionisation current, is amplified by a "push-pull" amplifier circuit, the plate current in which is recorded by a milliammeter. The milliammeter reading is then directly proportional to the pressure in the gauge.

A. B. MANNING.

Simple spectral apparatus of high light intensity. I. Spectral photography of weak luminescence phenomena. K. SCHAUM and W. KRAEMAR (Z. wiss. Phot., 1926, **24**, 219—223).—A Seibert direct-vision spectroscope was provided with a specially calculated two-lens achromat of aperture 0·07 as collimator and a three-lens achromat of aperture 0·11 as resolving objective, and with a

small camera. The luminescence of vapours was studied, at atmospheric pressure, in a Kauffmann "elektrisator" (ozoniser) (Z. physikal. Chem., 1898, **26**, 719; 1899, **28**, 673), using a Tesla discharge, and at low pressures in a Tesla tube using a high-frequency field. A Geissler tube could not be used owing to rapid decomposition of the substances studied. Observed lines and bands are tabulated for aniline, dimethylaniline, α-naphthylamine, *o*-phenetidine, and "tetralin" in the "elektrisator," and for aniline, dimethylaniline, and α-naphthylamine in the Tesla tube.

W. CLARK.

Lens-polariscopes. H. SCHULZ (Z. tech. Physik, 1925, **6**, 614—618; from Chem. Zentr., 1926, 1, 1674—1675).—The substitution of lenses for prisms in polariscopes is recommended. Using lenses of calcite, observations may be made in the ultra-violet region. By using a combination of a calcite and a glass lens the relation of focal length for the ordinary and extraordinary rays can be adjusted to have any value, and a system suitable for a variety of purposes obtained. J. S. CARTER.

Stirring apparatus for use in potash analysis according to the tartaric acid method of Przibylla. G. MÜLLER (Kali, 1926, **20**, 31; from Chem. Zentr., 1926, I, 1859).—The individual stirrers are arranged in a circular fashion round a central driving pulley under such conditions that each stirrer may be used at will. The solutions are contained in wide-necked, weighted flasks of about 160 c.c. capacity which stand in two semi-circular water-baths.

J. S. CARTER.

Weighing by hydrostatic compensation. M. GUICHARD (Bull. Soc. chim., 1926, [iv], **39**, 1113—1115; cf. A., 1925, ii, 427).—A balance is described in which the pan which normally carries the weights is replaced by a plunger dipping into a vessel of oil. By means of an attached burette, the amount of oil can be regulated so that the apparent weight of the plunger balances a body placed in the other pan. After the balance has been once calibrated, the weight required can be determined from the burette reading. Such a balance is dead-beat. R. CUTHILL.

Improvement in MacMullin's automatic apparatus for determining the m. p. of organic compounds. H. F. PALMER and G. H. WALLACE (J. Amer. Chem. Soc., 1926, **48**, 2230—2232; cf. this vol., 593).—An arrangement is described whereby the maximum thermometer is raised automatically from the bath at the moment the substance melts.

F. G. WILLSON.

Differential method for the measurement of the vapour pressure of liquids. V. G. JOLLY and H. V. A. BRISCOE (J.C.S., 1926, 2154—2159).—The liquid is contained in a sealed U-tube the limbs of which are maintained at different constant temperatures. The liquid itself behaves as the manometer liquid, and from a knowledge of the vapour pressure at one temperature the values at other temperatures are readily obtained. The method, which may be used in dealing with intensively dried liquids, has the advantage that the presence of a foreign gas is not involved (cf. Campbell, A., 1915, ii, 516). The vapour pressures of water, benzene, and bromine are recorded; the values for bromine agree well with those of Ramsay and Young (J.C.S., 1886, **49**, 453).

S. K. TWEEDY.

Ignition of firedamp by momentary flames. N. S. WALLS and R. V. WHEELER.—See B., 1926, 730.

Ignition of firedamp by momentary flames. W. RINTOUL and A. G. WHITE.—See B., 1926, 730.

Laboratory electric furnace for temperatures up to 1400°. S. REINER (Chem.-Ztg., 1926, **50**, 578).—A simple furnace formed by placing suitably shaped blocks of refractory material about an iron or quartz tube is described. S. I. LEVY.

Apparatus for production of gases. H. HERBST (Chem.-Ztg., 1926, **50**, 579).—A cylinder containing the solid reagent is provided with a side tube sealed on near the bottom, and connected to a higher level vessel for the liquid reagent, the latter vessel being provided with a seal. The cylinder has a stopper carrying a three-way cock, which delivers the gas directly as required, or to a graduated measuring vessel provided with a pressure-equalising connexion.

S. I. LEVY.

Earliest human knowledge of copper. P. E. SPIELMANN (Nature, 1926, **118**, 411).—Where copper and petroleum occur in close proximity (as in the Caucasus, whence the earliest Egyptian immigrants may have come), ignition of the oil would produce metallic deposits liable to early discovery and use.

A. A. ELDRIDGE.

Mineralogical Chemistry.

Phosphate content of sea water in relation to the growth of the algal plankton. III. W. R. G. ATKINS (J. Mar. Biol. Assoc., 1926, **14**, 447—467).—The maximum concentration of phosphate as P_2O_5 in the English Channel is 40 mg. per cub. m. and the minimum 5·1 mg. for the depth 0—70 m. The deep water of the ocean is a reservoir of phosphate, containing 50—80 mg. per cub. m. In tropical waters, the intense light normally results in the utilisation of all phosphate down to at least 50 m. and the winter cooling never suffices to effect mixing with the deep water; further north, the mixing is more complete, and the seasonal phosphate cycle becomes more pronounced (cf. this vol., 42). W. THOMAS.

Precipitation of calcium and magnesium from sea water. L. IRVING (J. Mar. Biol. Assoc., 1926, **14**, 441—446).—Calcium and magnesium may be precipitated under possible conditions of natural sea-water alkalinity. The same conditions governing

precipitation outside of the organism may explain the excess of calcium over magnesium in organic "formed" precipitates, as alkalinity necessary for magnesium precipitation is much more difficult for the organism to attain, especially within its tissues.
W. THOMAS.

Occurrence of iodine in Nature. X. Geochemistry of iodine. T. VON FELLENBERG and G. LUNDE (Biochem. Z., 1926, **175**, 162—171).—The amounts of iodine and bromine contained in various rocks and minerals are tabulated.
P. W. CLUTTERBUCK.

Cornuite. F. V. VON HAHN (Zentr. Min. Geol., 1925, A, 353—356; from Chem. Zentr., 1926, I, 1787—1788).—The green diatomite of Neu-Ohe contains inclusions of an amorphous, transparent yellow mineral to which the name cornuite is given. The mineral contains about 97% of water and 0·08% of ash, and appears to be a protein, since it gives a number of reactions characteristic of albumin.
W. A. CASPARI.

Lead hydrogen arsenate as a mineral. L. J. SPENCER (Nature, 1926, **118**, 411—412).—Colourless monoclinic plates ($a:b:c=0·8643:1:0·7181$, $\beta=84°\ 36'$) from Tsumeb, South-West Africa, were found to have the composition $PbHAsO_4$. They are identical with the crystals prepared by de Schulten (A., 1905, ii, 174), and the new mineral is named "schultenite."
L. J. SPENCER.

Stibiobismuthinite. E. QUERCIGH (Atti R. Accad. Lincei, 1926, [vi], **4**, 68—72).—Koenig (A., 1917, ii, 487) described stibiobismuthinite as a new mineral $(Bi,Sb)_4S_7$. Artificial preparations of antimony and bismuth sulphides by the method of Geitner (Annalen, 1864, **129**, 359) contain included sulphur, as do mixed sulphides $(Bi,Sb)_2S_3$, to which type it is suggested that the mineral belongs.
E. W. WIGNALL.

New Russian occurrence of vanadium and uranium minerals. S. KURBATOV (Bull. Acad. Sci. St. Pétersbourg, 1925, 315; from Chem. Zentr., 1926, I, 1789).—A yellow mineral containing about 33% of vanadium pentoxide, 52% of cupric oxide, and 0·59% of uranium oxide occurs near copper mines in Minusinsk. The mineral consists of a mixture of calcium volborthite with allophane, opal, and brown hæmatite.
W. A. CASPARI.

Pectolites from Russian Lapland. E. KOSTYLEVA (Bull. Acad. Sci. St. Pétersbourg, 1925, 383; from Chem. Zentr., 1926, I, 1788).—Three specimens of pectolite from the Chibinsk Tundra contained 49·00—53·80% SiO_2, 0·68—2·06% Al_2O_3, 0·95—1·39% Fe_2O_3, 32·04—32·46% CaO, 0·55—2·17% MnO, 1·09% MgO, 7·38—8·99% Na_2O, 0·53—0·60% K_2O, and 2·85—4·08% of water. A new mineral, *juxporite*, $(HNaK)_2(CaMgMn)SiO_3$, is found accompanying the above; it forms pink fibres and scales of silky lustre, fusible in the blowpipe.
W. A. CASPARI.

Organic Chemistry.

Thermal decomposition of methane by a glowing filament. G. M. SCHWAB and E. PIETSCH.—See this vol., 918.

Production of propylene. L. J. BONHAM (J. Amer. Pharm. Assoc., 1925, **14**, 114—118).—*n*-Propyl alcohol, b. p. 96—98°, is vaporised in a glycerol bath at 125—130° and passed through a hard glass tube containing a catalyst prepared by precipitating aluminium hydroxide from the sulphate with ammonia, washing by decantation until free from ammonium sulphate, drying in pans at 80—90°, and breaking into pellets which were subsequently dried in a slow stream of air at 510°. At 510°, 25 c.c. of the alcohol gave 8200 c.c. of gas; at 365°, the product was purer and the catalyst could be used repeatedly. On regeneration of the catalyst, then containing carbon, by heating for 30 min. at a high temperature, it exhibited increased activity, and the product was purer.
CHEMICAL ABSTRACTS.

Photolysis of alcohols. VOLMAR.—See this vol., 920.

Formation of carbon dioxide from alcohols. W. A. LAZIER and H. ADKINS.—See this vol., 918.

Mechanism of the catalytic dehydration of methyl alcohol. H. C. HOWARD, jun.—See this vol., 918.

Synthetic manufacture of alcohol and acetic acid [and acetone]. P. PASCAL.—See B., 1926, 767.

Action of sodium acetate on *iso*butylene dibromide and trimethylethylene dibromide. K. KRASSOURSKY and F. SCHENDEROWITCH (Ukraine Chem. J., 1925, **1**, 633—637).—On heating *iso*butylene dibromide for 3 hrs. with acetic acid and sodium acetate, 33% of the theoretical quantity of iso*butenyl acetate*, $CH_2{:}CMe{\cdot}CH_2{\cdot}OAc$, b. p. 120—123°, was obtained.

Trimethylethylene dibromide treated in the same way gave *β-methyl-Δ^β-buten-γ-yl acetate*, $CMe_2{:}CMe{\cdot}OAc$, b. p. 133—139°. It probably contains some of the isomeric acetate, $CH_2{:}CMe{\cdot}CHMe{\cdot}OAc$.
S. BOTCHARSKY.

Natural methylheptenone. II. Alcohols, dienes, and *cyclo*geraniolenes. I. R. ESCOURROU (Bull. Soc. chim., 1926, [iv], **39**, 1121—1138).—Natural methylheptenone, b. p. 173—174°, d^{10} 0·8691, n_D^{14} 1·44345, prepared from citral, gives good yields of tertiary alcohols when treated with magnesium alkyl halides. The following are obtained in this way: βζ-dimethyl-Δ^β-hepten-ζ-ol, b. p. 77—78°/13 mm., $d^{10·5}$ 0·8564, n_D^{19} 1·45197 (*acetate*, b. p. 184—186°/740 mm., d^{11} 0·883, n_D^{11} 1·44235); βζ-dimethyl-Δ^β-octen-ζ-ol, b. p. 92·5°/13 mm., d^{17} 0·8572, n_D^{15} 1·45658 (*acetate*, b. p. 214°/738 mm., d^{12} 0·8841, n_D^{15} 1·44606); [βζ-di-

methyl-Δ^{β}-nonen-ζ-ol, b. p. 102—103°/13 mm., d^{11} 0·8592, n_D^{11} 1·45727 (*acetate*, b. p. 112—113°/13 mm., d^{10} 0·8863, n_D^{10} 1·45247); $\beta\zeta\eta$-*trimethyl*-Δ^{β}-*octen*-ζ-*ol*, b. p. 97—98°/12 mm., d^{10} 0·8717, $n_D^{10\cdot5}$ 1·46295; $\beta\zeta$-*dimethyl*-Δ^{β}-*decen*-ζ-*ol*, b. p. 95—96°/5 mm., $d^{10\cdot5}$ 0·8603, n_D^{10} 1·45997 (*acetate*, b. p. 122—123°/13 mm., $d^{10\cdot5}$ 0·8903, n_D^{11} 1·45177); $\beta\zeta\iota$-*trimethyl*-Δ_{β}-*decen*-ζ-*ol*, b. p. 123—124°/14 mm., d^{11} 0·8566, $n_D^{10\cdot5}$ 1·45657; ζ-*phenyl*-β-*methyl*-Δ^{β}-*hepten*-ζ-*ol*, b. p. 155—156°/19 mm., d^{10} 0·9679, n_D^{13} 1·52316; β-*methyl*-ζ-*benzyl*-Δ^{β}-*hepten*-ζ-*ol*, b. p. 153—154°/10 mm., $d^{10\cdot5}$ 0·9654, n_D^{10} 1·52632. On redistillation, and especially if a trace of acid be present, these alcohols tend to decompose, yielding methylheptenone and the hydrocarbon corresponding with the alkyl radical present in the original magnesium alkyl halide. R. W. West.

Ethers derived from ββ′-dihalogenated *iso*propyl alcohols and halogenated propylene glycols. L. Blanchard (Bull. Soc. chim., 1926, [iv], **39**, 1119—1121).—A mixture of trioxymethylene and αα′-dichlorohydrin, saturated with hydrogen chloride, yields *chloromethyl dichloroisopropyl ether* $CH_2Cl{\cdot}O{\cdot}CH(CH_2Cl)_2$, b. p. 95—96°/17 mm. (cf. Hamonet, A., 1905, i, 403). In similar manner, α-monochlorohydrin yields the *ether*, $CH_2Cl{\cdot}O{\cdot}CH_2{\cdot}CH(O{\cdot}CH_2Cl){\cdot}CH_2Cl$. These substances react with magnesium alkyl halides, yielding ethers of the type $>CH{\cdot}O{\cdot}CH_2R$ (cf. Hess and Fink, A., 1916, i, 158). R. W. West.

Addition of methyl hypobromite and methyl hypochlorite to certain ethylene derivatives. E. L. Jackson (J. Amer. Chem. Soc., 1926, **48**, 2166—2174; cf. A., 1924, i, 962).—The presence of water is unnecessary for the addition of methyl hypobromite to ethylene derivatives when their methyl-alcoholic solutions are treated with bromine. In absolute methyl-alcoholic solution, phenyl styryl ketone yields in this way α-bromo-β-methoxy-β-phenylpropiophenone, together with ketone dibromide; cinnamic acid affords methyl esters of the corresponding additive products, which are also obtained similarly from methyl cinnamate; whilst stilbene yields stilbene dibromide and *α-bromo-β-methoxy-αβ-diphenylethane*, m. p. 115·5—116·5°. The action of bromine on cinnamic acid in 50% aqueous methyl-alcoholic solution brings about the simultaneous addition of bromine, hypobromous acid, and methyl hypobromite. Treatment of phenyl styryl ketone in absolute methyl alcohol with chlorine affords two isomerides of *α-chloro-β-methoxy-β-phenylpropiophenone*, m. p. 69—70° and 98—99°, respectively, the former predominating. Cinnamic acid affords similarly the dichloride, together with *α-chloro-β-methoxy-β-phenylpropionic acid*, m. p. 163—164°, and its *methyl* ester, m. p. 54—55°, the latter being obtained analogously from methyl cinnamate. Reaction between chlorine, cinnamic acid, and methyl alcohol proceeds similarly, but less smoothly, in carbon tetrachloride solution. Treatment of stilbene with chlorine in methyl-alcoholic solution affords two isomerides of *α-chloro-β-methoxy-αβ-diphenylethane*, m. p. 96—97° and 55—57°, respectively, together with stilbene dichloride. An analogous reaction with iodine was not observed.

F. G. Willson.

Varying valency of platinum with respect to mercaptanic radicals. III. P. C. Rây, B. C. Guha, and K. C. Bose-Rây (J. Indian Chem. Soc., 1926, **3**, 155—160; cf. A., 1925, ii, 1121).—The molecular compound of platinous chloride and ethyl sulphide is decomposed by ammonia with formation of tetrammineplatinous dichloride, whilst pyridine yields a mixture of the corresponding tetrapyridine compound with the non-electrolyte dipyridineplatinous chloride. The same platinotetrammine is produced by the action of ammonia on the compound $PtCl_3,2Et_2S$. The platinic chloride compound $PtCl_4,2Et_2S$ is decomposed by ammonia, yielding tetramminedichloroplatinic dichloride and by pyridine to give dipyridinetetrachloroplatinum.

G. M. Bennett.

Triethylene trisulphide and 1 : 4-dithian. P. C. Rây and K. C. Bose-Rây (J. Indian Chem. Soc., 1926, **3**, 73—74).—The identification of "triethylene trisulphide" with 1 : 4-dithian (cf. Bennett and Berry, A., 1925, i, 695) is confirmed, but the authors prefer, notwithstanding the evidence as to the mol. wt. of the substance both in solution and as vapour, to retain the formula $(C_2H_4S)_3$, mainly on the ground of the isolation of a *compound*, $(C_2H_4)_3S_2PtCl_3$, by the action of aqueous platinic chloride solution.

G. M. Bennett.

Lengthened chain compounds of sulphur. P. C. Rây and K. C. Bose-Rây (J. Indian Chem. Soc., 1926, **3**, 75—80).—The "polymeride" of dithian prepared as described by V. Meyer (A., 1887, 228) is found to contain substances of high mol. wt. of the general formula $Br(C_2H_4S)_n{\cdot}C_2H_4Br$ isolated by extraction with solvents such as nitrobenzene. The following *compounds* are described: n=48, m. p. 163°; n=40, m. p. 170°; n=32, m. p. 157—159°; n=26, m. p. 145—155°; n=24, m. p. 147°; n=16, m. p. 162°; n=12, m. p. 100°; and n=10, m. p. 120°. The mol. wt. of the first of these (n=48) in boiling ethylene dibromide is half that expected, the reason suggested being that the solvent reacts with the substance to yield the compound having n=24.

G. M. Bennett.

Action of aluminium selenide, telluride, and arsenide and of magnesium arsenide on alcohols and ethers. G. Natta (Giorn. Chim. Ind. Appl., 1926, **8**, 367—370).—Analogues of alkyl mercaptans, sulphides, and disulphides are obtained by passing the vapour of alcohols over analogues of aluminium sulphide heated at 250—300° (cf. A., 1924, i, 952). Aluminium selenide (prepared without explosion if the mixed elements are ignited by a hot wire; cf. Chikashige and Aoki, A., 1918, ii, 114) gives, with ethyl alcohol, ethyl selenol, selenide, and diselenide; with *iso*propyl alcohol, *isopropyl selenol*, b. p. 70—75°, accompanied at higher temperatures with *isopropyl diselenide*, b. p. 210°, and some *isopropyl selenide*. Ethers react less readily than alcohols: ethyl ether yields ethyl diselenide and selenide, with hydrogen selenide and unsaturated hydrocarbons. Aluminium telluride with methyl alcohol gives dimethyl telluride and with ethyl alcohol perhaps ethyl tellurol; ethers scarcely react at their decomposition point. Aluminium arsenide gives with methyl alcohol trimethyl-

arsine, some dimethylarsine, and a black substance, probably $(CH_3As)_x$ (cf. A., 1906, i, 150). With ethyl alcohol, an analogous *substance*, perhaps $(C_2H_5As)_x$, is obtained, but at temperatures giving stable products the reaction is very feeble. Magnesium arsenide, prepared in a very violent reaction on igniting the mixed elements, reacts with ethyl alcohol at the b. p. to give arsine and organo-magnesium compounds, and at 280—295° to give ethyl- and diethyl-arsine, with a trace of triethylarsine. E. W. WIGNALL.

Determination of the mol. wt. of fatty acids. M. TRAUTZ and W. MOSCHEL.—See this vol., 997.

Diagnosing potential optical activity. II. Optical activity of chlorobromoacetic acid. J. READ and A. M. MCMATH (J.C.S., 1926, 2183—2191).—Chlorobromomalonic acid, m. p. 83° (cf. Vanderstichele, *ibid.*, 1923, **123**, 1225), is produced by the successive action of bromine and sulphuryl chloride on a solution of malonic acid in anhydrous ether; the normal *brucine* salt and *brucine hydrogen* salt, $[\alpha]_D$ −15·2°, are described. When heated at 130°, chlorobromomalonic acid is converted quantitatively into chlorobromoacetic acid, which can be resolved into optically active components by crystallisation of the *l*-hydroxyhydrindamine salt. *l-Hydroxyhydrindamine* dl-*chlorobromoacetate* has m. p. 165° (decomp.), $[\alpha]_D$ −20·2° in dry methyl alcohol, −56° in acetone (with slow mutarotation). *l-Hydroxyhydrindamine* d-*chlorobromoacetate*, m. p. 157° (decomp.), is readily racemised when dissolved in methyl alcohol or acetone; the racemising action of methyl alcohol is somewhat retarded by dilution with chloroform, transformation to the *dl*-compound occurring on heating. *l-Hydroxyhydrindamine dichloroacetate* has m. p. 139°, $[\alpha]_D$ −24·6° in methyl alcohol, $[\alpha]_D$ −24·7° in glacial acetic acid, $[M]_D$ −195° in acetone, with slow mutarotation. *Brucine chlorobromoacetate* has $[\alpha]_D$ −17·0° in chloroform. C. J. STILL.

Kinetics of chemical reactions. IV. Velocity equation of the hydrolytic decomposition of α-bromopropionic acid. V. α-Bromobutyric acid. J. ZAWIDZKI.—See this vol., 914.

Higher aliphatic compounds. II. Hydration of stearolic acid. G. M. ROBINSON and R. ROBINSON (J.C.S., 1926, 2204—2209).—ι-Ketostearic acid has been synthesised by an application of the method previously described. By reference to the f.-p. curve for mixtures of ι-ketostearic and κ-ketostearic acids, it is shown that the product obtained by treating stearolic acid with sulphuric acid and then with water consists of a mixture of 42·4% of ι-ketostearic acid and 57·6% of κ-ketostearic acid. *δ-Ketomyristic acid*, m. p. 87° (*oxime*, m. p. 74°), *κ-ketononadecoic acid*, m. p. 86—87° (*amide*, m. p. 83°), and *κ-ketobehenic acid*, m. p. 94° (*amide*, m. p. 99°), are described. C. J. STILL.

Configurational relationships of α-, β-, and γ-hydroxy-acids. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1926, **69**, 165—173; cf. this vol., 597).—Methyl *d*-β-hydroxybutyrate, $[\alpha]_D^{21}$ +8·6°, on reduction with sodium and glacial acetic acid gave *d*-αγ-dihydroxybutane, $[\alpha]_D^{22}$ +7·5°, which, in turn, gave the *d*-αγ-diphenylcarbamate, $[\alpha]_D^{22}$ +20°. *d*-γ-Hydroxyvaleric acid, $[\alpha]_D^{22}$ +14·0°, yielded, by the method of Hofmann, *d*-α-amino-γ-hydroxybutane (hydrochloride, $[\alpha]_D^{22}$ +13·3°), which, on deamination, gave *d*-αγ-dihydroxybutane. *d*-γ-Hydroxyvaleric acid is therefore related configuratively to *d*-β-hydroxybutyric acid and hence to *d*-lactic acid. C. R. HARINGTON.

Hydrolysis of ethyl acetoacetate by acids. A. SKRABAL and A. ZAHORKA.—See this vol., 914.

Configuration changes in substitution reactions. W. HÜCKEL (Z. angew. Chem., 1926, **39**, 842—851).—In an endeavour to determine which type of structure influences the configuration changes, in the sense of causing the Walden inversion, when substitution is effected in a group not directly attached to the asymmetric carbon atom, the author reviews a large number of reactions in which these changes take place. As a result, it appears that inversion almost invariably occurs when the molecule contains a ·CH·C:O group, the first carbon atom of which is asymmetric. This is particularly noticeable in the case of *cis–trans*-isomerides containing double linkings. Substitution reactions involving hydrolysis of the :C·O· group, when the carbon atom is asymmetric, usually result in configuration changes, although the asymmetric atom is apparently undisturbed. In certain other cases, racemisation of an optically active substance is effected by substitution in a position very remote from the asymmetric atom, *e.g.*, hydrogenation of optically active ricinoleic acid with the formation of inactive hydroxystearic acid. The author considers that reactions of this type need further investigation to determine whether true racemisation takes place or whether the product is really only very slightly optically active. A. R. POWELL.

Derivatives of ethyl β-aceto-α-methylsuccinate; constitution of hæmatoporphyrin. W. KÜSTER, H. MAURER, and A. PALM (Z. physiol. Chem., 1926, **156**, 1—34; cf. A., 1925, i, 992; this vol., 713).—A detailed account of work already published. The following is new. Oxidation of hæmatoporphyrin dimethyl ether, which has previously been reduced with zinc dust and acetic or hydrobromic–acetic acid, still gives only 1 mol. of the imide, $C_8H_{11}O_3N$, and 2 mols. of hæmatic acid, one pyrrole nucleus of the prosthetic group being destroyed. Ethyl hydrogen β-aceto-α-methylsuccinate, m. p. 66—67° (silver salt) and *barium* β-*aceto-α-methylsuccinate* are described. αγ-Dimethylparaconic acid (Fichter and Rudin, A., 1904, i, 472) when brominated with phosphorus and bromine and then boiled with water, gives the *lactone*, m. p. 110° (indef.), of hydroxydimethylitaconic (β - hydroxy - Δ^β - pentene - γδ - dicarboxylic) acid (fumaroid). Reduction of ethyl β-aceto-α-methylsuccinate with sodium amalgam in the cold gives ethyl hydrogen α-methyl-β(α-hydroxyethyl)succinate, $OH{\cdot}CHMe{\cdot}CH(CO_2H){\cdot}CHMe{\cdot}CO_2Et$, m. p. 81°, from which α-methyl-β-(α-hydroxyethyl) succinic acid, m.p. 105°, is obtained on hydrolysis. C. HOLLINS.

Synthesis of triacetolactone-5-carboxylic acid. R. MALACHOWSKI (Rocz. Chem., 1926, **6**, 23—26).—*Ethyl γ-acetylacetone-αγ-dicarboxylate*, b. p. 120—122°/5 mm. (*copper* salt, m. p. 124·5—125·5°), is prepared from the potassium salt of acetonedicarb-

oxylic ester by the action of acetyl chloride. This is converted by hydrolysis into the *γ-ethyl* ester, m. p. 96—98° (decomp.), which is condensed by sulphuric acid to *ethyl triacetolactone-5-carboxylate*, m. p. 63—65° (*copper* salt, m. p. 182°), and this on hydrolysis yields triacetolactone-5-carboxylic acid, m. p. 180° (*pyridine* salt, m. p. 117—118°). R. TRUSZKOWSKI.

Oxidation of tartaric acid by solutions of silver salts. D. R. MAXTED (J.C.S., 1926, 2178—2182).—When tartaric acid is oxidised with an excess (6—8 mols.) of silver nitrate in ammoniacal solution, 6 atoms of silver are deposited for each molecule of tartaric acid. Oxalic acid, formic acid, carbon dioxide, and water are formed in quantities agreeing with the equations: $C_4H_6O_6+3Ag_2O \rightarrow$ (*a*) $2(CO_2H)_2+6Ag+H_2O$; (*b*) $(CO_2H)_2+H{\cdot}CO_2H+CO_2+6Ag+H_2O$; (*c*) $2H{\cdot}CO_2H+2CO_2+6Ag+H_2O$.

The proportion of oxalic acid is increased when the solution is more alkaline. C. J. STILL.

Complex bismuthotartrates. R. PORTILLO (Anal. Fis. Quím., 1926, **24**, 420—431; cf. this vol., 939).—By dissolving bismuthoditartaric acid, $H[Bi(C_4H_4O_6)_2],3H_2O$, in hot, dilute sulphuric acid, a crystalline compound is obtained to which the formula $H_2[BiC_4H_2O_6],0{\cdot}5H_2SO_4,3H_2O$ is assigned. By a similar method, the author has prepared the *compounds*: $H_2[BiC_4H_2O_6]Cl,3H_2O$; $H_2[BiC_4H_2O_6]ClO_4,4H_2O$; $H_2[BiC_4H_2O_6]NO_3,5H_2O$; $H_2[BiC_4H_2O_6]NO_3,8H_2O$. Except in the case of the chlorine compound, the combined water is completely given up in a vacuum over sulphuric acid. In the case of the second compound, the combined water is only given up with decomposition above 120°. G. W. ROBINSON.

Natural occurrence of aconitic acid and its isomerides. O. A. BEATH (J. Amer. Chem. Soc., 1926, **48**, 2155—2158).—Samples of aconitic acid obtained from six species of delphiniums, from two species of *Aconitum*, and from the *columbianum*, had m. p. 172—173° in each case, identical with that of commercial aconitic acid. The m. p. was unchanged after esterification and hydrolysis. It is concluded that these acids are identical with the acid of the same m. p. described by Bland and Thorpe (J.C.S., 1912, **101**, 1490), and that the variations in m. p. recorded for naturally occurring aconitic acids are due to the samples being mixtures of isomerides.

F. G. WILLSON.

Structure of lactones from simple sugars. Trimethyl-γ-arabonolactone and the supposed β-gluconolactone and β-mannolactone. W. N. HAWORTH and V. S. NICHOLSON (J.C.S., 1926, 1899—1902).—Trimethyl-γ-arabinolactone, prepared from the γ-arabonolactone obtained by oxidation of *l*-arabinose, is identical with the product previously prepared by oxidation of trimethyl-γ-arabinose with nitric acid, thus confirming the presence of the butylene oxide ring in trimethyl-γ-arabinose. The unstable β-gluconolactone and β-mannolactone described by Nef (A., 1914, i, 490) are in reality δ-lactones containing a six-membered ring corresponding with the normal or amylene-oxide type.

C. J. STILL.

Lactone formation from gluconic acids and the structure of dextrose. P. A. LEVENE and H. S. SIMMS (J. Biol. Chem., 1926, **68**, 737—749).—Gluconic and βγ-dimethylgluconic acids, on keeping in aqueous solution, form lactones with both five- and six-membered rings; γεζ-trimethylgluconic acid forms only one lactone with a five-membered ring, whilst βγδ-trimethyl- and βγδζ-tetramethyl-gluconic acids each form only one lactone with a six-membered ring; since the last two acids were derived from methylglucoside and the γεζ-trimethylgluconic acid was derived from di*iso*propylideneglucose, it appears that the ring structure of the derivatives of dextrose does not indicate the structure of dextrose itself. In the present series of acids, the rates of lactone formation and hydrolysis are higher, and the equilibria are situated more to the acid side than in the series previously described. C. R. HARINGTON.

Optical resolution of chlorosulphoacetic acid. J. READ and A. M. MCMATH (J.C.S., 1926, 2192—2198).—By fractional crystallisation of the normal salt of chlorosulphoacetic acid with *l*-hydroxyhydrindamine, there is obtained l-*hydroxyhydrindamine* d-*chlorosulphoacetate*, m. p. 203° (decomp.), $[\alpha]_D$ −18·0° in methyl alcohol. *Brucine* d-*chlorosulphoacetate* has m. p. 196° (slight decomp.), $[\alpha]_D$ −2° in methyl alcohol; *ammonium* d-*chlorosulphoacetate*, $[\alpha]_{5461}$ +16·3°, $[\alpha]_D$ +13·8°, rotatory dispersion Hg_{5461}/Na_D 1·177 in water; *benzidine* d-*chlorosulphoacetate*, decomp. 245°, $[\alpha]_{5461}$ +15·7°. Impure l-*hydroxyhydrindamine* l-*chlorosulphoacetate*, *brucine* l-*chlorosulphoacetate*, and *ammonium* l-*chlorosulphoacetate* were also isolated. C. J. STILL.

Formation of formaldehyde by reduction of carbonic acid by hydrogen peroxide. E. RUPP and H. SCHLEE (Biochem. Z., 1926, **172**, 373—378).—From a mixture of sodium hydrogen carbonate, hydrogen peroxide, and an iron salt, carbon dioxide escapes and formic acid and formaldehyde are found in the liquid. The first product is probably formic acid, which is then converted into formaldehyde and carbonic acid by a Cannizzaro reaction.

C. RIMINGTON.

Process of making crotonaldehyde. F. W. LOMMEN.—See B., 1926, 770.

Action of organo-magnesium compounds on nitriles. Ketone cyanohydrins. J. GEURDEN (Bull. Soc. chim. Belg., 1926, **35**, 253—260).—The principal product of the action of magnesium alkyl, phenyl, and benzyl halides on the cyanohydrin of an aliphatic ketone is in each case the tertiary alcohol which would be obtained if the ketone itself were used in the reaction. Gauthier (A., 1911, i, 415, 513) mistook these tertiary alcohols for the ketonic alcohols which he expected to be produced. The true ketonic alcohol, β-*methylpentan-γ-on-β-ol*, b. p. 154°, d_4^{20} 0·9326 (*semicarbazone*, m. p. 129°), is also produced in small quantity in the action of magnesium ethyl bromide on acetone cyanohydrin, and from the corresponding reaction between magnesium methyl bromide and the cyanohydrin of methyl ethyl ketone the *semicarbazone* (m. p. 140°) of *γ-methylpentan-δ-on-γ-ol* is obtained. G. M. PENNETT.

Dynamic isomerism. XXII. Methyl alcohol as an amphoteric solvent for the mutarotation of the sugars. I. J. FAULKNER and T. M. LOWRY (J.C.S., 1926, 1938—1943).—Purified methyl alcohol, which gave a velocity coefficient of 0·00018 when used as a solvent for the mutarotation of tetramethylglucose, gave a maximum value for k of 0·0018 when mixed with three times its weight of cresol, and of 0·035 when mixed with two thirds its weight of pyridine. In purified ethyl alcohol, k=0·00016, a value about one eightieth of the velocity in water. C. J. STILL.

Oxidation of methylated glucoses. H. SOBOTKA (J. Biol. Chem., 1926, **69**, 267—275).—Since the reducing power of dextrose towards alkaline solutions of cupric salts is greater than can be accounted for by the oxidation of the aldehydic group of dextrose to carboxyl, it must be assumed that the hydroxyl groups also play some part in the reduction. In agreement with this, it is found that all methylated glucoses have less reducing power, as measured, *e.g.*, by the method of Bertrand, than dextrose itself. βγ-Dimethylglucose has less reducing power than γεζ-trimethylglucose, which is ascribed to the fact that the free hydroxyl group on the β-carbon atom in the latter substance facilitates enolisation. The reducing power of pentamethylglucose towards alkaline copper solutions approximates to its reducing power towards hypoiodite; the latter, being a measure of the reducing power of the aldehydic group only (cf. Willstätter and Schudel, A., 1918, ii, 337), is equal for dextrose itself and all its methyl ethers. C. R. HARINGTON.

Pentamethylglucose and its dimethylacetal. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1926, **69**, 175—180).—Methylation of diethylmercaptoglucose, first with methyl sulphate and then further by Freudenberg's method, yielded *pentamethyldiethylmercaptoglucose*, b. p. 152°/0·6 mm., $[\alpha]_D^{20}$ +19·2° in methyl alcohol; this, on treatment with mercuric chloride, gave *pentamethylglucose*, b. p. 108—110°/0·4 mm., $[\alpha]_D^{20}$ −35·1° in tetrachloroethane; $[\alpha]_D^{13}$ −33·5° to +11·5° in 18 hrs. in methyl alcohol; in methyl alcohol containing 0·25% of hydrochloric acid, $[\alpha]_D^{3}$ +15·5° immediately. The *dimethylacetal* had b. p. 95°/0·8 mm., $[\alpha]_D^{20}$ +15·09° in methyl alcohol. C. R. HARINGTON.

Action of aniline on dextrose in acetic acid solution. C. N. CAMERON (J. Amer. Chem. Soc., 1926, **48**, 2233—2238).—Aniline reacts with dextrose in acetic acid with formation of a *product*, apparently identical with that obtained by the action of acetic acid on glucoseanilide. Conversion of dextrose into the anilide is incomplete unless excess of aniline and acetic acid is present. Glucoseanilide has $[\alpha]_D^{21}$ −53·01° in alcohol, in presence of excess of aniline to suppress hydrolysis (cf. Irvine and Gilmour, J.C.S., 1908, **93**, 1429). F. G. WILLSON.

Reaction of paraldehyde applicable to carbohydrates. P. BRUÈRE (Bull. Soc. Chim. biol., 1926, **8**, 462—463).—Carbohydrates which furnish lævulose on hydrolysis give, with concentrated sulphuric acid and guaiacol, a colour almost identical with that given by paraldehyde; others give a bright red colour. C. P. STEWART.

Molecular dimensions of cellulose. H. BRUNSWIG (Cellulosechem., 1926, **7**, 118—121).—A graphic representation of the relations between the percentage of nitrogen in a cellulose nitrate and the percentage solubility at 1% concentration in ether–alcohol 2 : 1 by vol. shows a region of the graph between 10·2 and 12·8% N where the solubility may reach 100%. On both sides of this region, the line of solubility falls very abruptly to negligible proportions. For instance, a cellulose nitrate with 10·0% N has a solubility of 90%, and one with 13·0% N already contains 40—60% of insoluble cellulose nitrate. Hence it follows that the two cellulose nitrates representing the higher and lower limits of the region of 100% solubility must be single individuals of uniform composition. This was demonstrated in the case of the cellulose nitrate with 10·2% N by fractional precipitation of its acetone solution. The solubility in ether–alcohol is a direct function of chemical composition and does not depend on dispersion. The percentage of nitrogen in any cellulose nitrate may be varied upwards or downwards by re-immersion in another nitrating mixture of appropriate composition, and the solubility in ether–alcohol is modified strictly in accordance therewith. The simplest expressions for the two limiting cellulose nitrates which are 100% soluble are represented by the heptanitrate with 10·18% N and the decanitrate with 12·75% N, calculated on a cellulose molecule which is not smaller than $4C_6H_{10}O_5$. J. F. BRIGGS.

Constitutional formula for cellulose. H. LE B. GRAY (Ind. Eng. Chem., 1926, **18**, 811).—Chemical evidence (E.P. 231800 and 231811; cf. B., 1925, 913, 914) indicates that, in the cellulose molecule, one hydroxyl group per C_{24} is different from the other eleven, and to account for this a formula for cellulose consisting of four dextrose residues, three of which contain the amylene oxide ring and the fourth the butylene oxide ring, is proposed. This formula is in agreement with known data concerning the degradation products of cellulose. J. W. BAKER.

Esterification of alkali-cellulose. I and II. G. KITA, T. MAZUME, T. NAKASHIMA, and I. SAKRADA (Cellulosechem., 1926, **7**, 125—130, 130—133).—When alkali-cellulose is treated with stearyl chloride, the proportion of acid combining with the cellulose is diminished greatly by the presence of phosphoryl chloride and hydrochloric acid, and slightly by excess of alkali. Alkali-cellulose from 1 g. of cellulose requires about 3 g. of stearyl chloride to obtain maximum combination; additional stearyl chloride has little effect. The amount of combination is slightly increased by lowering the temperature at which the alkali-cellulose is prepared, but it is not affected by the temperature of esterification, or by the age of the alkali-cellulose; drying the alkali-cellulose prevents combination. The amount of stearyl chloride combining increases with the concentration of the sodium hydroxide up to 15 vol. %; it then remains constant to 35%, after which a further increase takes place. The curve thus obtained is similar to that of Vieweg for the amount

of alkali combining with cellulose. With naphthoyl chloride the amount of combination is constant from 20 to 45% of sodium hydroxide, but with benzoyl chloride there is a continuous increase up to 45%.

The addition of small quantities of sodium chloride to 13 or 15% sodium hydroxide, used in preparing alkali-cellulose, slightly increases the ability of the latter to combine with stearyl chloride. More sodium chloride has the reverse effect, but this is probably due to its influence on the esterification reaction. The addition of sodium carbonate to 15% sodium hydroxide increases the amount of combination. The addition of alcohol to sodium hydroxide of any concentration results in increased combining power, but the form of the curve, concentration–% combination, remains similar. It is concluded that the addition of alcohol causes further alkali to combine with the cellulose both chemically and physically. A. GEAKE.

Action of organo-magnesium compounds on nitriles. α-Aminonitriles. M. VELGHE.—See this vol., 1044.

Basis for the physiological activity of certain -onium compounds. V. Mobilities of the -onium ions. II. I. BENCOWITZ and R. R. RENSHAW (J. Amer. Chem. Soc., 1926, **48**, 2146—2155; cf. this vol., 497).—From conductivity measurements of aqueous solutions of tetramethylammonium bromide, tetraethylammonium chloride, and tetrapropylammonium iodide, values for the Λ_∞ of the tetramethyl-, tetraethyl-, and tetrapropyl-ammonium ion of 46·90, 34·09, and 23·57, respectively, are calculated. The Λ_c–$\sqrt{C}$ graphs of the above three alkylammonium salts, as well as those of two alkylsulphonium salts (cf. A., 1925, ii, 872), form straight lines. F. G. WILLSON.

Residual affinity and co-ordination. XXVIII. Ethylenediammine copper salts. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1926, 2018—2027).—The stabilising effect of ethylenediamine in preventing the change from cupric to cuprous compounds containing the iodide and cyanide radicals has been investigated. Cuprous iodide in the presence of aqueous ethylenediamine is rapidly oxidised by air to give *diaquobisethylenediamminocupric iodide*, $[2H_2O,Cu,2en]I_2$, which is stable in moist air; desiccation of this compound over sulphuric acid yields *monoaquobisethylenediamminocupric iodide*, $[H_2O,Cu,2en]I_2$, which reverts to the monoaquo-compound in a moist atmosphere. *Methanolbisethylenediamminocupric iodide*, $[MeOH,Cu,2en]I_2$, m. p. 225—230° (decomp.), separates on addition of methyl alcohol to a concentrated aqueous solution hydrated compound. Other complex co-ordination compounds are described. *Monoaquobisethylenediamminocupric cuprocyanide*, $[Cu,2en,H_2O][Cu(CN)_2]_2$, which on heating passes into *bisethylenediamminocupric dicuprocyanide*, $[Cu,2en][Cu_2(CN)_3]_2$; *monoaquobisethylenediamminodicupric cuprocyanide*, $[en{\cdot\cdot}Cu{\cdot\cdot}OH_2{\cdot\cdot}Cu{\cdot\cdot}en][Cu(CN)_2]_2$; a *compound*, $Cu_5(CN)_6,9C_2H_4(NH_2)_2,H_2CO_3,3H_2O$; *ethylenediammonium tricuprocyanide*, $[CH_2{\cdot}NH_3]_2[Cu_3(CN)_5]$ in hemihydrated and anhydrous forms; *ethylenediammonium cuprochloride* and *cuprobromide*, $[CH_2{\cdot}NH_3]_2[CuX_2]_2$. *Tetra-aquoethylenediammino-cupric perchlorate*, $[Cu,en,4H_2O][ClO_4]_2$, and *bismethanolbisethylenediamminocupric cyanate tetrahydrate*, $[Cu,2en,2MeOH](CNO)_2,4H_2O$, are also described. C. J. STILL.

Optical activity of cysteine. J. C. ANDREWS (J. Biol. Chem., 1926, **69**, 209—217).—The most complete reduction of cystine to cysteine was obtained by the use of tin and hydrochloric acid in large excess or by electrolytic reduction; in the latter case, racemisation occurred unless the solution was well cooled. Starting with *l*-cystine having $[\alpha]_D^{20}$ −215·5°, preparations of cysteine were obtained with $[\alpha]_D^{20}$ +9·7°. C. R. HARINGTON.

Urethanes. I. Mono- and di-carbethoxyguanidines: dicarbethoxyethyl*iso*carbamide. S. BASTERFIELD and L. E. PAYNTER (J. Amer. Chem. Soc., 1926, **48**, 2176—2179).—Dicarbethoxyguanidine has m. p. 165°, and monocarbethoxyguanidine m. p. 98° (hydrated) or 114° (anhydrous) (cf. Nencki, Ber., 1874, **7**, 1588). The former is practically inert pharmacologically, but the latter, when injected intravenously in aqueous solution, produces mild central depression with muscular hypertonus. Dicarbethoxyethyl*iso*carbamide (cf. Dains, A., 1899, i, 592) produces complete muscular relaxation in 20 min. F. G. WILLSON.

Production of formamide and hydrocyanic acid. BADISCHE ANILIN- U. SODA-FABR.—See B., 1926, 770.

Action of organo-magnesium compounds on nitriles. Benzoyl cyanide. A. DE COSTER (Bull. Soc. chim. Belg., 1926, **35**, 235—238).—Magnesium phenyl, benzyl, and ethyl bromides act on benzoyl cyanide to give a good yield of triphenylcarbinol, phenyldibenzylcarbinol, and phenyldiethylcarbinol, respectively. In the last case, there is also produced a little of the *hydrocyanide* (m. p. 117—119°) of *α-imino-α-benzoylpropane* (corresponding *hydrochloride*, m. p. 137—139°). G. M. BENNETT.

Trimeric crotononitrile. P. BRUYLANTS and L. MATHUS (Bull. Soc. chim. Belg., 1926, **35**, 239—253; cf. A., 1923, i, 311, 762).—The action of magnesium ethyl bromide on β-ethoxybutyronitrile, β-chlorobutyronitrile, β-dimethylaminobutyronitrile, or the isomeric crotononitriles produces a viscous mixture of polymeric crotononitriles from which is obtained a small yield of the trimeride, m. p. 174°. This substance is saturated, being converted by bromine into a *monobromo*-compound, $C_{12}H_{14}N_3Br$, m. p. 131°; it is also neutral and is inert towards alkyl iodides, picric, chloroplatinic, and nitrous acids. Hydrolysis with concentrated hydrochloric acid yields the *acid*, $C_{11}H_{15}N_2{\cdot}CO_2H$, m. p. 109°, which is converted by potassium permanganate in alkaline solution into the dibasic *acid*, $C_{10}H_{15}N(CO_2H)_2$, m. p. 179°, but is oxidised by nitric acid to the *acid*, $C_8H_{16}(CO_2H)_2$, m. p. 195° (*calcium* salt). A small quantity of *δ-ethyl-Δ$^{\beta}$-hexen-δ-ol*, b. p. 150—154°, was also isolated from the products of the original reaction. G. M. BENNETT.

Reversibility of triazan formation. K. E. Cooper and E. H. Ingold (J.C.S., 1926, 1894—1896).—The reversible formation of ethyl 1-phenyltriazan-2 : 3-dicarboxylate from aniline and ethyl azodicarboxylate is studied quantitatively. The preparation of *azodicarboxymethylamide*, m. p. 170° (decomp.), from methylamine and ethyl azodicarboxylate, of *hydrazinedicarboxymethylamide*, m. p. 247°, by reducing the azo-methylamide with aniline or hydrogen sulphide, and of hydrazinedicarboxyamide, m. p. 243—244°, by reducing azodicarboxyamide with aniline, is described. J. S. H. Davies.

Germanium. XVI. Germanium tetramethyl. Analysis by combustion of a liquid containing carbon and hydrogen. L. M. Dennis and F. E. Hance (J. Physical Chem., 1926, **30**, 1055—1059).—*Germanium tetramethyl*, prepared by the Grignard reaction, has m. p. approximately −88°, b. p. 43·4°, d^0 1·003—1·009, $n^{23·5}$ 1·3868. L. S. Theobald.

Tin alkyl compounds. I. Some stannoethanes. II. Trimethylbenzylstannane. C. A. Kraus and R. H. Bullard (J. Amer. Chem. Soc., 1926, **48**, 2131—2136).—*Trimethyltriethyldistannane*, liquid, obtained by condensation of sodium trimethylstannide with tin triethyl bromide, or of sodium triethylstannide with tin trimethyl bromide, is decomposed in boiling benzene, with formation of hexamethyl- and hexaethyl-distannanes. *Trimethyltriphenyldistannane*, m. p. 106°, is obtained quantitatively by condensation of sodium triphenylstannide with tin trimethyl bromide in liquid ammonia, but similar condensation of sodium trimethylstannide with tin triphenyl bromide affords also hexamethyl- and hexaphenyl-distannanes. *Trimethylbenzylstannane*, liquid, decomp. 215°, obtained from benzyl chloride and sodium trimethylstannide, affords benzyl bromide and tin trimethyl bromide when brominated in ethereal solution (cf. Grüttner and Krause, A., 1916, i, 684; 1917, i, 256; 1918, i, 158).
F. G. Willson.

Modification of Baeyer's strain theory. I. W. F. Short (Chem. News, 1926, **133**, 145—150).—The energy contents of the *cyclo*propane and *cyclo*butane rings are in agreement with the Baeyer strain angles when the thermal values obtained are divided by the number of carbon atoms in the ring (cf. Ingold, J.C.S., 1921, **119**, 305). The expression used by Ingold in calculating the angle between the carbon-to-carbon valencies is criticised and a new expression is given, based on the assumption that the angular space between the domains of each pair of attached carbon atoms subtended at the centre of the central atom is the same. This expression gives results in agreement with the relative ease of formation of the *cyclo*propane and *cyclo*butane rings, but not with their relative stabilities. It is concluded that the main factors controlling the relative ease of formation of carbon rings are (*a*) the "activities" of the atoms eliminated in ring formation as influenced by general and alternating polar effects produced by polar atoms, and (*b*) the spatial proximity of the polar atoms eliminated in ring formation. The second factor is most satisfactorily measured by the "approach values" calculated from the "normal" angle deduced by the tangent method. Ruzicka's assertion that a double linking is more easily formed than any other ring system (this vol., 727) is not valid in all cases (cf. Ingold, *loc. cit.*). The stability of a carbon ring system is measured approximately by the angle of strain, and, except in extreme cases when strongly polar groups are present, polar conditions in the ring will not exert a powerful influence on the relative ease of ring fission.
R. Brightman.

Oxidation in the benzene series by gaseous oxygen. I. Oxidation of methylbenzenes. H. N. Stephens (J. Amer. Chem. Soc., 1926, **48**, 1824—1826).—Methylbenzenes are oxidised by dry oxygen in diffused daylight at 100° in two stages, the first and main product being the aldehyde, which is subsequently partly oxidised to the acid. The rate of oxidation increases with accumulation of methyl groups in the molecule, but in no case was there indication of the oxidation of more than one methyl group. The presence of water retards the oxidation and in the case of *m*-xylene and mesitylene almost entirely inhibits the reaction. Appreciable amounts of reddish-brown gum or solid resin are formed in all cases, and in the case of cymene the cumaldehyde and cumic acid are also accompanied by some *p*-tolyl methyl ketone. R. Brightman.

Dimagnesium derivatives of benzene compounds. G. Bruhat and V. Thomas (Compt. rend., 1926, **183**, 297—299; cf. A., 1925, i, 1055).—The dimagnesium derivatives of *o*-, *m*-, and *p*-di-iodobenzene react with water, giving benzene; the *m*- and *p*-compounds react with carbon dioxide, giving *iso*phthalic and terephthalic acids, respectively, whilst the *o*-compound does not react in this way, benzoic acid being obtained. Benzonitrile reacts with the *o*-compound, giving *o*-dibenzoylbenzene and a small amount of benzophenone, with the *m*-compound, giving *iso*phthalophenone, and with the *p*-compound, giving terephthalophenone (oxime, m. p. 256—258°), and a *compound*, m. p. 160°. The dimagnesium derivatives react with aldehydes, and the products so obtained are decomposed by water, giving resinous products containing glycols which are not easily isolated; the *o*- and *p*-compounds react with benzophenone and the complexes obtained are decomposed by water, yielding tertiary glycols, whilst *m*-di-iodobenzene under these conditions yields a *compound*, m. p. about 213°. L. F. Hewitt.

2 : 3 : 4-Trinitrotoluene. F. H. Gornall and R. Robinson (J.C.S., 1926, 1981—1984).—2 : 3 : 4-Trinitrotoluene, obtained from crude trinitrotoluene residues, was converted by the action of aqueous sodium sulphite into sodium 2 : 4-dinitrotoluene-3-sulphonate, which on reduction gave *sodium 2 : 4-diaminotoluene-3-sulphonate*; this compound, as well as its *monoacetyl* derivative, has been used as a component for the preparation of a number of azo-dyes; a *monobenzoyl* derivative is also described. Oxidation of sodium 2 : 4-dinitrotoluene-3-sulphonate with alkaline permanganate yields sodium 2 : 4-*dinitro*-3-*sulphobenzoate*. 2 : 3 : 4-*Triaminotoluene*, m. p. 106°,

is produced by reduction of the 2 : 4-dinitro-*m*-toluidine obtained by heating 2 : 3 : 4-trinitrotoluene with alcoholic ammonia. 2 : 4-*Dinitro*-3-*methoxytoluene*, m. p. 86°, is obtained by the action of methyl-alcoholic potassium hydroxide on 2 : 3 : 4-trinitrotoluene, and also by methylation of 2 : 4-dinitro-*m*-cresol. 2 : 4-*Dinitro*-3-*benzylaminotoluene*, by condensation of 2 : 3 : 4-trinitrotoluene with benzylamine, has m. p. 115—116°, and the corresponding dibenzylamine derivative, m. p. 87—88°; other condensation products with amines are : 2 : 4-*dinitro*-m-*tolylpiperidine*, m. p. 101°, and 2 : 4-*dinitro*-m-*tolyl*-α-*naphthylamine*, m. p. 169—170° (decomp.). C. J. STILL.

Orientation effects in the diphenyl series. III. Mononitro-4 : 4′-dihalogenodiphenyls and allied compounds. R. J. W. LE FÈVRE and E. E. TURNER (J.C.S., 1926, 2041—2049).—The 4 : 4′-dibromo-2-nitrodiphenyl obtained by Lellmann (A., 1883, 343) has now been prepared by the regulated nitration of 4 : 4′-dibromodiphenyl, and by a similar process 4 : 4′-*dichloro*-2-*nitrodiphenyl*, m. p. 102°, is produced. 4 : 4′-*Dibromo*-3-*nitrodiphenyl*, m. p. 101—102°, when nitrated, yields a mixture of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl and 4 : 4′-dibromo-3 : 3′-dinitrodiphenyl, whereas 4 : 4′-dibromo-2-nitrodiphenyl gives a quantitative yield of 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl. Nitration of 4-bromo-2′-nitrodiphenyl and of 4-bromo-4′-nitrodiphenyl gives rise to the same product, 4-*bromo*-2′ : 3 : 4′-*trinitrodiphenyl*, m. p. 176—177°, and this, on treatment with piperidine, yields 2′ : 3 : 4′-*trinitro*-4-*piperidinodiphenyl*, m. p. 144—145°. The product obtained from 2-nitrobenzidine by the perbromide method of Griess and Saunders is believed to be 3′ : 4 : 4′-*tribromo*-2-*nitrodiphenyl*, and has m. p. 195—196°.

The preparation of 3-nitrobenzidine by the method of Koller (A., 1904, i, 778) was unsuccessful, as considerable quantities of 2-nitrobenzidine are produced instead.

Anilino-, methylanilino-, piperazino-, and some other derivatives of 4 : 4′-dichloro- and 4 : 4′-dibromo-2 : 3′-dinitrodiphenyls are described. 4-*Bromo*-2 : 3′-*dinitro*-4′-*anilinodiphenyl*, m. p. 151°, 4-*chloro*-2 : 3′-*dinitro*-4′-*anilinodiphenyl*, m. p. 129—130°, 4-*bromo*-2 : 3′-*dinitro*-4′-*methylanilinodiphenyl*, m. p. 142—143°, 4-*chloro*-2 : 3′-*dinitro*-4′-*methylanilinodiphenyl*, m. p. 134°, 4-*bromo*-2 : 3′-*dinitro*-4′-*phenoxydiphenyl*, m. p. 124—125°, 4-*chloro*-2 : 3′-*dinitro*-4′-*phenoxydiphenyl*, m. p. 113°, 4-*bromo*-2 : 3′-*dinitro*-4′-*piperazinodiphenyl*, m. p. 250°, 4-*chloro*-2 : 3′-*dinitro*-4′-*piperazinodiphenyl*, 4-*chloro*-2 : 3′-*dinitro*-4′-*aminodiphenyl*, m. p. 218—219°, 4-*bromo*-2 : 3′-*dinitro*-4′-*aminodiphenyl*, m. p. 219°. Products were also obtained from 4 : 4′-dibromo-3 : 3′-dinitrodiphenyl : 3 : 3′-*dinitro*-4 : 4′-*dianilinodiphenyl*, m. p. 242°, 3 : 3′-*dinitro*-4 : 4′-*dimethylanilinodiphenyl*, m. p. 250°, 3 : 3′-*dinitro*-4 : 4′-*diphenoxydiphenyl*, m. p. 139—140°. C. J. STILL.

β-Xenylhydroxylamine and its rearrangement. H. GILMAN and J. E. KIRBY (J. Amer. Chem. Soc., 1926, **48**, 2190—2193).—Reduction of *p*-nitrodiphenyl with zinc dust and ammonium chloride in 95% alcohol affords p-*hydroxylaminodiphenyl* (β-*xenylhydroxylamine*), m. p. 158° (decomp.) after softening. This is stable only in presence of dilute acetic acid, in absence of which it oxidises rapidly to 4 : 4′-azoxybisdiphenyl, m. p. 207·5° (cf. Zimmermann, A., 1881, 175). It does not rearrange to 4-amino-4′-hydroxydiphenyl. Condensation with benzaldehyde affords the *compound*, $CHPh{:}NO{\cdot}C_6H_4Ph$, m. p. 174—175° (cf. Gattermann, A., 1897, i, 189).

F. G. WILLSON.

Nitro- and *gem*-dinitro-ethylenes. P. LIPP [with W. LÜDICKE, N. KALINOV, and A. P. PETKOV] (Annalen, 1926, **449**, 15—29).—Nitrous gases from nitrite and sulphuric acid react with αα-diphenylethylene in light petroleum at low temperatures to give a blue, oily nitrosite, which on keeping at 0° evolves gas and forms β-nitro-αα-diphenylethyl alcohol, m. p. 106—107°, and β-nitro-αα-diphenylethylene, m. p. 86°, the latter being most readily obtained by heating the blue oil with acetyl chloride. Nitrodiphenylethylene is decomposed by boiling alcoholic potassium hydroxide into benzophenone and probably nitroacetic acid. ββ-Dinitro-αα-diphenylethylene (Anschütz and Romig, A., 1886, 1033) reacts with boiling methyl-alcoholic potassium hydroxide to give ββ-*dinitro*-αα-*diphenylethyl alcohol* [from the *potassium* salt, $CPh_2(OH){\cdot}C(NO_2){:}NO_2K$, by the action of water], which quickly decomposes into benzophenone and dinitromethane.

β-Nitro-αα-diphenylethylene is reduced by aluminium amalgam in ether to αα-diphenylethylamine (cf. Konovalov and Jatzewitsch, A., 1905, i, 763, who obtained a "syrupy base" and a hydrochloride, m. p. 170—173°), m. p. about 35—40°, b. p. 149°/4 mm. (corr.) (hydrochloride, m. p. 263—265°; *phenylcarbamide*, m. p. 191—192°; phenylthiocarbamide, m. p. 172—173°). The neutral products of the reduction are *bis*(*diphenylvinyl*)*amine*, m. p. 142—146°, and diphenylacetaldoxime, m. p. 110—115°, b. p. 156—158°/0·3 mm. (corr.). The secondary amine is hydrolysed by cold hydrochloric–acetic acid to diphenylacetaldehyde, b. p. about 170°/12 mm. (semicarbazone, m. p. 161—163°).

ββ-Dinitro-αα-diphenylethylene is similarly reduced to diphenylacetamidoxime, m. p. 138—139° (hydrochloride, decomp. about 190°), which is also prepared from diphenylacetonitrile and hydroxylamine together with (probably) diphenylacetamide, m. p. 171—172°. Diphenylacetonitrile, m. p. 73—74°, b. p. 134°/0·6 mm., is amongst the neutral products of reduction. C. HOLLINS.

Action of sunlight on tetranitrostilbene. A. PLISSOV (Ukraine Chem. J., 1925, **1**, 643).—A solution of tetranitrostilbene in pyridine is coloured bright green in sunlight. The constitution of the substance formed, m. p. 219°, is not known.

S. BOTCHARSKY.

Replaceability of the halogen atom in 2-chloro- and 2-bromo-1 : 6 : 8-trinitronaphthalene. E. J. VAN DER KAM (Rec. trav. chim., 1926, **45**, 564—581).—Trinitration of 2-chloro-, 2-bromo-, 2-methoxy-, and 2-ethoxy-naphthalene furnishes the corresponding 1 : 6 : 8-*trinitro*-derivatives, m. p. 194°, 205°, 215°, and 186°, respectively, together with lower nitration

products. The substituents in position 2 are replaced by the amino- or methylamino-group on treatment with the requisite reagents in alcoholic solution at 100° under pressure, yielding 1 : 6 : 8-*trinitro*-β-*naphthylamine*, m. p. 300° (decomp.), and 1 : 6 : 8-*trinitro*-β-*naphthylmethylamine*, m. p. 257° (decomp.), respectively. The former yields 4 : 6-dinitrophthalic acid with alkaline permanganate. Reaction velocity determinations show that the replacement of the halogen atoms by ethoxyl is more rapid than by methoxyl, that the chlorine atom is more readily replaced by alkyloxy-groups than is the bromine atom, and that, from the point of view of replacement by methoxyl, the chloro-compound is twice or three times as reactive as the bromo-compound, and is intermediate between chloro-2 : 4-dinitro- and chloro-2 : 4 : 6-trinitro-benzene.

J. S. H. DAVIS.

Alkylanthracenes and "transannular tautomerism." E. DE B. BARNETT and M. A. MATTHEWS (Ber., 1926, **59**, [*B*], 1429—1438).—Evidence is adduced in favour of the view that alkylidene-9 : 10-dihydroanthracenes are intermediately formed during reactions of alkylanthracenes. Since the migration of a hydrogen atom across the central ring is involved, the term "transannular tautomerism" is suggested.

9-Methylanthracene is converted by the calculated quantity of bromine in carbon disulphide into 10-*bromo*-9-*methylanthracene*, m. p. 173°, and by the halogen (2 mols.) into 10-*bromo*-9-*bromomethylanthracene*, m. p. 200° [corresponding *pyridinium* salt, m. p. 232° (decomp.)], [giving 10-*bromo*-9-*acetoxymethylanthracene*, m. p. 167°, and 10-*bromo*-9-*hydroxymethylanthracene*, m. p. 229° (decomp.) after darkening at 200°]. 9-Methylanthracene and bromine (4 mols.) afford 10-*bromo*-9-*bromomethylanthracene tetrabromide*, m. p. 140° (decomp.), oxidised by chromic acid to 2 : 3-dibromoanthraquinone. 9-Ethylanthracene yields successively 10-*bromo*-9-*ethylanthracene*, m. p. 104°, and 10-*bromo*-9-*ethylanthracene tetrabromide*, m. p. 177° (decomp.); the latter substance is converted by potassium hydroxide into 2 : 3 : 10-*tribromo*-9-*ethylanthracene*, m. p. 169°, oxidised to 2 : 3-dibromoanthraquinone. 9-iso*Propylanthracene*, m. p. 76°, prepared from anthrone and magnesium *iso*propyl bromide, gives 10-*bromo*-9-iso*propylanthracene*, m. p. 97°, 10-*bromo*-9-iso*propylanthracene tetrabromide*, m. p. 163° (decomp.), and 2 : 3 : 10-*tribromo*-9-iso*propylanthracene*, m. p. 210°, oxidised to 2 : 3-dibromoanthraquinone. 10-*Bromo*-9-iso*amylanthracene tetrabromide*, m. p. 162° (decomp.), and 2 : 3 : 10-*tribromo*-9-iso*amylanthracene*, m. p. 121°, are described. 9 : 10-*Dimethylanthracene*, m. p. 181° [picrate, m. p. 175—176° (decomp.)], prepared from 9-methylanthrone and magnesium methyl iodide, is identical with the substance described as 9 : 10-dimethyl-9 : 10-dihydroanthracene; with bromine it affords 9 : 10-*dibromomethylanthracene*, darkening at 315° [*dipyridinium* salt; *picrate*, m. p. 247° (decomp.)]. 10-*Phenyl*-9-*methylanthracene*, m. p. 112°, prepared from 9-methylanthrone and magnesium phenyl bromide or phenylanthrone and magnesium methyl iodide yields 10-*phenyl*-9-*bromomethylanthracene*, m. p. 177°, whereas 9 : 10-*diphenylanthracene*, m. p. 241—243°, affords 9 : 10-*diphenylanthracene tetrabromide*, m. p. 160° (decomp.).

H. WREN.

Mechanism of substitution reactions in the aromatic nucleus. VII. E. DE B. BARNETT, M. A. MATTHEWS, and J. L. WILTSHIRE Rec. trav. chim., 1926, **45**, 558—563).—1 : 4-Dichloroanthracene, m. p. 180°, forms a stable *dibromide*, m. p. 169° (decomp.), which has the *cis*-configuration, and on boiling with toluene reverts to the parent compound. With aniline, methylaniline, dimethylaniline, and piperidine, the dibromide forms 1 : 4-*dichloro*-9 : 10-*dianilino*-, *dimethyldianilino*-, *tetramethyldiaminodiphenyl*-, and *dipiperidino*-9 : 10-*dihydroanthracene*, m. p. 141°, 214°, 297°, 198°, respectively, without re-establishment of the "bridge" linking. With pyridine, 1 : 4-*dichloro*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide* is formed, which, in common with most salts of this type, loses 1 mol. of pyridine bromide on boiling in aqueous solution, and forms 1 : 4-*dichloroanthranylpyridinium bromide*, m. p. 315° (decomp.), with re-establishment of the bridge. Unlike 1 : 5-dichloroanthracene dibromide, the 1 : 4-dichloro-isomeride, on hydrolysis with aqueous acetone in presence of calcium carbonate, yields only a single *dihydroxy*-derivative, m. p. 204° (decomp.), together with 1 : 4-dichloroanthracene. 2 : 3-Dichloroanthracene, m. p. 261°, does not form a dibromide, but instead 2 : 3-*dichloro*-9 : 10-*dibromoanthracene*, m. p. 244°. With nitric and acetic acids, it gives 2 : 3-*dichloro*-9-*nitroanthracene*, m. p. 232°, or a mixture of this with 2 : 3-*dichloro*-9-*nitro*-9 : 10-*dihydroanthranyl acetate*, m. p. 181° (decomp.), according to the conditions. 2 : 3-*Dichloroanthrone*, m. p. 202°, obtained by reducing 2 : 3-dichloroanthraquinone with tin and hydrochloric–acetic acid, or, better, with sulphuric acid and aluminium powder, appears to yield a pinacol condensation *product*, m. p. 210°, with zinc dust and acetic–hydrochloric acid, and when heated with pyridine and acetic anhydride yields 2 : 3-*dichloroanthranyl acetate*, m. p. 168°. Poor yields of 1 : 4-dichloroanthraquinone were obtained by the chromic acid oxidation of 1 : 4-*dichloroanthraquinone tetrachloride*, m. p. 255—257° (decomp.), prepared by the action of phosphorus pentachloride on quinizarin suspended in nitrobenzene, whilst synthesis from phthalic anhydride, *p*-dichlorobenzene, and aluminium chloride was unsuccessful.

J. S. H. DAVIES.

M. p. of 4-chloro-2 : 6-dibromoaniline. E. C. GILBERT (J. Amer. Chem. Soc., 1926, **48**, 2242).—4-Chloro-2 : 6-dibromoaniline has m. p. 92·9° (lit. 95° and 97°).

F. G. WILLSON.

Preparation and properties of *o*-toluidine. H. G. TANNER and P. A. LASSELLE (J. Amer. Chem. Soc., 1926, **48**, 2163—2166).—*o*-Toluidine, prepared synthetically from phthalimide, gives, when treated with potassium dichromate by Schoen's method (A., 1890, 839), a greenish-black precipitate, the filtrate from which is practically identical with that given by *p*-toluidine; the presence of traces of the *p*-compound in *o*-toluidine cannot therefore be recognised by this test. *o*-Toluidine has b. p. 200·6°/754·6 mm., d_{20}^{23} 1·0053, n_D^{23} 1·5688.

F. G. WILLSON.

Substituted amides. I. Preparation of substituted acetamides and the corresponding primary amines. H. O. NICHOLAS and J. E. L. ERICKSON (J. Amer. Chem. Soc., 1926, **48**, 2174—2176).—The yield of benzylacetamide obtained by heating acetamide with benzyl chloride is very small, owing to the production of a large proportion of ammonium chloride (cf. Rudolph, A., 1879, 921). Treatment of anhydrous acetamide with hydrogen bromide at 200—220° affords ammonium bromide and diacetamide. The following substituted acetamides were obtained by heating together 1·6 mols. of acetamide and 0·4 mol. of the appropriate alkyl bromide at 200—220°, the yields being quoted in brackets: benzyl-, m. p. 61°, b. p. 157°/2 mm. (80%); β-phenylethyl-, m. p. 45°, b. p. 154°/2 mm. (40%); ethyl-, b. p. 206° (66%); *n*-propyl-, b. p. 225° (70%); *n*-butyl-, b. p. 229° (66%); and *iso*amyl-acetamide, b. p. 232° (42%). Hydrolysis of the above acetamides affords the corresponding amines in 80—90% yields.

F. G. WILLSON.

Autoxidation and antioxygenic action. Catalytic action of various nitrogen compounds. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1926, **183**, 408—412; cf. A., 1923, ii, 308; 1924, i, 635, ii, 602, 841).—Of 83 nitrogen compounds examined, secondary amines, diamines, and aminophenols possess the strongest antioxygenic properties. Thus diphenylamine, monomethylaniline, *o*-, *m*-, and *p*-aminophenol, *p*-phenylenediamine, *p*-anisidine, and *p*-phenetidine at concentrations of 1 in 10,000 inhibit the autoxidation of acraldehyde, whilst with aniline, triphenylamine, and dimethylaniline a concentration of 1 in 1000 is necessary. *N*-Methyl derivatives of diamines or aminophenols are equally active, and derivatives such as tetramethyldiaminodiphenylmethane and Michler's ketone also possess antioxygenic properties, although in a lesser degree. Substitution of both amino- and phenolic groups, as in *p*-acetophenetidide, leads to inactivity, although *N*-acyl derivatives such as *o*-acetamidophenol are active. αα- and ββ-Dinaphthylamines are good stabilisers for acraldehyde, but cyclic compounds are much less active antioxidants, and pyridine and quinoline do not affect the autoxidation of benzaldehyde, although they are slightly active with furfuraldehyde. Amino-acids and amides generally have little or no antioxygenic properties. The following substances were used as autoxidants: acraldehyde, benzaldehyde, furfuraldehyde, heptaldehyde, propionaldehyde, styrene, turpentine, linseed oil, and sodium sulphite (10% aqueous solution).

R. BRIGHTMAN.

Dependence of rotatory power on chemical constitution. XXIX. Resolution of sulphoxides into their optically active forms. P. W. B. HARRISON, J. KENYON, and H. PHILLIPS (J.C.S., 1926, 2079—2090).—It is shown that mixed sulphoxides exist in enantiomorphous forms, and the formula $\bar{O}—\overset{+}{S}<^{R}_{R'}$ is proposed (cf. Phillips, this vol., 159). dl-p-*Aminophenyl* p-*tolyl sulphoxide*, m. p. 169—170° (*acetyl* derivative, m. p. 183—184°) (prepared, together with di-*p*-tolyl disulphoxide, by heating aniline and *p*-toluenesulphinic acid at 110—115°), is resolved, by use of *d*- and *l*-camphorsulphonic acids, into d-p-*aminophenyl* p-*tolyl sulphoxide*, m. p. 151°, $[\alpha]^{25}_{5461}$ +123° in ethyl alcohol (d-*camphorsulphonate*, m. p. 133—134°, $[\alpha]^{25}_{5461}$ +17·2° in ethyl alcohol; *acetyl* derivative, $[\alpha]^{25}_{5461}$ +66·4° in ethyl alcohol); and l-p-*aminophenyl* p-*tolyl sulphoxide*, m. p. 151°, $[\alpha]^{25}_{5461}$ −122° in ethyl alcohol (l-*camphorsulphonate*, m. p. 133—134°, $[\alpha]^{25}_{5461}$ −18·1° in ethyl alcohol; *acetyl* derivative, m. p. 173—174°, $[\alpha]^{25}_{5461}$ −66·2°). dl-m-*Carboxyphenyl methyl sulphoxide*, m. p. 170—172° (prepared by oxidation of an aqueous solution of *m*-methylthiolbenzoic acid by hydrogen peroxide in presence of potassium carbonate) is resolved, by means of brucine and *l*-menthylamine, into d-m-*carboxyphenyl methyl sulphoxide*, m. p. 134°, $[\alpha]_{5461}$ +137·6° in methyl alcohol (*brucine* salt, m. p. 136—137°; l-*menthylamine* salt, m. p. 171°, $[\alpha]_{5461}$ +68·9°) and l-m-*carboxyphenyl methyl sulphoxide*, m. p. 133°, $[\alpha]_{5461}$ − 133·5°. Optically inactive p-*acetamidophenyl*-p-*tolylsulphone*, m. p. 192—194°, is obtained by oxidation of *d*-*p*-acetamidophenyl *p*-tolyl sulphoxide, and also from *dl*-*p*-aminophenyl *p*-tolyl sulphoxide; *d*-*m*-carboxyphenyl methyl sulphoxide is oxidised to optically inactive *m*-carboxyphenylmethylsulphone. *l*-*p*-Aminophenyl *p*-tolyl sulphoxide, its acetyl derivative, and *d*-*m*-carboxyphenyl methyl sulphoxide exhibit complex rotatory dispersion. The sign of rotation of *l*-*p*-aminophenyl *p*-tolyl sulphoxide is reversed in hydrochloric acid solution; its rotatory power and that of *d*-*m*-carboxyphenyl methyl sulphoxide are tabulated for various wave-lengths and in different solvents.

F. M. HAMER.

Preparation of *N*-aralkylated aromatic amines [by hydrogenation of Schiff's bases]. J. D. RIEDEL A.-G.—See B., 1926, 771.

Preparation of s-diaminodiarylcarbamides. I. G. FARBENIND. A.-G. See B., 1926, 769.

Manufacture of diarylguanidines. BRIT. DYESTUFFS CORPN., C. J. T. CRONSHAW, and W. J. S. NAUNTON.—See B., 1926, 769.

Optically active dyes. III. Physical properties, dyeing reactions, and mechanism of dyeing. IV. Asymmetric dyes from *m*-aminomandelic acid. W. R. BRODE and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2193—2201, 2202—2206; cf. A., 1924, i, 1242).—III. The active isomerides of the optically active dyes previously prepared by coupling β-naphthol and dimethylaniline with *d*-, *l*-, and *dl*-*p*-diazobenzamidophenylacetic acid have the same physical properties, including adsorption by active and inert materials, colour, and fastness to light. Their rotatory dispersion curves, as well as those of the intermediates used, are normal. Whilst the racemic dyes appear to be adsorbed to a greater extent than the active substances by both active and inactive adsorbing agents, no apparent difference in adsorption of the two active forms could be detected, and it is considered that Morgan and Skinner's results (A., 1925, i, 1191) are probably due to experimental error.

Condensation of 5-benzeneazosalicylaldehyde with

α-2-hydroxy-1-naphthylbenzylamine affords 5-*benzeneazosalicylidene*-α-2-*hydroxy*-1-*naphthylbenzylamine*, yellow-orange, m. p. 210—212°, of which the active modifications, m. p. 220—225°, were prepared. These are too insoluble in water for dyeing experiments.

IV. Repetition of the experiments of Porter and Hirst (A., 1919, i, 558) and of Porter and Ihrig (A., 1923, i, 1027) have failed to confirm the observation of these authors that one of the optically active isomerides of these dyes is selectively adsorbed, and the data so far obtained indicate that dyeing is not a chemical process. The absorption spectra of the azo-dyes obtained by coupling diazotised *m*-aminomandelic acid with phenol and β-naphthol, respectively, are described with curves. F. G. Willson.

Halogen and nitro-derivatives of benzene- and toluene-azonaphthylamine, their solid diazonium salts, and conversion of the latter into the corresponding hydrazinesulphonic acids. J. Tröger and R. Schaefer (J. pr. Chem., 1926, [ii], **113**, 268—292).—The following compounds were prepared by addition of aqueous solutions of diazonium salts to alcoholic α-naphthylamine solution in presence of sodium acetate, at 35—50°: o-*chlorobenzeneazo*-α-*naphthylamine*, red-brown, m. p. 129°; m-*chlorobenzene*-, similar, m. p. 116° (hydrochloride, reddish-violet); o-*bromobenzene*-, red-brown, m. p. 117°; m-*bromobenzene*-, reddish-yellow, m. p. 103°; o-*nitrobenzene*-, dark red-brown, with green reflex, m. p. 170—171°; m-*nitrobenzene*-, light red, m. p. 179—180°; p-*nitrobenzene*-, blue-violet, m. p. 248°; 4-*nitro*-6-*methylbenzene*-, dark red, m. p. 198° (*hydrochloride*, violet-black); 3-*nitro*-2-*methylbenzene*-, light red, m. p. 202°; 5-*nitro*-2-*methylbenzene*-, red-brown, m. p. 186°; and 6-*nitro*-2-*methylbenzene-azo*-α-*naphthylamine*, deep red-brown, with green reflex, m. p. 162°. Diazotisation is effected by addition of powdered nitrite to suspensions of the above bases in hydrochloric acid, with subsequent agitation at temperatures up to 45°, the diazonium salts then crystallising from the warm solutions. o-*Chlorobenzeneazo*-α-*naphthalenediazonium chloride*, brown-yellow, loses nitrogen when kept. m-*Chlorobenzeneazo*-α-*naphthalene-azoresorcinol*, brown, amorphous, and -*azo*-β-*naphthol*, violet-brown, were prepared from m-*chlorobenzeneazo*-α-*naphthalenediazonium chloride*, brown-yellow. The following compounds, prepared analogously, are described: o-*bromobenzeneazo*-α-*naphthalenediazonium chloride*, yellowish-brown; m-*bromobenzeneazo*-α-*naphthalenediazonium chloride*, red-brown, decomp. when kept a few hrs.; p-*bromobenzeneazo*-α-*naphthalenediazonium chloride*, cherry-red; p-*bromobenzeneazo*-α-*naphthaleneazoresorcinol*, dark red; p-*bromobenzeneazo*-α-*naphthaleneazo*-β-*naphthol*, dark violet; o-*nitrobenzeneazo*-α-*naphthalenediazonium chloride*, light brown; m-*nitrobenzeneazo*-α-*naphthalenediazonium chloride*, reddish-brown; p-*nitrobenzeneazo*-α-*naphthalenediazonium chloride*, similar; 3-*nitro*-2-*methylbenzeneazo*-α-*naphthalenediazonium chloride*, loam-coloured; 4-*nitro*-2-*methylbenzeneazo*-α-*naphthalenediazonium chloride*, yellow-brown; 4-*nitro*-2-*methylbenzeneazo*-α-*naphthaleneazoresorcinol*, dark violet; 4-*nitro*-2-*methylbenzeneazo*-α-*naphthalene*-β-*naphthol*, similar; 5-*nitro*-2-*methylbenzeneazo*-α-*naphthalenediazonium chloride*, yellow-brown; and 6-*nitro*-2-*methylbenzeneazo*-α-*naphthalenediazonium chloride*, similar. In the above chloro-, bromo-, and nitro-benzene derivatives, the *ortho*-, *meta*-, and *ortho*-compounds, respectively, are the most stable, whilst in the toluene group the 5-nitro-derivatives are the most stable. Treatment of the above diazonium salts with aqueous alkaline hydrogen sulphite affords the corresponding diazosulphonates, which are converted, on reduction with ammonium sulphide or stannous chloride, into the corresponding hydrazinesulphonic acids (cf. Tröger and Piotrowski, A., 1917, i, 669). The following are described: *sodium* m-*chlorobenzeneazo*-α-*naphthalenediazosulphonate*, blood-red (labile) or golden-yellow; m-*chlorobenzeneazo*-α-*naphthylhydrazinesulphonic acid*, deep red (*salicylaldehyde* condensation product, yellowish-red, m. p. 155—157°); *sodium* o-*bromobenzeneazo*-α-*naphthalenediazosulphonate*, golden-yellow; *sodium* m-*bromobenzeneazo*-α-*naphthalenediazosulphonate*, similar; *sodium* p-*bromobenzeneazo*-α-*naphthalenediazosulphonate*, similar; p-*bromobenzeneazo*-α-*naphthylhydrazinesulphonic acid*, blue-black with green reflex (*salicylaldehyde* condensation product, wine-red, m. p. 198°); and *sodium* p-*nitrobenzeneazo*-α-*naphthalenediazosulphonate*, golden-yellow. 4-*Nitro*-2-*methylbenzeneazo*-α-*naphthylhydrazinesulphonic acid*, deep violet, is obtained by saturating a solution of the above corresponding diazonium chloride with sulphur dioxide, a similar reaction being also occasionally observed with *m*-chloro- and *p*-bromo-benzeneazo-α-naphthalenediazonium chlorides. *Sodium* 5-*nitro*-2-*methylbenzeneazo*-α-*naphthalenediazosulphonate*, reddish-yellow, yields the corresponding *acid*, brownish-black, on treatment with hydrochloric acid, and, on reduction with stannous chloride, 5-*nitro*-2-*methylbenzeneazo*-α-*naphthylhydrazinesulphonic acid*, reddish-violet (*salicylaldehyde* condensation product, magenta-red, m. p. 165°). F. G. Willson.

Chromium compounds of azo dyes. Soc. Chem. Ind. in Basle.—See B., 1926, 702.

Esterification of *cyclo*hexanol and some of its homologues. I. Viscosity, surface tension, and thermochemistry. (Mlle.) G. Cauquil.—See this vol., 914.

Alcohols of the hydroaromatic and terpene series. V. Geometrical and optical isomerism of the methyl*cyclo*hexanols. G. A. C. Gough, H. Hunter, and J. Kenyon (J.C.S., 1926, 2052—2071).—Two geometrically isomeric forms of 2-methyl*cyclo*hexanol, two of 3-methyl*cyclo*hexanol (all resolvable into optical antipodes), and two of 4-methyl*cyclo*hexanol are described. After hydrogenation of *o*-cresol, the methyl*cyclo*hexanols obtained by fractional distillation are converted into dl-α-2-*methyl*cyclo*hexyl hydrogen phthalate*, m. p. 124—125° (β-*eucaine* salt, m. p. 173—174°), which is hydrolysed to dl-α-2-*methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., d_4^{25} 0·9228, n_{5893}^{25} 1·4596, η^{25} 0·336 (*acetate*, b. p. 79—80°/20 mm., d_4^{25} 0·9430, n_{5893}^{25} 1·4389, η 0·0233; *phenylcarbamate*, m. p. 105—106°; p-*nitrobenzoate*, m. p. 65°; *hydrogen succinate*, m. p. 44—46°; p-*toluenesulphonate*, m. p. 27—28°), and dl-β-2-*methyl*cyclo*hexyl hydrogen phthalate*, m. p. 89—90° (β-*eucaine*

salt, m. p. 154°), or dl-β-2-*methyl*cyclo*hexyl* p-*nitrobenzoate*, m. p. 35—36°, may be prepared, either being hydrolysable to dl-β-2-*methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., d_4^{25} 0·9228, n_{5893}^{25} 1·4616, η^{25} 0·155 (*acetate*, b. p. 79—80°/20 mm., d_4^{25} 0·9434, n_{5893}^{25} 1·4376, η^{25} 0·0211; *phenylcarbamate*, m. p. 78—80°; *hydrogen succinate*, m. p. 30—31°). Similarly are obtained from *p*-cresol α-4-*methyl*cyclo*hexyl hydrogen phthalate*, m. p. 119—120° (β-*eucaine* salt, m. p. 170—171°), yielding α-4-*methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., d_4^{25} 0·9080, n_{5893}^{25} 1·4544, η^{25} 0·385 (*acetate*, b. p. 78—80°/20 mm., d_4^{25} 0·9380, n_{5893}^{25} 1·4373, η^{25} 0·0217; *phenylcarbamate*, m. p. 124—125°; p-*nitrobenzoate*, m. p. 67°; p-*toluenesulphonate*, m. p. 71—72°), and β-4-*methyl*cyclo*hexyl hydrogen phthalate*, m. p. 72—73° (β-*eucaine* salt, m. p. 170—171°), yielding β-4-*methyl*cyclo*hexanol*, b. p. 78—79°/20 mm., d_4^{25} 0·9180, n_{5893}^{25} 1·4584, η^{25} 0·247 (*acetate*, b. p. 78—79°/20 mm., d_4^{25} 0·9337, n_{5893}^{25} 1·4365, η^{25} 0·0196; *phenylcarbamate*, m. p. 124°; p-*nitrobenzoate*, m. p. 94°). From hydrogenated *m*-cresol are prepared dl-α-3-*methyl*cyclo*hexyl* p-*nitrobenzoate*, m. p. 58°, hydrolysable to dl-α-3-*methyl*cyclo*hexanol*, b. p. 77—79°/20 mm., d_4^{25} 0·9104, n_{5893}^{25} 1·4530, η^{25} 0·251 [*acetate*, b. p. 81—82°/20 mm., d_4^{25} 0·9454, n_{5893}^{25} 1·4313, η^{25} 0·0174; *hydrogen phthalate*, m. p. 93—94° (β-*eucaine* salt, m. p. 149—150°); *phenylcarbamate*, m. p. 92—93°; p-*toluenesulphonate*, m. p. 39—40°], and dl-β-3-*methyl*cyclo*hexyl* p-*nitrobenzoate*, m. p. 65°, hydrolysable to dl-β-3-*methyl*cyclo*hexanol*, b. p. 77—78°/20 mm., d_4^{25} 0·9091, n_{5893}^{25} 1·4554, η^{25} 0·197 [*acetate*, b. p. 78—79°/20 mm., d_4^{25} 0·9430, n_{5893}^{25} 1·4369, η^{25} 0·0195; *hydrogen phthalate*, m. p. 82—83° (β-*eucaine* salt, m. p. 171—172°); *phenylcarbamate*, m. p. 101—103°; p-*toluenesulphonate*, m. p. 46—47°]. With the methyl*cyclo*hexanols the convention is adopted of naming the more viscous isomeride the α- and the less viscous the β-; their viscosities, and those of their acetates, are studied, and the relationship between chemical constitution and viscosity is discussed (cf. Thole, J.C.S., 1912, **101**, 552); it appears that the α-isomerides are probably the *trans*- and the β- the *cis*-methyl*cyclo*hexanols. The proportions of α- and β-2-methyl*cyclo*hexanols, produced by various methods of preparation, have been investigated by means of a viscosity–composition diagram.

Crystallisation of the *strychnine* salt, m. p. 190°, of *dl*-α-2-methyl*cyclo*hexyl hydrogen phthalate gives rise to the d- and l-α-2-*methyl*cyclo*hexyl hydrogen phthalates*, $[\alpha]_{5893}$ ±63° in benzene, whence are obtained the d- and l-α-2-*methyl*cyclo*hexanols*, $[\alpha]_{6708}$ ±13° (l-α-2-*methyl*cyclo*hexyl acetate*, d_4^{20} 0·9458, α_{6708} −19·27°). By use of *l*-α-phenylethylamine and strychnine, *dl*-β-2-methyl*cyclo*hexyl hydrogen phthalate was resolved with difficulty into the α- and l-β-2-*methyl*cyclo*hexyl hydrogen phthalates*, $[\alpha]_{5461}$ +46° in benzene, whence are obtained d-β-2-*methyl*cyclo*hexanol* and l-β-2-*methyl*cyclo*hexanol*, d_4^{20} 0·9272, α_{6708}^{20} −4·62° (*acetate*, d_4^{20} 0·9454, α_{6708} −9·11°). *l*-α-2-Methyl*cyclo*hexanol is oxidised to l-2-*methyl*cyclo*hexanone*, b. p. 59—60°/20 mm., $[\alpha]_{4359}^{25}$ −43·0°, d_4^{25} 0·9230, and *l*-β-2-methyl*cyclo*hexanol to d-2-*methyl*cyclo*hexanone*, $[\alpha]_{5893}^{18}$ +14·21°, d_4^{18} 0·9262. Crystallisation of the *p*-nitrobenzoic esters of the 3-methyl*cyclo*hexanols, obtained by reduction of *d*-3-methyl*cyclo*hexanone (from pulegone), yields l-α-3-*methyl*cyclo*hexyl* p-*nitrobenzoate*, $[\alpha]_{5461}$ −3·8° in methyl alcohol, m. p. 45·5—46·5°, which is hydrolysed to l-α-3-*methyl*cyclo*hexanol*, $[\alpha]_{5461}^{26\cdot5}$ −4·22°, $d_4^{26\cdot5}$ 0·9131, η^{25} 0·251 (*hydrogen phthalate*, m. p. 94—95°, $[\alpha]_{5461}^{19}$ −17·39° in benzene; *acetate*, d_4^{16} 0·9511, α_{6708} −8·13°), oxidisable to d-3-*methyl*cyclo*hexanone*, b. p. 66—67°/25 mm., α_{5893}^{23} +11·54° (also obtained by oxidation of *l*-β-3-methyl*cyclo*hexanol).

dl-α-2-Methyl*cyclo*hexyl *p*-toluenesulphonate is converted by potassium acetate into a methyl*cyclo*hexyl acetate, which on hydrolysis yields *dl*-β-2-methyl*cyclo*hexanol (cf. Phillips, J.C.S., 1923, **123**, 43). Similarly, *dl*-α-3- and α-4-methyl*cyclo*hexyl *p*-toluenesulphonates give *dl*-β-3- and β-4-methyl*cyclo*hexanols, respectively. l-α-3-*Methyl*cyclo*hexyl* p-*toluenesulphonate*, m. p. 36—37°, $[\alpha]_{5461}^{19}$ −26·3° in benzene, is similarly converted into l-β-3-*methyl*cyclo*hexanol*, $d_4^{16\cdot5}$ 0·9245, α_{6708} −2·53°, η^{25} 0·196 (*acetate*, d_4^{20} 0·9448, α_{6708} −3·40°; *hydrogen phthalate*, m. p. 70—71°, $[\alpha]_{5461}^{19}$ −32·7° in benzene), and *dl*-β-3-methyl*cyclo*hexyl *p*-toluenesulphonate into *dl*-α-3-methyl*cyclo*hexanol. The density at different temperatures and rotatory power for different wave-lengths for some of the optically active methyl*cyclo*hexanols and their acetates are tabulated.

F. M. Hamer.

***cis–trans* Isomerism and steric hindrance. III. 2-*cyclo*Hexyl*cyclo*hexanols.** G. Vavon, Anziani, and Herynk (Bull. Soc. chim., 1926, [iv], **39**, 1138—1147).—When 2-*cyclo*hexyl*cyclo*hexanone is reduced using hydrogen and platinum-black it yields mainly *cis*-2-*cyclo*hexyl*cyclo*hexanol, b. p. 130—131°/10 mm., m. p. 60° (phenylurethane, m. p. 148°; *hydrogen succinate*, m. p. 114—114·5°; *hydrogen phthalate* in two interconvertible forms, m. p. 112—113° and 126—127°). If sodium and alcohol are used as the reducing agent *trans*-2-*cyclo*hexyl*cyclo*hexanol, m. p. 53—54° (phenylurethane, m. p. 132°; *hydrogen succinate*, m. p. 131°; *hydrogen phthalate*, m. p. 123—124°), is obtained. Steric considerations of *cyclo*hexyl derivatives suggest that the reactions of *cis*-forms should be much slower than those of the *trans*-isomerides (cf. Vavon, this vol., 837). Experiments on the esterification of *cis*- and *trans*-2-*cyclo*hexyl-*cyclo*hexanols show that the esterification rates of *cis*- and *trans*- are in the ratio 1 : 1·8, using acetic acid, and 1 : 4·5, using acetic acid containing 2% of sulphuric acid. Hydrolysis experiments also support this steric theory, the *trans*-hydrogen succinate hydrolysing thirty times as fast as the *cis*-isomeride and the *trans*-hydrogen phthalate thirteen to fourteen times as fast as the *cis*-form. R. W. West.

Colour reactions of phenols with sodium nitroprusside. L. Ekkert and L. W. Winkler (Pharm. Zentr., 1926, **67**, 566—568).—Characteristic colour reactions are obtained by pouring concentrated sulphuric acid to form a layer beneath an aqueous (or alcoholic) solution of a phenol, dusting sodium nitroprusside on to the surface, and shaking gently until the surface of contact becomes coloured. Thus with phenol the upper layer is red and the surface of contact dark green. On mixing the two layers, the liquid is first violet and then green. Addition

of a small quantity of water gives a bluish colour, excess of water a red, and ammonia to alkalinity a bluish-green. Distinctive colorations are similarly described for thymol, pyrocatechol, resorcinol, quinol, orcinol, pyrogallol, phloroglucinol, crude cresol, Fagi creosote, and α- and β-naphthol. R. BRIGHTMAN.

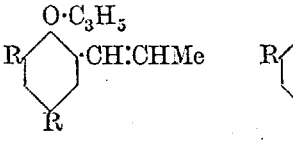
Use of leucotrope [phenylbenzyldimethylammonium chloride] as benzylating agent. H. BAW (J. Indian Chem. Soc., 1926, **3**, 101—104).—The benzylation of phenols by means of leucotrope and of the corresponding *m*- and *p*-nitrobenzyl compounds is described. o-, m- and p-*Chlorophenyl benzyl ethers* have been prepared, having b. p. 296°, m. p. 59°, and m. p. 71°, respectively, the last being identical with that obtained by Sintenis (Annalen, 1872, **161**, 345). 2 : 4-*Dichlorophenyl benzyl ether* has m. p. 60°. G. M. BENNETT.

Nitrosation of phenols. III. Nitrosation of 4-halogeno-*o*- and -*m*-cresols and oximation of the 4-halogeno-2 : 5-toluquinones. H. H. HODGSON and F. H. MOORE (J.C.S., 1926, 2036—2040; cf. *ibid.*, 1923, **123**, 2499; A., 1925, i, 1408).—Nitrosation of 4-chloro-*o*-cresol, 4-*bromo*-o-*cresol*, m. p. 78°, and 4-*iodo*-o-*cresol*, m. p. 65°, obtained from the 4-halogeno-*o*-nitrotoluenes by reduction and diazotisation, yields 4-*chloro*-5-*nitroso*-o-*cresol*, m. p. 197° (decomp.), 4-*bromo*-5-*nitroso*-o-*cresol*, m. p. 197° (decomp.), and 4-*iodo*-5-*nitroso*-o-*cresol*, m. p. 200° (decomp.), respectively. Reduction gives 4-*chloro*-5-*amino*-o-*cresol*, 4-bromo-5-amino-*o*-cresol, m. p. 189° (lit. m. p. 180°), and 4-*iodo*-5-*amino*-o-*cresol*, m. p. 170°. The three nitroso-*o*-cresols exist in only one modification, and the high m. p. of the chloro- and bromo-compounds compared with those of 4-nitroso-3-chlorophenol, m. p. 135°, and 5-nitroso-*o*-cresol, m. p. 134·5°, are accepted as evidence for their quinoneoxime structure. Support for this view is obtained from the behaviour of 4-*chloro*-m-*cresol*, m. p. 45°, and 4-*bromo*-m-*cresol*, m. p. 38°, which yield, on nitrosation, 4-*chloro*-6-*nitroso*-m-*cresol*, m. p. 191° (decomp.), and 4-*bromo*-6-*nitroso*-m-*cresol*, m. p. 190° (decomp.), which are also obtained by the action of hydroxylamine hydrochloride on 4-chloro- and 4-bromo-2 : 5-toluquinones. 4-Iodo-*m*-cresol gives 4-*iodo*-6-*nitroso*-m-*cresol*, m. p. 170° (decomp.), whereas the product of oximation of 4-*iodo*-2 : 5-*toluquinone*, m. p. 92°, decomposes at 181°. The difference is ascribed to impurity and not to isomerism. Reduction of the nitroso-*m*-cresols gives 4-chloro-6-amino-*m*-cresol, m. p. 227° (slight decomp.) (cf. Kehrmann, A., 1916, i, 657); 4-bromo-6-amino-*m*-cresol, m. p. 222° (slight decomp.) (cf. Kehrmann, A., 1899, i, 129, m. p. 205—208°). 4-*Iodo*-6-*amino*-m-*cresol*, prepared from the quinoneoxime, has m. p. 208°. 4-Chlorotoluquinone-5-monoxime has m. p. 190°, 4-bromotoluquinone-5-monoxime, m. p. 190°, and 4-iodotoluquinone-5-monoxime, m. p. 181° (decomp.). No isomerism could be detected (cf. Kehrmann, *loc. cit.*). M. CLARK.

3 : 5-Dihalogenophenols. H. H. HODGSON and J. S. WIGNALL (J.C.S., 1926, 2077—2079).—The 3-halogeno-5-nitroanisoles are prepared from 5-nitro-*m*-anisidine, m. p. 120°, and from them the 3-halogeno-5-nitrophenols. The 5-halogeno-*m*-anisidines are prepared from the corresponding nitro-compounds, and are converted into the 3 : 5-dihalogenoanisoles. The 3 : 5-dihalogenophenols are obtained by hydrolysing the 5-halogeno-*m*-anisidines, diazotising, and applying the Sandmeyer process. The following compounds are described: 3-*iodo*-5-*nitroanisole*, m. p. 84°; 3-*chloro*-5-*nitrophenyl benzoate*, m. p. 78°, *acetate*, m. p. 84°; 3-*bromo*-5-*nitrophenyl acetate*, m. p. 99°; 3-*iodo*-5-*nitrophenol*, m. p. 136°, *benzoate*, m. p. 100·5°, *acetate*, m. p. 110°; 2 : 4 : 6-*tribromo*-3-*iodo*-5-*nitrophenol*, m. p. 176°; 5-*chloro*-m-*anisidine*, m. p. 33°; 5-*bromo*-m-*anisidine*, m. p. 52°; 5-*iodo*-m-*anisidine*, m. p. 86·5°; 3-*chloro*-5-*iodoanisole*, b. p. 267—268°; 3 : 5-*di*-*iodoanisole*, m. p. 85°; 3-*chloro*-5-*bromoanisole*, m. p. 33°; 3-*bromo*-5-*iodoanisole*, m. p. 54°; 3 : 5-*dichlorophenyl benzoate*, m. p. 55°, *acetate*, m. p. 38°; 3 : 5-*dibromophenyl benzoate*, m. p. 77°, *acetate*, m. p. 53°; 3 : 5-*di*-*iodophenyl benzoate*, m. p. 93°; 2 : 4 : 6-*tribromo*-3 : 5-*di*-*iodophenol*, m. p. 226—228°; 3-*chloro*-5-*bromophenol*, m. p. 70°, *benzoate*, m. p. 62°, *acetate*, m. p. 45°; 3-*chloro*-2 : 4 : 5 : 6-*tetrabromophenol*, m. p. 205°; 3-*chloro*-5-*iodophenol*, m. p. 60°, *benzoate*, m. p. 54°, *acetate*, m. p. 47°; 3-*chloro*-2 : 4 : 6-*tribromo*-5-*iodophenol*, m. p. 195°; 3-*bromo*-5-*iodophenol*, m. p. 82·5°, *benzoate*, m. p. 76°, *acetate*, m. p. 46°; 2 : 3 : 4 : 6-*tetrabromo*-5-*iodophenol*, m. p. 220—221°. F. M. HAMER.

Action of sodium methoxide on some derivatives of o-dichlorobenzene. G. M. KRAAY (Diss., Amsterdam, 1926, 1—68).—*o*-Dichlorobenzene, substituted in the *p*-position by fluorine, chlorine, bromine, iodine, nitro-, sulphonic, methyl, carboxyl, amino-, hydroxyl, nitroso-, cyano-, formyl, or benzoyl atoms or groups, was treated with methyl-alcoholic sodium methoxide at 180°. A halogen atom is first replaced by a methoxyl group, the anisole then reacting further with sodium methoxide, giving the sodium derivative of a phenol and dimethyl ether. The following substances are described: 3 : 4-*dichlorofluorobenzene*, b. p. 171°; 3 : 4-*dichloroiodobenzene*, m. p. 30·5°; 3 : 4-*dichlorobenzonitrile*, m. p. 72·1°; 3 : 4-*dichloronitrosobenzene*, m. p. 88°; 3 : 4-*dichlorophenylhydroxylamine*, m. p. 75° (decomp.); 3 : 3′ : 4 : 4′-*tetrachloroazoxybenzene*, m. p. 139—139·5°; 3 : 4-*dichlorobenzyl alcohol*, m. p. 38°; 4-*chloro*-m-*cresol*, m. p. 46°; 2-*chloro*-5-*bromophenol*, m. p. 57°; 2-*chloro*-5-*iodophenol*, m. p. 56·5°; 2-*chloro*-5-*iodonitrobenzene*, m. p. 74·5°; 2-*chloro*-5-*iodoaniline*, m. p. 61·5°. Selective replacements of the halogens are discussed from the point of view of polarity. CHEMICAL ABSTRACTS.

Migration of allyl in phenyl allyl ethers from oxygen to an unsaturated *ortho* side-chain. L. CLAISEN and E. TIETZE (Annalen, 1926, **449**, 81—101).—The *O*-allyl group in phenyl allyl ethers of the type (I) is shown to migrate to the β-position in the side-chain, giving (II), the transformation being analogous to migration to a *para* carbon atom, *i.e.*, across two conjugated double linkings.

(I.)  (II.)

When m-4-*xylyl allyl ether*, b. p. 105·5°/15 mm., is heated under reflux, the temperature of the liquid rises from 224° to 238° in about 20 min. and is then constant, the ether having been converted into 5-*allyl*-m-4-*xylenol*, b. p. 245—245·5°/757 mm., 116—117°/11 mm. (*phenylurethane*, m. p. 109°; *methyl ether*, b. p. 230—233°). This, heated with a little pyridine hydrochloride, yields 2 : 5 : 7-*trimethylcoumaran*, b. p. 230—230·5°, or is reduced by the Paal–Skita method to 5-n-*propyl*-m-4-*xylenol*, m. p. 31—32°, b. p. 243·5—245°, 125—126°/17 mm. (*phenylurethane*, m. p. 112—112·5°). Allylxylenol is isomerised by hot methyl-alcoholic potassium hydroxide to 5-*propenyl*-m-4-*xylenol*, m. p. 73·5—74°, b. p. 134—136°/17 mm. (*phenylurethane*, m. p. 135·5—136°; *methyl ether*, b. p. 244—244·5°). 5-*Propenyl*-m-4-*xylyl allyl ether* (I, R = Me), b. p. 141·5—143°/17 mm., is converted by heating under reduced pressure into α-(2-*hydroxy*-3 : 5-*dimethylphenyl*)-β-*methyl*-$\Delta^{\alpha\delta}$-*pentadiene* (II, R=Me), b. p. 149—152°/16 mm. (*methyl ether*, b. p. 269° or 142°/14 mm.), from which may be obtained the $\Delta^{\alpha\gamma}$-*isomeride*, b. p. 158—161°/14 mm. (*methyl ether*, b. p. 155—158°/14 mm.), by the action of alcoholic alkali, and by the Paal–Skita reduction method α-(2-*hydroxy*-3 : 5-*dimethylphenyl*)-β-*methylpentane*, b. p. 144—146°/16·5 mm. No migration to either of the *meta*-positions occurs, for when the allyl ether of 5-allyl- or 5-propyl-*m*-4-xylenol is heated, the *O*-allyl group is eliminated in the form of diallyl (and, to a smaller extent, allene), leaving the free allyl- or propyl-xylenol.

Dihydroeugenol (2-methoxy-4-*n*-propylphenol), b. p. 249—250°/752 mm., 128°/15 mm. (phenylurethane, m. p. 117·5—118°), forms an *allyl ether*, b. p. 159°/16 mm., which is converted by heating in hydrogen at 190—200° into 2-*methoxy*-4-n-*propyl*-6-*allylphenol*, b. p. 282—283° or 157—158°/14·5 mm. (*phenylurethane*, m. p. 103·5°). The isomeric 2-*methoxy*-4-n-*propyl*-6-n-*propenylphenol*, m. p. 59·5—60°, b. p. 165—167°/15 mm. (*phenylurethane*, m. p. 98—99°), obtained by the action of methyl-alcoholic potassium hydroxide on the 6-allyl compound, gives an *allyl ether*, b. p. 174—176°/15 mm., which is converted by heating under reduced pressure into α-(2-*hydroxy*-3-*methoxy*-5-n-*propylphenyl*)-β-*methyl*-$\Delta^{\alpha\delta}$-*pentadiene*, b. p. 180°/12 mm. (*phenylurethane* syrupy, *methyl ether*, b. p. 166—169°/12 mm.).

Similarly, from 2 : 4-dichlorophenol are obtained 2 : 4-dichloro-6-allylphenol (phenylurethane, m. p. 120°), 2 : 4-*dichloro*-6-n-*propenylphenol*, m. p. 47—48°, b. p. 146—147°/15 mm. (prepared also from salicylaldehyde and ethyl magnesium bromide), its *allyl ether*, b. p. 156—157°/15 mm., and α-(2-*hydroxy*-3 : 5-*dichlorophenyl*)-β-*methyl*-$\Delta^{\alpha\delta}$-*pentadiene*, b. p. 169—172°/16 mm. C. Hollins.

Derivatives of homocatechol. I. F. R. Graesser-Thomas, J. M. Gulland, and R. Robinson (J.C.S., 1926, 1971—1976; cf. Oberlin, this vol., 283).—Treatment of *iso*creosol (4-methoxy-*m*-cresol; *acetyl* derivative, m. p. 56—57°; *benzoyl* derivative, m. p. 80—81°) in ethereal solution with nitrous acid yields 2 : 6-*dinitroisocreosol*, m. p. 152—153° (decomp.) [*sodium* salt; *phenylhydrazine* salt, $+2H_2O$, m. p. 109° (decomp.); *hydroxylamine* salt, pasty at 166°, m. p. 208°; *acetyl* derivative, m. p. 106°]. Nitration of acetylcreosol in acetic anhydride yields 6-nitroacetylcreosol together with 2 : 6-*dinitrohomocatechol*, m. p. 92°. Further nitration gives 2 : 6-dinitroacetylcreosol, m. p. 103° (cf. Oberlin, *loc. cit.*, m. p. 101—102°), hydrolysed to 2 : 6-dinitrocreosol, which yields a *quinoline* salt, m. p. 110° (decomp.) after treatment with cold fuming nitric acid. The *quinoline* salt of 3 : 5 : 6-trinitroguaiacol has m. p. 185° (decomp.). Methylation of 2 : 6-dinitro*iso*creosol or of 2 : 6-dinitrocreosol gives 2 : 6-dinitrohomoveratrole, m. p. 92° (Oberlin, m. p. 90—91°), which reacts with cotarnine in methyl alcohol to give *anhydrocotarnine*-2 : 6-*dinitrohomoveratrole*, m. p. 141°. M. Clark.

Derivatives of homocatechol. II. J. M. Gulland and R. Robinson (J.C.S., 1926, 1976—1981).—Homoveratrole-6-sulphonyl chloride, m. p. 75°, yields the amide, m. p. 193—194° (cf. Robinson, *ibid.*, 1917, **111**, 955, oily chloride yielding amide, m. p. 191°). Nitration of the chloride yields 5-*nitrohomoveratrole*-6-*sulphonyl chloride*, m. p. 140—141°. Nitration of *iso*creosol in ethereal solution gives a *compound*, m. p. 166—167°, and, under certain conditions, 2 : 6-dinitro*iso*creosol. Nitration of acetyl-*iso*creosol yields a *compound*, $C_9H_9O_5N$, m. p. 104—105° (probably 5-nitro-3-acetoxy-*p*-cresol, since treatment with alcoholic potassium hydroxide yields 5-nitrohomocatechol), and a *compound*, $C_{10}H_{11}O_5N$, m. p. 60—61° (probably 5-nitro-3-acetoxy-*p*-tolyl methyl ether). Reduction of 2 : 6-dinitro*iso*creosol with sodium sulphide yields 2-*nitro*-6-*amino*iso*creosol*, m. p. 168—169° (decomp.) [N-*acetyl* derivative $+H_2O$, m. p. 183° (*sodium* salt, yellow needles)]. Reduction of 2 : 6-dinitrohomoveratrole with sodium sulphide gives a mixture of bases, m. p. 90—100°, from which 2-nitro-6-aminohomoveratrole, m. p. 90—92° (cf. Oberlin, *loc. cit.*, m. p. 92—93° or 104—105°), is obtained through the *hydrochloride*, m. p. about 210°, or through the *piperonylidene* derivative, m. p. 130—132°. By the Sandmeyer reaction, the nitroamine gives 6-*bromo*-2-*nitrohomoveratrole*, m. p. 102°, and a *by-product*, m. p. 241°. The action of sulphurous acid and copper powder on the diazosulphate gives a neutral *compound*, $C_{18}H_{19}O_9N_5S$, m. p. 142°, and a little nitrohomoveratrolesulphinic acid, which yields, on oxidation and hydrolysis, a *nitrophenol*, m. p. 62°, probably 2-nitro-3-hydroxy-*p*-tolyl methyl ether. Reduction of nitrohomoveratrolediazonium chloride with stannous chloride gives a *nitrohydrazinohomoveratrole*, in two physical modifications, m. p. 147—149° and 163—164° (*piperonylidene* derivative, m. p. 172—173°), converted by oxidation with copper sulphate in dilute acetic acid solution followed by permanganate oxidation into a mixture of 2- and 6-nitroveratric acids. M. Clark.

Derivatives of guaiacol and veratrole substituted in the 3- and 6-positions. A. E. Oxford (J.C.S., 1926, 2004—2011).—The action of acetyl nitrate at −15° on *o*-anisyl acetate yields equal proportions of 3-*nitroguaiacol*, m. p. 68·5—69·5° (*sodium* salt; *acetyl* derivative, b. p. 168—169°/12—13 mm.; benzoyl derivative, m. p. 88—89°, identical with Meldola's benzoyl-*o*-nitroguaiacol,

Proc. C.S., 1896, **11**, 127), and 5-nitroguaiacol. The constitution of the 3-nitro-compound follows from formation of 3-nitroveratrole on methylation. Reduction of 6-nitroguaiacol with sodium hyposulphite yields 6-*aminoguaiacol*, m. p. 83·5° (*triacetyl* derivative, m. p. 122—124°). Further nitration of 3-nitroguaiacol in acetic acid solution yields 3 : 4-*dinitroguaiacol*, m. p. 109·5—110° (*sodium* salt; *acetyl* derivative, m. p. 99—100·5°; *benzoyl* derivative, m. p. 132—133°), and 3 : 6-*dinitroguaiacol*, m. p. 69—70° (*sodium* salt; *acetyl* derivative, m. p. 56°). Methylation of the last-named compound gives 3 : 6-*dinitroveratrole*, m. p. 56°, reduced to 3 : 6-*diaminoveratrole*, m. p. 82° (triacetyl derivative, m. p. 96—97°). 3 : 4-Dinitroguaiacol and 3 : 4-dinitroveratrole yield, on reduction, diamines condensing with the sodium hydrogen sulphite compound of phenanthraquinone to give the corresponding ethers of 1 : 2-dihydroxyphenanthraphenazine. Direct nitration of 3-nitroguaiacol by concentrated nitric acid or further nitration of 3 : 6-dinitroguaiacol gives 3 : 4 : 6-*trinitroguaiacol*, existing in two modifications, m. p. 108—109° and 113·5° [*sodium* salt; *quinoline* salt, softening at 185°, decomp. 190°; *pyridine* salt, softening at 146°, m. p. 150—153° (decomp.); *benzoyl* derivative, m. p. 146—147°]. 4 : 5 : 6-Trinitroguaiacol, m. p. 144—147° (decomp.) [quinoline salt, m. p. 207—209° (decomp.)], is obtained by direct nitration of 5-nitroguaiacol [cf. Kohn, A., 1925, i, 1265, m. p. 143—149° (decomp.), quinoline salt, m. p. 201° (decomp.)]. M. CLARK.

Hydrogenated dihydroxydiphenylmethane compounds. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING) and H. JORDAN.—See B., 1926, 720.

Co-ordination valency of two hydroxyl groups in the *ortho* position. II. Complexes of hydroxyquinol, 1 : 2-dihydroxynaphthalene, and protocatechualdehyde with acids of the molybdenum group. L. FERNANDES (Gazzetta, 1926, **56**, 416—424; cf. A., 1925, i, 912).—Hydroxyquinol and 1 : 2-dihydroxynaphthalene form with molybdates and tungstates coloured complexes which can be detected as maxima on a concentration–absorption curve obtained from absorption spectra. In this way, the six complexes $MoO_3,mC_6H_3(OH)_3,(NH_4)_2O,nH_2O$; $MoO_3,mC_{10}H_6(OH)_2,(NH_4)_2O,nH_2O$, and $WO_3,mC_6H_6O_3,(NH_4)_2O,nH_2O$, where $m = 1$ and 2, are detected.

The following complexes are isolated in microcrystalline form by precipitation: *pyridinium hydroxyquinol-aquouranate*, $[UO_3,C_6H_6O_3,H_2O](C_5H_6N)H$, maroon; *pyridinium* 1 : 2-*dihydroxynaphthalene-aquouranate*, $[UO_3,C_{10}H_6O_2,H_2O](C_5H_6N)H$, red; *ammonium mono-* and *di-protocatechualdehyde-aquomolybdates*, $[MoO_3,(CHO{\cdot}C_6H_3{\cdot}O_2),H_2O](NH_4)H$, orange, $[MoO_2,(CHO{\cdot}C_6H_3{\cdot}O_2)_2](NH_4)H$, maroon; *diguanidinium diprotocatechualdehyde-molybdate*, $[MoO_2,(CHO{\cdot}C_6H_3{\cdot}O_2)_2]CNH_2(NH_2)_2$, brick-red; *thallium protocatechualdehyde-aquomolybdate*, $[MoO_3,(CHO{\cdot}C_6H_3{\cdot}O_2),H_2O]TlH$, red; *diammonium mono-* and *di-protocatechualdehyde-aquotungstates*, $[WO_3,CHO{\cdot}C_6H_3{\cdot}O_2,H_2O](NH_4)_2$ and $[WO_2{\cdot}(CHO{\cdot}C_6H_3{\cdot}O_2)_2](NH_4)_2$, maroon.

E. W. WIGNALL.

Typical reactions for phenols. K. BRAUER [with RUTHSATZ] (Chem.-Ztg., 1926, **74**, 553—554).—The reaction recently described (B., 1926, 595) of resins or varnishes with phosphomolybdic acid and ammonia is characteristic of phenolic hydroxyl groups and can be used to differentiate *o*-, *m*-, and *p*-substitution in the polyhydric phenols. The green coloration given by *o*-dihydroxyphenols, such as pyrocatechol and pyrogallol, and phosphomolybdic acid is turned to blue on addition of ammonia, whilst the blue coloration obtained with *p*-dihydric phenols is unchanged by ammonia, and *m*-dihydric phenols, *e.g.*, resorcinol, phloroglucinol, give a (blue) coloration only after addition of ammonia. Hydroxyquinol gives the reaction for a *p*-dihydric phenol. The reaction is very sensitive and can be applied in either ethereal or aqueous solution or suspension. Introduction of carboxyl groups weakens the reaction, and salol, for instance, gives a much weaker coloration than phenol. R. BRIGHTMAN.

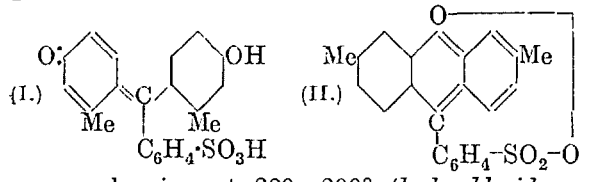
Apiole of *anethum* and its propenyl isomeride. M. DELÉPINE and A. LONGUET (Bull. Soc. chim., 1926, [iv], **39**, 1019—1024).—When treated in ethereal solution with iodine and mercuric oxide, apiole (5 : 6-dimethoxy-3 : 4-methylenedioxyallylbenzene, cf. A., 1909, i, 642) yields the *ethylene oxide*, $C_9H_9O_4{\cdot}CH_2{\cdot}CH{\cdot}CH_2$ (O), b. p. 195—200°/15 mm., which could not be transformed into the isomeric aldehyde.

The addition of bromine to *iso*apiole (5 : 6-dimethoxy-3 : 4-methylenedioxypropenylbenzene) in ethereal solution yields a *dibromide*, $C_{12}H_{14}O_4Br_2$, m. p. 105°, which reacts with dilute acetone to give a *glycol bromohydrin*, probably $C_9H_9O_4{\cdot}CH(OH){\cdot}CHBrMe$. This alcohol is converted by potassium hydroxide into the *oxide*, b. p. 185—192°/15 mm., which isomerises on distillation to a *ketone*, probably either $C_9H_9O_4{\cdot}CO{\cdot}CH_2Me$ or $C_9H_9O_4{\cdot}CH_2{\cdot}COMe$, b. p. 260° (*semicarbazone*, m. p. 159—160°). Potassium acetate reacts with the dibromide, yielding the *glycol diacetate*, m. p. 124°.

When treated with sodium iodide, bromo*iso*apiole dibromide yields 2-*bromo*-5 : 6-*dimethoxy*-3 : 4-*methylenedioxypropenylbenzene* (*bromoisoapiole*), m. p. 66° (*picrate*, m. p. 72°), whilst boiling with alcohols yields alkoxy-derivatives, $C_9H_8O_4Br{\cdot}CH(OR){\cdot}CHBrMe$ (*methoxy-*, m. p. 59°; *ethoxy-*, m. p. 82—83°; *propoxy-*, m. p. 64°), and a *substance*, $C_{11}H_9O_4Br$, m. p. 108° (*bromo*-derivative, m. p. 151—152°), possibly 3-*bromo*-6-*methoxy*-4 : 5-*methylenedioxymethylbenzfuran*. The following reactions of bromo*iso*apiole dibromide are described: dilute acetone yields the *glycol bromohydrin*, $C_9H_8O_4Br{\cdot}CH(OH){\cdot}CHBrMe$, m. p. 125° (*benzoate*, m. p. 132°); alcoholic potassium hydroxide yields the *oxide*, $C_{12}H_{13}O_5Br$, m. p. 99—100°, which yields the *glycol monoacetate*, $C_{14}H_{17}O_7Br$, m. p. 121—123°; potassium acetate in acetic acid solution yields the *glycol diacetate*, $C_9H_8O_4Br{\cdot}[CH{\cdot}OAc]_2{\cdot}Me$, m. p. 88—90°. R. W. WEST.

***m*-Cresolsulphonephthalein, 3 : 6-dimethylsulphonefluoran, and some of their derivatives.** W. R. ORNDORFF and A. C. PURDY (J. Amer. Chem. Soc., 1926, **48**, 2212—2221).—Condensation of *o*-sulphobenzoic anhydride or chloride with *m*-cresol

in presence of zinc chloride at 105—110° affords *m*-cresolsulphonephthalein, (I), deep red with green reflex, decomp. 250—300° after darkening and shrinking. The air-dried material contains about 1% of water, and is therefore to be considered as a solid solution of the inner carbonium or oxonium salt and the quinonoid hydrate (cf. Cohen, U.S. Pub. Health Reports, 1923, **38**, 199; Orndorff and Cornwell, this vol., 610). The *triammonium* salt, deep red, *monoammonium* salt, light red, *barium* salt (+2EtOH), dark red, *diacetate*, m. p. 172—173°, and *dibenzoate*, m. p. 208—209°, were prepared. When boiled with methyl alcohol, *m*-cresolsulphonephthalein affords a dark red *monomethyl ether*, m. p. 176—178°, and a colourless *dimethyl ether*, m. p. 164—165° after turning red, which is converted into a deep red *isomeride* (*ammonium* salt, red) when heated at 170° in carbon dioxide. Bromination in cold glacial acetic acid affords *tetrabromo*-m-*cresolsulphonephthalein*, colourless, m. p. 218—219° (*heptahydrate*, brick-red, amorphous, m. p. 218—219° after becoming orange at 90° and colourless at 190°; *ammonium* salt; *diacetate*, m. p. 235—236°; *dibenzoate*, m. p. 205—206°). Condensation of *m*-cresol with *o*-sulphobenzoic anhydride at 125—145°, in absence of condensing agent, affords 3 : 6-*dimethylsulphonefluoran* (II),



orange, charring at 280—290° (*hydrochloride*, red), bromination of which in glacial acetic acid affords *dibromo*-3 : 6-*dimethylsulphonefluoran*, orange, darkening at 200°, m. p. not below 300° (*triammonium* salt), whilst reduction with zinc dust and boiling water yields the *zinc* salt of "*dimethylhydrosulphofluoranic acid*" (3 : 6-*dimethyl*-9-*phenylxanthen*-o-*sulphonic acid*). F. G. WILLSON.

Action of benzoyl peroxide on benzene at low temperatures in presence of anhydrous metal chlorides. J. BÖESEKEN and A. F. A. REYNHART (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 598—602; cf. Gelissen and Hermans, A., 1925, i, 379, 545).—Benzoyl peroxide acts on an excess of benzene at 0° in presence of aluminium chloride (1 mol.) to yield almost quantitatively benzoic acid (1 mol.) and phenyl benzoate (1 mol.), the production of carbon dioxide being negligible. Since carbon dioxide and diphenyl result in the absence of the aluminium chloride, the latter functions by activating the linking between the central oxygen atoms of the peroxide. In a similar reaction in presence of ferric chloride, no phenyl benzoate is isolated, but more than 1 mol. of benzoic acid together with dark-coloured compounds containing iron. Diphenyl and carbon dioxide are also produced, and the proportion of these increases as the temperature of reaction is raised to 35°. If the proportion of ferric chloride is much less (0·1 mol.), both phenyl benzoate and diphenyl are produced. The two reactions evidently proceed side by side. Zinc chloride has no catalytic action; stannic chloride has a slow effect similar to that of aluminium chloride. Antimony pentachloride causes a violent reaction at 0°, some benzophenone being formed. G. M. BENNETT.

Preparation of nitriles by the diazo reaction. A. KORCZYNSKI and B. FANDRICH (Compt. rend., 1926, **183**, 421—423).—The following nitriles have been obtained in greater purity and higher yields by the use of nickel cyanide instead of cuprous cyanide in the diazo-reaction (cf. A., 1920, i, 643): *o*- and *p*-toluonitrile, *o*- and *p*-anisonitrile, *o*-chlorobenzonitrile, m. p. 43—44°, *m*-chlorobenzonitrile, m. p. 40·5°, *o*-bromobenzonitrile, m. p. 53°, and *p*-bromobenzonitrile. The cyanides of iron, chromium, manganese, zinc, molybdenum, cadmium, tin, or thorium cannot be used. R. BRIGHTMAN.

Derivatives of anæsthesin [ethyl *p*-aminobenzoate]. G. GORI (Gazzetta, 1926, **56**, 430—434).—Ethyl *p*-aminobenzoate has been condensed to give: with succinic acid, *ethyl* p-*succinimidobenzoate*, m. p. 150°; with phthalic anhydride, *ethyl* p-*phthalimidobenzoate*, m. p. 150—151°; with tetrachlorophthalic anhydride, *ethyl* p-*tetrachlorophthalimidobenzoate*, pale yellow, m. p. 255°; with piperonal, *ethyl* p-*piperonylideneaminobenzoate*, m. p. 109—110°; with 1-chloro-2 : 4-dinitrobenzene in the presence of sodium acetate, *ethyl* 2 : 4-*dinitrodiphenylamine*-4′-*carboxylate*, orange, m. p. 112—113°; with carbon disulphide in alcoholic solution, *ethyl* s-*diphenylthiocarbamide*-4 : 4′-*dicarboxylate*, yellow, m. p. 153°. In all these derivatives the anæsthetic property is lost (cf. Thoms and Ritsert, A., 1921, i, 343). E. W. WIGNALL.

Relationship between hydrogen-ion concentration and chemical constitution in certain local anæsthetics. E. B. VLIET and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2158—2162).—The basicities of a series of compounds of the type $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot [CH_2]_x \cdot NRR'$ have been measured. The basicity decreases with increase in size of the groups R and R′, except that dimethylamino-derivatives are slightly less basic than the corresponding diethylamino-compounds. Di*iso*propylamino-derivatives are slightly more basic than di-*n*-propylamino-derivatives, di*iso*- and di-*n*-amylamino-compounds have the same basicity, but that of the di*iso*butylamino-compounds is less than that of the *n*- and *sec.*-butyl isomerides. Increase in the value of *x* causes increase in basicity, but branching of this chain reduces it. When the $[CH_2]_x$ group is replaced by the *cyclo*hexyl group, the compounds behave as if the nitrogen and oxygen atoms were connected by two straight chains of carbon atoms, the basicity being determined by the length of the shorter chain. The two geometrical isomerides of *o*-dimethylaminohexahydrophenyl *p*-aminobenzoate have the same basicity, although differing greatly in physical properties and anæsthetic effect. Borates of γ-di-*n*-butylaminopropyl and β-*n*-butylallylaminoethyl *p*-aminobenzoates are completely hydrolysed by water. F. G. WILLSON.

Isomeric phenylserines. M. O. FORSTER and K. A. N. RAO (J.C.S., 1926, 1943—1951).—Erlenmeyer's condensation of glycine with benzaldehyde

yields *trans*-phenylserine, m. p. 202° (decomp.) (A., 1899, i, 759). Reduction of α-triazo-β-hydroxy-β-phenylpropionic acid with ammonium sulphide yields cis-*phenylserine*, m. p. 230—232° (decomp.), hydrated form, m. p. 213° [*ethyl ester picrate*, m. p. 170°; N-*benzoyl* derivative, m. p. 197°; O-*methyl* derivative, m. p. 227—232° (decomp.), $+2H_2O$, m. p. 215—216°, with *ethyl ester picrate*, m. p. 155°; O-*methyl*-N-*benzoyl* derivative, m. p. 208°; *amide*, m. p. 199—200°]. Evidence for the *cis*-configuration of the new acid is found in the formation of a benzoyl derivative without dehydration, whereas benzoylation of *trans*-phenylserine gives Erlenmeyer's benzamidocinnamic acid lactimide and a *compound*, m. p. 160°. Further support is derived from its synthesis by the action of ammonia on cinnamic acid chlorohydrin or sodium oxidophenylacrylate. Erlenmeyer erroneously described the product of these two reactions as phenyl-*iso*serine. Attempts to convert the phenylserines into the parent compound of picrorocellin were unsuccessful, but Abderhalden and Komm's colour test (A., 1925, i, 175) showed that a diketopiperazine was formed when the phenylserines were heated at their decomposition temperature. M. CLARK.

Reactions of nitroso-derivatives with unsaturated compounds. IV. Dinitrones corresponding with α-diketonic acids. L. ALESSANDRI (Gazzetta, 1926, **56**, 398—416).—The dinitrone from ethyl phenylpropiolate and *p*-nitrosodimethylaniline, m. p. 168—169° (decomp.) (cf. this vol., 287), hydrolyses to the latter, ethyl benzoylglyoxylate, and *p*-aminodimethylaniline. In ethyl alcohol, the additive product previously described is obtained, orange-red with metallic reflex, m. p. 138—139° (slight decomp.), from which the dinitrone can be regenerated; and in methyl alcohol, the *product*, $C_{27}H_{30}O_4N_4$,MeOH, reddish-purple with metallic reflex, m. p. 143—144° (slight decomp.).

From ethyl phenylpropiolate and *p*-nitrosomethylaniline, proceeding as before, there is obtained the *dinitrone*, $C_{25}H_{26}O_4N_4$, red, m. p. 189—190° (decomp.), which hydrolyses to *p*-nitrosomethylaniline and ethyl benzoylglyoxylate. E. W. WIGNALL.

2 : 3-Aminonaphthoic acid. SOC. CHEM. IND. IN BASLE.—See B., 1926, 736.

1 : 4- and 1 : 5-Naphthylaminesulphonic acids. E. F. EHRHARDT and R. M. HEREWARD.—See B., 1926, 736.

Optical activity and the polarity of substituent groups. IV. *sec.*-β-Octyl esters of *o*-, *m*-, and *p*-methoxy- and nitro-benzoic acids. H. G. RULE and (MISS) A. H. NUMBERS (J.C.S., 1926, 2116—2123).—In an examination of the influence of nuclear substitution on the optical rotatory power of β-octyl benzoate, the following were prepared, by condensation of *sec.*-β-octyl alcohol, $[\alpha]_D^{19}$ ±8·14°, with the required acid chloride in presence of pyridine: l-β-*octyl* o-*methoxybenzoate*, b. p. 187·5°/13 mm., $d_4^{20\cdot3}$ 1·0004, $[\alpha]_D^{20}$ −12·59°; m-*methoxybenzoate*, b. p. 187·5°/12 mm., $d_4^{20\cdot4}$ 0·9939, $[\alpha]_D^{20}$ −35·48°; *anisate*, b. p. 189°/13 mm., d_4^{20} 0·9968, $[\alpha]_D^{20}$ −42·88°; o-*nitrobenzoate*, b. p. 204°/15 mm., d_4^{20} 1·0735, $[\alpha]_D^{20}$ −43·56°; m-*nitrobenzoate*, b. p. 212°/18 mm.; p-*nitrobenzoate*, m. p. 29·5—30°. Densities, rotatory powers, and specific rotations of *l*-β-octyl *o*-, *m*-, and *p*-methoxybenzoate, of *l*-β-octyl *o*-nitrobenzoate, and of *d*-β-octyl *m*- and *p*-nitrobenzoate, for various temperatures and wave-lengths, are tabulated, and also the molecular rotations and dispersion ratios of *d*-β-octyl *o*-, *m*-, and *p*-methoxybenzoates and *o*-, *m*-, and *p*-nitrobenzoates. The *o*-, *p*-directive methoxy-group causes a depression and the *m*-directive nitro-group an exaltation of rotatory power. The nitro-groups affect both rotation and acidic strength in the order $o\text{-}NO_2 > p\text{-}NO_2 > m\text{-}NO_2 > H$; the weaker methoxy-groups give the sequence, for rotatory powers, $p\text{-}OMe > m\text{-}OMe > H > o\text{-}OMe$, and for acidic strength $o\text{-}OMe > H > p\text{-}OMe$. Except in the case of octyl *o*-methoxybenzoate, the rotation of each ester falls with rise of temperature. F. M. HAMER.

Synthesis of iridic acid. F. MAUTHNER (Annalen, 1926, **449**, 102—108).—3-Hydroxy-4 : 5-dimethoxybenzoic acid, m. p. 193—194°, is easily prepared by methylation of methyl gallate with methyl sulphate, followed by hydrolysis with alkali (cf. Herzig and Pollak, A., 1903, i, 89; Fischer and Freudenberg, *ibid.*, 1912, i, 471, 887). The acid is condensed with methyl chloroformate to give 3-*methylcarbonato*-4 : 5-*dimethoxybenzoic acid*, m. p. 146—147°, from which, by reduction of the acid *chloride*, m. p. 65—66°, with hydrogen and palladium, is obtained 3-*methylcarbonato*-4 : 5-*dimethoxybenzaldehyde*. This is hydrolysed to 3-*hydroxy*-4 : 5-*dimethoxybenzaldehyde*, m. p. 60—61° (*semicarbazone*, m. p. 211—212°; p-*nitrophenylhydrazone*, m. p. 212—213°), which is converted, by way of the *azlactone* (condensation product with hippuric acid), m. p. 140—141°, into iridic acid (3-hydroxy-4 : 5-dimethoxyphenylacetic acid), m. p. 118°, identical with the natural product (de Laire and Tiemann, A., 1894, i, 47).

C. HOLLINS.

Formation and stability of *spiro*-compounds. XIII. *spiro*-Compounds from substituted lævulic acids. E. ROTHSTEIN and J. F. THORPE (J.C.S., 1926, 2011—2017).—The failure of diethylglutaric acid and *cyclo*hexanediacetic acid to give cyclic pentadiones when condensed with ethyl oxalate was ascribed to overlapping of the end reacting groups in the intermediate oxalyl compound, $>C<^{CH(CO_2Et)\cdot CO}_{CH_2\cdot CO_2Et\ CO_2Et}$, owing to the presence of the α- and α′-carbethoxy-groups, as the tetrahedral angle between the groups $CH_2\cdot CO_2Et$ became increasingly diminished by substitution (Dickens, Kon, and Thorpe, *ibid.*, 1922, **121**, 1496). A four-membered ring is formed in the case of the diethyl compound, whereas with the *cyclo*hexane derivative, where further overlapping occurs, no ring formation takes place. There is no possibility here of the three-membered ring formation which might be expected on the analogy of the production of *cyclo*hexane*spiro*-*cyclo*propan-2-ol-2 : 3-dicarboxylic acid from α-keto-*cyclo*hexanediacetic acid on boiling with concentrated potassium hydroxide solution. The correctness of these explanations is confirmed by preparation of

*cyclo*pentane compounds from ethyl 1-acetyl*cyclo*hexane-1-acetate and ethyl ββ-dimethyl-lævulate by direct ring closure under the influence of dry sodium ethoxide. The distance between the two reacting groups is sufficiently increased by the substitution of the carbethoxy-groups by hydrogen atoms to make possible the formation of the five-membered ring, and the *cyclo*hexane compound now gives a higher yield of cyclic dione than the ββ-dimethyl ester.

1-Carboxy*cyclo*hexane-1-acetic acid, m. p. 134° (cf. Lapworth, *ibid.*, 1922, **121**, 2754, m. p. 132°), yields the *anhydride*, m. p. 55°, and the *ethyl* ester, b. p. 175—180°/11 mm. The latter is converted through the acid chloride, by the action of zinc methyl iodide, into *ethyl* 1-*acetyl*cyclo*hexane*-1-*acetate*, b. p. 155°/14 mm. The free *acid* has m. p. 82° (*semicarbazone*, m. p. 212°). The ethyl ester does not give a *spirocyclo*propane ring when boiled with concentrated potassium hydroxide solution, but yields, with sodium ethoxide, cyclo*hexane*spirocyclo*pentane*-2 : 4-*dione*, m. p. 180°. The constitution of the last-named compound is shown by oxidation with alkaline sodium hypochlorite to 1-carboxy*cyclo*hexane-1-acetic acid. cyclo*Hexane*spiro-3-*bromo*-Δ^2-cyclo*penten*-2-*ol*-4-*one* has m. p. 238°. Ethyl ββ-dimethyl-lævulate yields 1 : 1-dimethyl*cyclo*pentane-2 : 4-dione, whence 3-*bromo*-1 : 1-*dimethyl*-Δ^2-cyclo*penten*-2-*ol*-4-*one*, m. p. 203°, is obtained. M. CLARK.

Glutaconic acids. XX. Tetrahydro*iso*phthalic acid. E. H. FARMER and H. L. RICHARDSON (J.C.S., 1926, 2172—2178).—Δ^2-Tetrahydro*iso*phthalic acid, prepared by reduction of *iso*phthalic acid as described by Perkin and Pickles (*ibid.*, 1905, 87, 293), does not yield a hydroxy-anhydride by the methods applicable to glutaconic acids, whilst its ester cannot be methylated. When its anhydride is heated with ethyl alcohol, two forms of *ethyl hydrogen* Δ^2-*tetrahydroisophthalate* are obtained, m. p. 44—45° and 40—41°. The anhydride with methyl alcohol yields one *methyl hydrogen* ester, m. p. 59°, which on addition of bromine followed by treatment with diethylamine gives bromotetrahydro*iso*phthalic acid ester, reducible to a *substance*, m. p. 41—43°, the original acid ester, and the *isomeric* methyl hydrogen ester, b. p. 172—174°/1 mm. The action of methyl iodide on the silver salt of the acid forms *methyl* Δ^2-*tetrahydroisophthalate*, b. p. 134—135°/7 mm.; *amide*, m. p. 239°. After an attempt to methylate the Δ^2-ester by means of methyl iodide in the presence of sodium methoxide, the ester recovered was methyl Δ^3-tetrahydro-*iso*phthalate. Oxidation of the original acid with ozone gives tricarballylic acid, which cannot arise from the true Δ^2-form. The behaviour of the Δ^2-acid is unusual for a glutaconic acid and it is suggested that it is actually the *cis*-Δ^4-compound.

F. M. HAMER.

Constitution of the yellow sodium compounds from ethyl citraconate (or itaconate) and ethyl sodiomalonate. C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1926, 1912—1917; cf. Ingold, Shoppee, and Thorpe, this vol., 939).—The yellow sodium compound formed as a by-product when ethyl malonate acts on ethyl citraconate (or itaconate) in the presence of excess of sodium ethoxide is a mixture of two closely similar isomerides, which yield, on acidification, the corresponding ketonic esters. The mixture is produced by reaction of the primary condensation products, (I) and (II), with a second molecule of citraconic or itaconic ester, followed by elimination of alcohol to give the products (V) and (VI):

$$CHMe(CO_2Et)\cdot CH(CO_2Et)\cdot CH(CO_2Et)_2 \text{ (I.)} \longrightarrow CHMe(CO_2Et)\cdot CH(CO_2Et)\cdot C(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et \text{ (III.)}$$

$$\rightarrow CHMe(CO_2Et)\cdot CH(CO_2Et)\cdot \underset{\text{(V.)}}{\underset{|}{C}(CO_2Et)\cdot CO\cdot \underset{|}{C}H\cdot CO_2Et} \quad CH_2 \text{———} CH\cdot CO_2Et$$

$$CH(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et \text{ (II.)} \longrightarrow \text{(III.)}$$

and (V.) or $\longrightarrow CH_2(CO_2Et)\cdot CH(CO_2Et)\cdot CH_2\cdot C(CO_2Et)_2\cdot CH_2\cdot CH(CO_2Et)\cdot CH_2\cdot CO_2Et$ (IV.) $\longrightarrow$

$$CH_2(CO_2Et)\cdot CH(CO_2Et)\cdot CH_2\cdot \underset{\text{(VI.)}}{\underset{|}{C}(CO_2Et)\cdot CO\cdot \underset{|}{C}H\cdot CO_2Et} \quad CH_2 \text{———} CH\cdot CO_2Et$$

The results show that, under the experimental conditions used, ethyl citraconate and ethyl itaconate are interconvertible, their primary additive products with ethyl malonate being (I) and (II), respectively.

The constitution of both keto-esters follows from the fact that (I) condensed with either citraconic or itaconic ester gives only a liquid ester, *ethyl* α-1 : 3 : 4-*tricarbethoxy*-2-*keto*cyclo*pentyl*-β-*methylsuccinate* (V), whilst (II) condensed in the same way gives a mixture of (V) with *ethyl* ω-1 : 3 : 4-*tricarbethoxy*-2-*keto*cyclo-*pentylmethylsuccinate* (VI), m. p. 83°. Hydrolysis of (V) gives α-4-*carboxy*-2-*keto*cyclo*pentyl*-β-*methylsuccinic acid*, m. p. 148—149°. Hydrolysis of (VI) gives ω-4-*carboxy*-2-*keto*cyclo*pentylmethylsuccinic acid*, m. p. 173° [*ethyl* ester, b. p. 247°/18 mm. (*semicarbazone*, m. p. 105°)], oxidised by permanganate to βδ-dicarboxysuberic acid, m. p. 206—207°. *Butane*-αα*β*γ-*tetracarboxyamide*, m. p. 267°, is obtained from (I) by the action of ammonia. M. CLARK.

Isomerism of the oximes. XXV. Dissociation constants of some isomeric aldoximes. O. L. BRADY and R. F. GOLDSTEIN (J.C.S., 1926, 1918—1924).—Measurement of the dissociation constants of four pairs of isomeric aldoximes, α- and β-benzaldoxime, α- and β-*o*- and *m*-nitrobenzaldoxime, and α- and β-cinnamaldoxime, shows that, in each case, the α- is a stronger acid than the β-isomeride. One other β- and eight other α-aldoximes were investigated to determine whether the acidity of the α-isomeride bore any relation to the ease of formation of the β-compound, but without positive result. The evidence regarding the configuration of the aldoximes afforded by their physical properties is at variance with the deductions drawn from their chemical reactions. M. CLARK.

Nitration of chlorinated 3-hydroxybenzaldehydes and some consequences of adjacent substitution. H. H. HODGSON and H. G. BEARD (J.C.S., 1926, 2030—2036).—Nitration of 2-chloro-3-hydroxybenzaldehyde yields 2-*chloro*-4-*nitro*-3-*hydroxybenzaldehyde*, m. p. 166° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 294—295° (decomp.); *semicarbazone*, m. p. 271—272° (decomp.); *oxime*, m. p. 170°; *methyl ether*, m. p. 107°], and 2-*chloro*-6-*nitro*-

3-*hydroxybenzaldehyde*, m. p. 153° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 232—233°; *semicarbazone*, m. p. 234° (decomp.); *oxime*, m. p. 175°; *methyl ether*, m. p. 134°]. Nitration of 4-chloro-3-hydroxybenzaldehyde gives a little 4-*chloro*-2-*nitro*-3-*hydroxybenzaldehyde*, m. p. 161° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 281—282° (decomp.); *semicarbazone*, m. p. 270—271° (decomp.)], with 4-*chloro*-6-*nitro*-3-*hydroxybenzaldehyde*, m. p. 175° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 275—276° (decomp.); *semicarbazone*, m. p. 265—266° (decomp.)], as main product. Nitration of 6-chloro-3-hydroxybenzaldehyde gives 6-chloro-2-nitro-3-hydroxybenzaldehyde [*silver* salt; p-*nitrophenylhydrazone*, m. p. 256—257° (decomp.); *semicarbazone*, m. p. 249—250° (decomp.)] and 6-chloro-4-nitro-3-hydroxybenzaldehyde [*silver* salt; p-*nitrophenylhydrazone*, m. p. 284—286° (decomp.); *semicarbazone*, m. p. 266—267° (decomp.)].

Mononitration of 2 : 4- and 2 : 6-dichloro-3-hydroxybenzaldehydes gives 2 : 4-*dichloro*-6-*nitro*-3-*hydroxybenzaldehyde*, m. p. 107° (*silver* salt; p-*nitrophenylhydrazone*, m. p. 279—280°; *semicarbazone*, $+H_2O$, softening at 140—150°), and 2 : 6-*dichloro*-4-*nitro*-3-*hydroxybenzaldehyde*, m. p. 80° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 279—280° (decomp.); *semicarbazone*, m. p. 255—256°; *oxime*, m. p. 195°]. Dinitration of 2-, 4-, and 6-chloro-3-hydroxybenzaldehydes gives 2-*chloro*-4 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 110° [*ammonium* and *silver* salts; p-*nitrophenylhydrazone*, m. p. 277—279° (explosive decomp.); *semicarbazone*, m. p. 240—242° (decomp.); *oxime*, m. p. 142°]; 4-*chloro*-2 : 6-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 118—119° (*silver* salt; p-*nitrophenylhydrazone*, exploding 235—236°; *semicarbazone*, exploding at about 200°); and 6-*chloro*-2 : 4-*dinitro*-3-*hydroxybenzaldehyde*, m. p. 121·5° [*silver* salt; p-*nitrophenylhydrazone*, m. p. 285—286° (decomp.); *semicarbazone*, m. p. 267—269° (decomp.)].

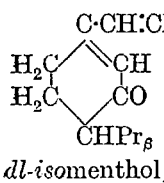
The potent influence on adjacent groups of chlorine substitution in position 2 is illustrated by reference to the volatility in steam of the 2-chloro-3-methoxy-derivatives (where the methoxy-group is shown to function in this connexion as a phenolic hydroxyl) and to the anomalous colour reaction of 2-chloro-4 : 6-dinitro-3-hydroxybenzaldehyde-*p*-nitrophenylhydrazone in aqueous sodium hydroxide. Chlorinated 4-nitro-3-hydroxybenzaldehydes are, in general, sparingly soluble in water but readily soluble in non-hydroxylic solvents. The reverse holds for the 6-nitro-isomerides. The last-named compounds induce sneezing. M. CLARK.

Three-carbon system. VI. Systems containing the benzoyl group. M. D. FARROW and G. A. R. KON (J.C.S., 1926, 2128—2138).—α-Δ^1-cyclo*Hexenylacetophenone*, b. p. 172—178°/14 mm., d_4^{21} 1·04157, n_D^{21} 1·55630 [*oxime*, m. p. 101—102°; *methyl* derivative, b. p. 168—170°/15 mm., $d_4^{18\cdot5}$ 0·99896, $n_D^{18\cdot5}$ 1·54314, *semicarbazone*, m. p. 191—192°; *ethyl* derivative (prepared by ethylation; it could not be prepared by the action of magnesium phenyl bromide on α-cyclo*hexylidenebutyronitrile*, d_4^{21} 0·92283, n_D^{21} 1·48917, obtained by ethylating ethyl α-cyano-*cyclo*hexylideneacetate and treating the product with sodium ethoxide), b. p. 184—185°/19 mm., d_4^{21} 1·01155, n_D^{21} 1·54077, *semicarbazone*, m. p. 212°], is prepared by condensation of *cyclo*hexanone and acetophenone in the presence of sodium ethoxide and also, together with diphenyl, by the action of magnesium phenyl bromide, or, better, its zinc chloride double compound, on α-Δ^1-*cyclo*hexenylacetyl chloride or *cyclo*hexylideneacetyl chloride. The *semicarbazone* from either source has m. p. 94—115°, 120—121°, and the ketone is oxidised by ozone to an aldehydic oil, hydrolysable to benzoic acid, but the existence of the αβ-phase of the ketone is indicated in that with ethyl sodioacetoacetate it gives a *compound*, $C_{17}H_{20}O$, b. p. 210—220°/20 mm., m. p. 69—70° (*semicarbazone*, m. p. 219°), which is regarded as $CH_2<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CPh\\CH_2\text{---}CO\end{matrix}>CH$. With sodium ethoxide, the ketone yields a *substance*, $C_{28}H_{32}O_2$, m. p. 201° (considered to be produced by condensation of the αβ-phase with the sodio-derivative of the βγ-phase), which with acetic acid gives a *compound*, $C_{28}H_{30}O$, m. p. 106°. From α-Δ^1-*cyclo*pentenylacetyl chloride or *cyclo*pentylideneacetyl chloride is prepared α-Δ^1-cyclo*pentenylacetophenone*, b. p. 163—165°/16 mm., d_4^{20} 1·04982, n_D^{20} 1·56437 (*semicarbazone*, m. p. 157°; *ethyl* derivative, b. p. 162°/11 mm., $d_4^{18\cdot5}$ 1·01725, $n_D^{18\cdot5}$ 1·54191, *semicarbazone*, m. p. 196·5°); the product of its condensation with ethyl sodioacetoacetate gives a *semicarbazone*, m. p. 193°.

Condensation of acetophenone with ββ-diethylacryl chloride yields *α-phenyl-γ-ethyl-Δ^β-penten-α-one*, b. p. 138°/8 mm., d_4^{18} 0·98638, n_D^{18} 1·54353 (*semicarbazone*, m. p. 90°; hydroxylamine yields the *oximino-oxime*, m. p. 158°, and a *compound*, m. p. 101—102°). Use of the chloride of γ-ethyl-Δ^γ-pentenoic acid yields *α-phenyl-γ-ethyl-Δ^γ-penten-α-one*, b. p. 146°/17 mm., $d_4^{19\cdot5}$ 0·98513, $n_D^{19\cdot5}$ 1·53372. These two ketones form an equilibrium mixture in the presence of sodium ethoxide. With ethyl sodioacetoacetate both give the same product (*semicarbazone*, m. p. 178—179°). All the four ketones are hydrolysed on boiling with acids and alkalis, yielding, respectively, *cyclo*hexanone, *cyclo*pentanone, and diethyl ketone, together with acetophenone; *cyclo*hexenylacetone undergoes a similar fission. All the ketones show exaltation of the molecular refraction, and resemble closely the corresponding methyl ketones. F. M. HAMER.

Piperitone. VIII. Condensation of piperitone with aldehydes. J. C. EARL and J. READ (J.C.S., 1926, 2072—2076; cf. *ibid.*, 1921, **119**, 784).—Piperitone condenses with anisaldehyde in alcoholic solution, in presence of sodium ethoxide, giving *anisylidene*-dl-*piperitone*, m. p. 98°, rhombic crystals, $a : b : c = 0{\cdot}91900 : 1 : 0{\cdot}82044$. *Piperonylidene*-dl-*piperitone*, m. p. 128°, and *opianylidene*-dl-*piperitone*, m. p. 157° (*calcium* salt described), are similarly prepared. *Salicylidene*-dl-*piperitone*, m. p. 177°, obtained by use of aqueous sodium hydroxide, is reduced by zinc dust and alkali to two isomeric *dihydro*-derivatives, $C_{17}H_{22}O_2$. The aldehyde condensations also take place, to a small extent, in presence of hydrochloric acid. Since benzylidene-piperitone is oxidised by potassium permanganate

to α-*iso*propylglutaric acid, it is concluded that condensation of piperitone with benzaldehyde occurs in the 7-position; the products previously described (A., 1924, i, 301) are regarded as 7-benzylidene-*dl*-piperitone (I), 7-benzyl-*dl-iso*menthone, 7-benzyl-*dl-iso*menthol, and 2-benzylidene-7-benzyl-*dl-iso*menthone.



(I.)

F. M. HAMER.

p'-Methylchalkone [p-tolyl styryl ketone]. Isomerism of the *cis*-cinnamic acids. C. WEYGAND and A. MATTHES (Annalen, 1926, **449**, 29—62; cf. Weygand, A., 1924, i, 521).—The m. p. previously given for α- and β-forms of *p*-tolyl styryl ketone are now corrected to 74—75·4° (α) and 55—56° (β). A third (γ) isomeride, m. p. 45°, is obtained when either is heated for a short time at 200° and rapidly cooled. This passes spontaneously into the β- or α-form, and is extraordinarily sensitive to traces of the isomerides.

The α-form under all conditions gives only a monopicrate, m. p. 99—100°; β gives the same monopicrate, but only after about 30 min. (conversion into α). When the orange-yellow solution of α or β in sulphuric acid is diluted with water, the β-form (not α- as previously reported) is precipitated, the conversion of α into β taking place by way of the halochromic compound >CO . . . . HX. The α-form exhibits behaviour which varies according to the previous history—age, heat treatment, vacuum distillation, crystallisation, etc.—and may give, after melting, a stable β-form, or β quickly changing to α, or the very labile γ-form. This supports the suggestion (cf. Schaum, Schaeling, and Klausing, A., 1916, i, 405) that solid solutions of two kinds of molecules are normally obtained. It is concluded that polymorphism is a special case in the relations of a pseudo-ternary system.

Phenyl styryl ketone gives under all conditions a dipicrate, m. p. 97—98°. Phenyl *p*-methylstyryl ketone, m. p. 96·5°, and p-*tolyl* p-*methylstyryl ketone*, m. p. 127·5—129° (from *p*-methylacetophenone and *p*-tolualdehyde), are α-compounds and also yield only *dipicrates*, m. p. 92—94° and 101—102·5°, respectively. *p*-Ethylphenyl styryl ketone, m. p. 61—61·5°, b. p. 218—221°/11 mm. (from *p*-ethylacetophenone, b. p. 116°/14 mm., and benzaldehyde), is a β-compound, whilst p-n-*propylphenyl styryl ketone*, m. p. 46—47·1° (from *p*-propylacetophenone, b. p. 140—142°/26 mm.), is a γ-compound; neither forms a picrate.

A review of the accumulated data on the isomeric *cis*-triads in the cases of cinnamic acid, *p*-tolyl styryl ketone, and phenyl β-bromo-α-ethoxystyryl ketone leads to the conclusion that isomerism may result from the intermolecular saturation of residual valencies (*e.g.*, between the carbonyl group and a benzene nucleus) in different ways. C. HOLLINS.

Benzylbenzoin [benzoylphenylbenzylcarbinol]. J. PASCUAL (VILA) and J. CEREZO (Anal. Fís. Quím., 1926, **24**, 395—399; cf. A., 1925, i, 557).—Experimental details relating to a previous communication are given. *Benzylbenzoin acetate* has m. p. 128—129°. G. W. ROBINSON.

Catalytic hydrogenation of the carbonyl group in aromatic compounds under pressure in presence of copper. I. B. KUBOTA and T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res., 1926, **5**, 1—6; cf. this vol., 727).—Aromatic ketones undergo reduction to alcohols when treated with hydrogen under pressure in presence of copper. Benzil at 100° and 76—92 atm. when so treated gives benzoin, hydrobenzoin, and *iso*hydrobenzoin; benzoylacetone at 83° gives β-*hydroxy*-β-*phenylethyl methyl ketone*, b. p. 134—136°/10 mm., *phenylhydrazone*, m. p. 120—122° (partial decomp.), and a small quantity of phenyl β-hydroxy-*n*-propyl ketone, whilst at 105° it gives α-phenyl-*n*-butane-αγ-diol. Phthalic anhydride at 120° yields "hydrophthalyl-lactonic acid" (benzylphthalide-*o*-carboxylic acid) and *dihydroxyphthalan*, $C_6H_4<\begin{matrix}CH(OH)\\CH(OH)\end{matrix}>O$, a colourless liquid giving a *dibenzoate*. B. W. ANDERSON.

Hexoylresorcinol [2 : 4-dihydroxyphenyl *n*-amyl ketone] and some of its derivatives. D. TWISS (J. Amer. Chem. Soc., 1926, **48**, 2206—2212).—Hexoylresorcinol, m. p. 56—57°, b. p. 217—218°/14 mm., or b. p. 343—345° (decomp.) at atmospheric pressure (cf. Dohme, Cox, and Miller, this vol., 838), is obtained by boiling ethyl hexoate with resorcinol and zinc chloride. The following derivatives are described: *monomethyl ether*, b. p. 189—192°/12—13 mm.; (?) *dimethyl ether*, m. p. 35—36°; *oxime*, m. p. 190—191° (decomp.); p-*nitrobenzoate*, m. p. 89—91°; *monoacetate*, b. p. 213—215°/14 mm.; *diacetate*, b. p. 229—232°/13 mm. (decomp.); *mononitro*-derivative, m. p. 73—74°; and *dibromo*-derivative, m. p. 102—103°. Hexylresorcinol (2 : 4-dihydroxy-*n*-hexylbenzene), m. p. 67—68°, b. p. 198—200°/13—14 mm., or b. p. 333—335° (decomp.) at atmospheric pressure, is obtained by reducing hexoylresorcinol with amalgamated zinc and hydrochloric acid. The *dimethyl ether*, b. p. 164—165°/12 mm., and *diacetate*, b. p. 198—199°/15 mm., are described. The influence of the keto-group in hexoylresorcinol is shown by the fact that this compound when methylated with methyl iodide or sulphate gives only a monomethyl ether, whilst hexylresorcinol readily gives the dimethyl ether. The monomethyl ether is probably 2-*hydroxy*-4-*methoxyphenyl* n-*amyl ketone*. Condensation of hexylresorcinol with ethyl acetoacetate in presence of 82% sulphuric acid affords 7-*hydroxy*-4-*methyl*-6-*hexylcoumarin*, m. p. 165°. F. G. WILLSON.

Action of thionyl chloride on hydroxyanthraquinones. III. A. GREEN (J.C.S., 1926, 2198—2204; cf. A., 1924, i, 1080).—By boiling purpurin with thionyl chloride, it is converted into 1 : 2-*thionylpurpurin*, m. p. 211—213°, which is rapidly reconverted into purpurin by the action of moisture, and with boiling acetic acid yields 2-acetylpurpurin. Anthrapurpurin and thionyl chloride give 1 : 2-*thionyl*-7-*chlorothionylanthrapurpurin*, m. p. 179° (decomp.), converted by boiling acetic acid into 2-*acetylanthrapurpurin*, m. p. 296—298° (decomp.), by benzoic acid at 170° into 2-*benzoylanthrapurpurin*, m. p. 203—205°, and by boiling acetic anhydride into triacetylanthrapurpurin, m. p. 225—227°. *Thionylhystazarin*,

m. p. 200°, when boiled with acetic acid, reverts to hystazarin, and with boiling acetic anhydride slowly yields diacetylhystazarin, m. p. 211—213°. 2 : 3-*Thionylanthragallol* with acetic acid gives anthragallol, m. p. 313—314°, and 3-*acetylanthragallol*, m. p. 210—212°, and by its regulated interaction with acetic anhydride gives 2 : 3-diacetylanthragallol, m. p. 223—224°, which indicates that the thionyl group is not linked to the 1-position of the anthragallol nucleus. Anthraquinone, 5-*chloro*-1-*hydroxyanthraquinone*, m. p. 223—224° (prepared from 5-chloro-1-aminoanthraquinone) (*acetyl* derivative, m. p. 205°), 1-hydroxy-, 4-chloro-1-hydroxy-, 1 : 8-dihydroxy-, and 2-hydroxy-anthraquinone do not react with boiling thionyl chloride. M. p. of hydroxyanthraquinones and their acetyl derivatives are tabulated.

F. M. HAMER.

Benzanthrone derivatives [from α-naphthaleneazobenzene-*m*-carboxylic acids]. G. KALISCHER, R. MÜLLER, and F. FRISTER.—See B., 1926, 735.

Catalytic hydrogenation of carone. S. N. IYER and J. L. SIMONSEN (J.C.S., 1926, 2049—2052).—When carone is reduced using platinic chloride and hydrogen, it behaves like an αβ-unsaturated ketone. After the absorption of 1 mol. of hydrogen, the product consists mainly of *p*-menthan-2-one, whilst on complete reduction (2 mols. of hydrogen) *p*-menthane (in small quantity), *p*-menthan-2-ol [phenylurethane, (carbamate), m. p. 107—108°], and *l*-*p*-menthane-2 : 8-diol are obtained. R. W. WEST.

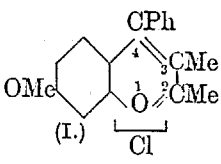
Identity of uncineol with eudesmol. A. R. PENFOLD (J. Proc. Roy. Soc. N.S. Wales, **59**, 124—127).—The stearoptene, uncineol, isolated from the essential oil of *Melaleuca uncinata*, has been shown to be identical with eudesmol contained in eucalyptus oils. The pure substance has m. p. 80·5—81°, and after fusion m. p. 82°, b. p. 155—156°/10 mm., $[\alpha]_D^{20}$ +33·45° in chloroform; the hydrochloride has m. p. 75—76°. C. J. STILL.

Steric hindrance and *cis-trans*-isomerism. II. Borneol, *iso*borneol, and their esters. G. VAVON and P. PEIGNIER (Bull. Soc. chim., 1926, [iv], **39**, 924—942).—Camphor is hydrogenated with difficulty in acetic acid using platinum-black, yielding 90% of *iso*borneol. This is then further dehydrated and reduced to *iso*camphane. Comparative measurements show that bornyl esters are more readily formed and also more readily hydrolysed than those of *iso*borneol. Moreover, borneol reacts more readily with magnesium ethyl bromide than does *iso*borneol. The lesser reactivity of the latter must be due to steric hindrance, and this fact, together with its direct formation from camphor, indicate that *iso*borneol has the *cis*-configuration, *i.e.*, the hydroxyl group and the bridge are on the same side of the *cyclo*hexane ring. d-*Bornyl* iso*valerate*, b. p. 151—152°/26 mm., $[\alpha]_{578}$ +36·7°, d_4^{18} 0·9486, n_D^{18} 1·4605; l-iso*bornyl* iso*valerate*, b. p. 142—144°/18 mm., $[\alpha]_{578}$ −56°, d_4^{18} 0·9523, n_D^{18} 1·462, and l-iso*bornyl benzoate*, b. p. 185°/11 mm. (corr.), $[\alpha]_{578}$ −78°, d_4^{16} 1·057, n_D^{16} 1·529, are described. H. E. F. NOTTON.

Caryophyllene alcohols and their occurrence in nature. J. M. ROBERTSON (Nature, 1926, **118**, 156).—The non-occurrence of caryophyllene alcohol in nature is not surprising in view of the observation (Henderson, Robertson, and Kerr, this vol., 298) that in its preparation from caryophyllene by Wallach's hydration method ring-closure occurs with the irreversible production of a tricyclic structure. Dicyclic caryophyllol (*loc. cit.*), however, should occur in nature, and this substance may, in fact, be identical with the dicyclic sesquiterpene alcohol obtained from clove stems by Semmler (A., 1912, i, 479).

A. A. ELDRIDGE.

Styrylbenzopyrylium salts. VII. Conversion of 7-methoxy-2 : 3-dimethylchromone into styrylpyrylium salts. I. M. HEILBRON and A. ZAKI (J.C.S., 1926, 1902—1906).—When 7-methoxy-2 : 3-dimethylchromone is treated in benzene solution with 2 mols. of magnesium phenyl bromide, it yields 7-*methoxy*-4-*phenyl*-2 : 3-*dimethylbenzopyrylium chloride* (I) (*ferrichloride*, m. p. 114°; *perchlorate*, m. p. 206°), which readily condenses with aromatic aldehydes in alcoholic solution to yield 2-styrylbenzopyrylium salts (cf. Buck and Heilbron, *ibid.*, 1923, **123**, 2521). The substitution of auxochromic groups in the phenyl group in position 4 has a decided influence on the colour of the salts. The following compounds are obtained by condensing (I) with aldehydes : 7-*methoxy*-4-*phenyl*-2-p-*hydroxystyryl*-3-*methylbenzopyrylium chloride*, m. p. 275° (decomp.) (*perchlorate* described); 2-p-*methoxystyryl* compound (*ferrichloride* described); 2-p-*hydroxy*-m-*methoxystyryl* compound (*ferrichloride* described); 2-p-*dimethylaminostyryl* compound (*ferrichloride*, *diperchlorate*, and *monoperchlorate* described). When 7-methoxy-2 : 3-dimethylchromone is treated with magnesium *p*-anisyl bromide, it yields 7-*methoxy*-4-p-*anisyl*-2 : 3-*dimethylbenzopyrylium chloride*, m. p. 160° (*ferrichloride* described), whilst with magnesium *p*-dimethylaminophenyl iodide it yields 7-*methoxy*-4-p-*dimethylaminophenyl*-2 : 3-*dimethylbenzopyrylium chloride* (*perchlorate* described). The 4-*p*-anisyl chloride condenses with aldehydes in manner similar to that of the 4-phenyl analogue, and thus affords : 7-*methoxy*-4-p-*anisyl*-2-p-*hydroxystyryl*-3-*methylbenzopyrylium chloride* (*ferrichloride* described); 2-p-*methoxystyryl* compound (*ferrichloride* described); and 2-p-*dimethylaminostyryl* compound (*ferrichloride*, m. p. 125°). R. W. WEST.



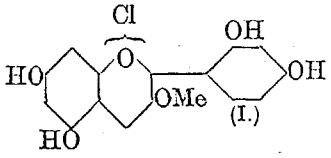
(I.)

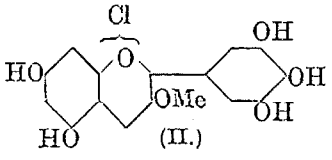
Synthesis of pyrylium salts of anthocyanidin type. IX. Hydroxyflavylium salts. A. ROBERTSON and R. ROBINSON (J.C.S., 1926, 1951—1959).—Condensation of salicylaldehyde with acetoveratrone yields 3 : 4-*dimethoxyphenyl* 2-*hydroxystyryl ketone*, m. p. 150—151°, which is readily converted into 3′ : 4′-*dimethoxyflavylium chloride* (*ferrichloride*, m. p. 196—196·5°). This on demethylation yields 3′ : 4′-*dihydroxyflavylium chloride*, which gives an intense ferric chloride reaction. β-Resorcylaldehyde condenses with acetoveratrone to yield 7-*hydroxy*-3′ : 4′-*dimethoxyflavylium chloride* (*ferrichloride*, m. p. 182—183°), which on demethylation yields 7 : 3′ : 4′-*tri*-

hydroxyflavylium chloride (butinidin chloride), of which the alkali reactions resemble those of mecocyanin. By condensations and demethylation of the products, the following compounds are obtained: from salicylaldehyde and ω-methoxyacetoveratrone, 3 : 3′ : 4′-*trimethoxyflavylium ferrichloride*, m. p. 173°, and 3 : 3′ : 4′-*trihydroxyflavylium chloride*; from orcylaldehyde and ω-methoxyacetoveratrone, 7-*hydroxy*-3 : 3′ : 4′-*trimethoxy*-5-*methylflavylium ferrichloride*, m. p. 182—183°, and 3 : 7 : 3′ : 4′-*tetrahydroxy*-5-*methylflavylium chloride*, the ferric chloride and alkali reactions of which resemble those of cyanidin; from 6 : 4′-dimethoxyflavylium chloride by demethylation, 6 : 4′-*dihydroxyflavylium chloride*; from 2-hydroxy-5-methoxybenzaldehyde and acetoveratrone, 6 : 3′ : 4′-*trimethoxyflavylium ferrichloride*, m. p. 186°, and 6 : 3′ : 4′-*trihydroxyflavylium chloride*; from 2-hydroxy-5-methoxybenzaldehyde and ω-methoxyacetoveratrone, 3 : 6 : 3′ : 4′-*tetramethoxyflavylium ferrichloride*, m. p. 198—199°, and 3 : 6 : 3′ : 4′-*tetrahydroxyflavylium chloride*; from *o*-vanillin and acetoveratrone, 8 : 3′ : 4′-*trimethoxyflavylium ferrichloride*, m. p. 193—194°; from *o*-vanillin and ω-methoxyacetoveratrone, 3 : 8 : 3′ : 4′-*tetramethoxyflavylium ferrichloride*, m. p. 162—163°, and 3 : 8 : 3′ : 4′-*tetrahydroxyflavylium chloride*.

In the alkali reaction, hydroxyl in position 6 tends to increase the intensity and stability of the colour, whilst hydroxyl in position 8 tends towards a reverse effect. R. W. WEST.

Synthesis of pyrylium salts of anthocyanidin type. X. Delphinidin chloride 3-methyl ether. E. S. GATEWOOD and R. ROBINSON (J.C.S., 1926, 1959—1967).—2 : 4-Diacetoxy-ω-methoxyacetophienone condenses with 2 : 4 : 6-triacetoxybenzaldehyde in a formic acid solution of hydrogen chloride yielding a product which on hydrolysis gives *morinidin chloride* 3-*methyl ether* (I). Sodium hydroxide causes con-

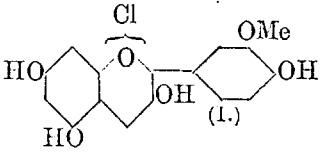




densation of 2-hydroxy-4 : 6-dimethoxybenzaldehyde with 3 : 4 : 5-trimethoxyacetophenone, m. p. 76—77°, yielding 3 : 4 : 5-*trimethoxyphenyl* 2-*hydroxy*-4 : 6-*dimethoxystyryl ketone*, m. p. 151—152°, which is readily converted by hydrochloric acid into 5 : 7 : 3′ : 4′ : 5′-*pentamethoxyflavylium chloride*, m. p. 150° (*ferrichloride*, m. p. 199—201°, *perchlorate*, and *mercurichloride* described). Demethylation of the chloride using phenol and hydriodic acid ultimately yields 7(or 5) : 3′ : 4′ : 5′-*tetrahydroxy*-5(or 7)-*methoxyflavylium chloride*.

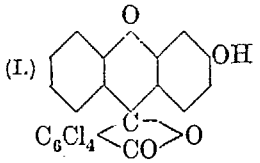
When 3 : 4 : 5-triacetoxybenzoyl chloride reacts in ether solution with methyl sodio-αγ-dimethoxyacetoacetate, the products after hydrolysis with aqueous-alcoholic potassium hydroxide may be separated by extraction first with ether and then with butyl alcohol. The ether-soluble product after acetylation is probably 3 : 4 : 5-*triacetoxy*-ω-*methoxyacetophenone*, m. p. 132—133°, but it will not condense with triacetoxybenzaldehyde to give a flavylium salt analogous to (I). The product which is soluble in butyl alcohol probably contains the group $(OH)_3C_6H_2\cdot CO\cdot CH(OMe)\cdot CO\cdot R$, since on acetylation it yields an oil which condenses with 2 : 4 : 6-triacetoxybenzaldehyde, the group ·CO·R being expelled, to give a product which hydrolyses to 5 : 7 : 3′ : 4′ : 5′-*pentahydroxy*-3-*methoxyflavylium chloride* (II). This delphinidin 3-methyl ether (II) is not identical with either myrtillidin chloride or petunidin chloride, and one of the possible formulæ for these compounds is thus eliminated. R. W. WEST.

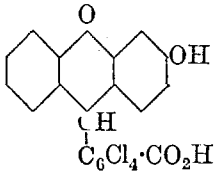
Synthesis of pyrylium salts of anthocyanidin type. XI. Synthesis of peonidin chloride. T. J. NOLAN, D. D. PRATT, and R. ROBINSON (J.C.S., 1926, 1968—1971).—When ω-chloro-4-acetoxyacetophenone is boiled with alcoholic potassium acetate, it yields 4-*hydroxy*-ω-*acetoxyacetophenone*, m. p. 127°, which on acetylation yields ω : 4-*diacetoxyacetophenone*, m. p. 98°. Hydrogen chloride in formic acid solution causes condensation of ω : 4-diacetoxyacetophenone with 2 : 4 : 6-triacetoxybenzaldehyde, and the product after hydrolysis gives a poor yield of pelargonidin chloride, $(OH)_2C_6H_2{\cdot}C_3HO(OH)\cdot C_6H_4\cdot OH$Cl. 4-*Hydroxy*-ω-*acetoxy*-3-*methoxyacetophenone*, m. p. 110°, is obtained from ω-chloroacetovanillone by the action of alcoholic potassium acetate, and on acetylation yields ω : 4-*diacetoxy*-3-*methoxyacetophenone*, m. p. 73°. Both these acetoxy-derivatives condense with 2 : 4 : 6-triacetoxybenzaldehyde, yielding products which give peonidin chloride (I) after hydrolysis.



R. W. WEST.

3-Hydroxytetrachlorofluoran and 3 : 4-dihydroxytetrachlorofluoran and some of their derivatives. W. R. ORNDORFF and C. H. JOHNSON (J. Amer. Chem. Soc., 1926, 48, 2221—2230).—Condensation of resorcinol with *o*-hydroxybenzoyltetrachlorobenzoic acid (cf. this vol., 290) in tetrachloroethane in presence of stannic chloride at 120—125° affords *tetrachloro*-3-*hydroxyfluoran* (I), m. p. not below 300° [*monoammonium* salt, red-brown, m. p. 277—280° (decomp.); *monosodium* salt, orange-red; m. p. not below 300°; *barium* salt ($3H_2O$), orange-red, decomp. above 300° (anhydrous); *monoacetate*, m. p. 198—200°; *monobenzoate*, m. p. 248—249°]. Bromination in glacial acetic acid affords *tetrachloro*-2 : 4-*dibromo*-3-*hydroxyfluoran*, m. p. not below 300° [*mono-*





acetate, $(+1C_6H_6)$, m. p. 290—292°], whilst reduction with zinc and acetic acid yields *tetrachloro*-3-*hydroxyhydrofluoranic acid*, (II), m. p. 257—258° (cf. Meyer and Hoffmeyer, A., 1892, 1228) (*monoacetate*, m. p. 187—188°). Substitution of pyrogallol for resorcinol

in the above condensation affords *tetrachloro*-3 : 4-*dihydroxyfluoran*, m. p. not below 300° [*monosodium* and *disodium* salts, m. p. not below 300°; *monobenzoate*, m. p. 238—240°; *dibenzoate*, m. p. 140° (+0·5C_6H_6), m. p. 220°]. Bromination in acetic acid yields *tetrachloro*-2-*bromo*-3 : 4-*dihydroxyfluoran*, m. p. not below 300° [*diacetate* (+0·5C_6H_6), m. p. 268—270° (decomp.). Whilst tetrachlorohydroxyfluoran does not absorb dry ammonia, its dibromo-derivative absorbs 1 mol., tetrachlorodihydroxyfluoran absorbs 1·22 mols., and its bromo-derivative absorbs 2·74 mols., the salts being orange-yellow, dark brown, and bluish-black, respectively. F. G. Willson.

Thiophen series. XIX. Thiophen-eucaine-*A* and some other thiophen derivatives. W. Steinkopf and W. Ohse (Annalen, 1926, **448**, 205—210).—Analogues of cucaine-*A*, stovaine, and benzoylquinine are prepared by the usual methods with the substitution of 2-thienoyl (thiophen-2-carboxyl) chloride for benzoyl chloride.

4-Hydroxy-2 : 2 : 6 : 6-tetramethylpiperidine-4-carboxylic acid (D.R.-P. 91121, 91122) has m. p. 340—343°, not 285° as given in the patents. The methyl ester hydrochloride, when heated with 2-thienoyl chloride at 145—155°, yields *methyl* 4-*thienoyloxy*-2 : 2 : 6 : 6-*tetramethylpiperidine*-4-*carboxylate*, m. p. 91—92° [*hydrochloride*, m. p. 272—273°; *chloroplatinate*, m. p. 234—235° (decomp.)], from which by methylation with methyl iodide "*thiophen-eucaine*-A," m. p. 123° [*hydrochloride*, m. p. 219—220° (decomp.); *chloroplatinate*, m. p. 239° (decomp.)], was obtained. By thienoylation of α-dimethylamino-β-methylbutan-β-ol, "*thiophen-stovaine*," $C_4H_3S{\cdot}CO_2{\cdot}CMeEt{\cdot}CH_2{\cdot}NMe_2$ (*hydrochloride*, m. p. 188°; *chloroplatinate*, m. p. 153°; *picrate*, m. p. 122°), is obtained. 2-*Thienoylquinine* (cf. benzoylquinine, D.R.-P. 178172, 178173), m. p. 133°, $[\alpha]_D^{21\cdot5}$ —11·4° (*chloroplatinate*, decomp. 240°), and 2-*thienoyl*-p-*phenetidine*, m. p. 172°, are also described.

C. Hollins.

Action of organo-magnesium compounds on nitriles. α-Aminonitriles. M. Velghe (Bull. Soc. chim. Belg., 1926, **35**, 229—234; cf. A., 1925, i, 23).—Tertiary α-amino-nitriles react with organo-magnesium compounds by exchanging the nitrile group for the radical of the magnesium compound. Thus magnesium methyl, ethyl, and propyl bromides act on α-piperidino-α-methylpropionitrile to produce, respectively: 1-αα-*dimethylethylpiperidine*, $CMe_3{\cdot}NC_5H_{10}$, b. p. 166°, d_4^{20} 0·8465, n_D^{20} 1·4532 [*chloroplatinate*, m. p. 235° (decomp.)]; 1-αα-*dimethylpropylpiperidine*, b. p. 188°, d_4^{20} 0·8608, n_D^{20} 1·4593; and 1-αα-*dimethylbutylpiperidine*, b. p. 205—207°, d_4^{23} 0·8517, n_D^{20} 1·4592, [*chloroplatinate*, m. p. 221° (decomp.)]. Magnesium methyl bromide acts on α-dimethylamino-α-methylpropionitrile with production of ethane and βγ-*tetramethyldiamino*-βγ-*dimethylbutane*, b. p. 149°; magnesium ethyl bromide yields the same substance, and when the reaction is conducted at a low temperature and with high dilution, a little β-*dimethylamino*-β-*methylbutane*, b. p. 117—118°, is formed; whilst with magnesium propyl bromide the corresponding β-*dimethylamino*-β-*methylpentane*, b. p. 138—139°, d_4^{20} 0·7950 [*chloroplatinate*, m. p. 230° (decomp.)], is the main product of reaction. G. M. Bennett.

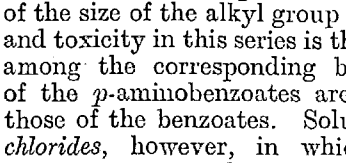
Piperidine derivatives. II. 3-Carbethoxy-1-alkyl-4-piperidyl benzoates. III. 3-Carbethoxy-1-alkyl-4-piperidyl *p*-aminobenzoates. S. M. McElvain (J. Amer. Chem. Soc., 1926, **48**, 2179—2185, 2239—2242; cf. A., 1924, i, 985).—The following alkyl-ββ′-dicarbethoxydiethylamines, $R{\cdot}N(CH_2{\cdot}CH_2{\cdot}CO_2Et)_2$, were prepared by condensation of the appropriate primary amines with ethyl β-bromopropionate and silver oxide in alcoholic solution (yields 65—75%): *ethyl*-, b. p. 126—128°/2 mm., d_{20}^{20} 1·0058, n_D^{20} 1·4385; n-*propyl*-, b. p. 132—134°/2 mm., d_{20}^{20} 0·9951, n_D^{20} 1·4393; iso*propyl*-, b. p. 128—130°/2 mm., d_{20}^{20} 0·9960, n_D^{20} 1·4388; n-*butyl*-, b. p. 154—156°/2 mm., d_{20}^{20} 0·9804, n_D^{20} 1·4400; iso*butyl*-, b. p. 153—156°/2 mm., d_{20}^{20} 0·9766, n_D^{20} 1·4384; sec.-*butyl*-, b. p. 145—148°/2 mm., d_{20}^{20} 0·9861, n_D^{20} 1·4415; n-*amyl*-, b. p. 164—168°/2 mm., d_{20}^{20} 0·9669, n_D^{20} 1·4375; and iso*amyl*-ββ′-*dicarbethoxydiethylamine*, b. p. 160—164°/2 mm., d_{20}^{20} 0·9689, n_D^{20} 1·4370. Treatment of the above tertiary amines with sodium in boiling xylene affords the corresponding 3-carbethoxy-1-alkyl-4-piperidones, which were isolated as the following hydrochlorides: *ethyl*-, m. p. 143—145°, n-*propyl*-, m. p. 138—140°; iso*propyl*-, m. p. 144—146°; n-*butyl*-, m. p. 127—129°; iso*butyl*-, m. p. 124—126°; sec.-*butyl*-, non-crystalline; n-*amyl*-, m. p. 141—143°; and 3-*carbethoxy*iso*amyl*-4-*piperidone hydrochloride*, m. p. 153—155°. When reduced with hydrogen in presence of platinum oxide, the above hydrochlorides yield the corresponding 4-hydroxy-3-carbethoxy-1-alkylpiperidines, of which only the *ethyl*-, b. p. 130—132°/2 mm., d_{20}^{20} 1·0754, n_D^{20} 1·4712 (*benzoate hydrochloride*, m. p. 214—216°), n-*propyl*-, b. p. 132—133°/2 mm., d_{20}^{20} 1·0502, n_D^{20} 1·4680 (*benzoate hydrochloride*, m. p. 208—210°), and 4-*hydroxy*-3-*carbethoxy*iso*propylpiperidine*, b. p. 128—130°/2 mm., d_{20}^{20} 1·0522, n_D^{20} 1·4695 (*benzoate hydrobromide*, m. p. 161—162°), could be purified by distillation, the remainder being isolated as the following benzoate salts: n-*butyl*-, *benzoate hydrobromide*, m. p. 194—196°; and *hydrochloride*, m. p. 175—177°; iso*butyl*-, *hydrochloride*, m. p. 177—179°; sec.-*butyl*-, *hydrobromide*, m. p. 162—164°; n-*amyl*-, *hydrochloride*, m. p. 164—166°; and 4-*benzoxy*-3-*carbethoxy*iso*amylpiperidine hydrochloride*, m. p. 179—181°. These salts have marked local anæsthetic action, the effect of which increases, whilst the toxicity decreases, with increase in size of the alkyl radical attached to the nitrogen atom. The amyl derivatives possess greater anæsthetic power than cocaine, and show only about one thirtieth of its toxicity. Aqueous solutions of the salts are acid, and cause irritation and hyperæmia.

III. The following 3-*carbethoxy*-1-*alkyl*-4-*piperidyl* p-*nitrobenzoate hydrochlorides* were prepared as described for the corresponding benzoates: *methyl*-, m. p. 193—195°; *ethyl*-, m. p. 214—216°; n-*propyl*-, m. p. 206—208°; iso*propyl*-, m. p. 203—205°; n-*butyl*-, m. p. 192—194°; iso*butyl*-, m. p. 204—206°; and 3-*carbethoxy*iso*amyl*-4-*piperidyl* p-*nitrobenzoate hydrochloride*, m. p. 167—169°. On reduction with hydrogen in alcohol in presence of platinum oxide catalyst, these are converted into the corresponding

3-*carbethoxy*-1-*alkyl*-4-*piperidyl* p-*aminobenzoates*, which were isolated as the *dihydrochlorides*: *methyl*-, m. p. 190—192°; *ethyl*-, m. p. 204—206°; n-*propyl*-, m. p. 221—223°; iso*propyl*-, m. p. 196—198°; n-*butyl*-, m. p. 228—230°; iso*butyl*-, m. p. 230—232°; and 3-*carbethoxy*iso*amyl*-4-*piperidyl* p-*aminobenzoate dihydrochloride*, m. p. 213—215°. Whilst the effect of the size of the alkyl group on the anæsthetic power and toxicity in this series is the same as that observed among the corresponding benzoates, the toxicities of the *p*-aminobenzoates are markedly higher than those of the benzoates. Solutions of the *monohydrochlorides*, however, in which form the *p*-aminobenzoates were administered, are neutral, and do not cause irritation and hyperæmia. The *iso*amyl derivative has about 2½ times the anæsthetic power, and one fourth the toxicity, of cocaine.

F. G. WILLSON.

Derivatives of 1-benzyltetrahydro*iso*quinoline. R. ROBINSON and H. WEST (J.C.S., 1926, 1985—1987).—By gradually adding anhydrocotarnine-2 : 4-dinitrotoluene to a cold mixture of stannous chloride, tin, acetic acid, and hydrochloric acid, reduction is effected, yielding *anhydrocotarnine*-2 : 4-*diaminotoluene* (I), m. p. 119° (*diacetyl* derivative, m. p. 211°; a monoacetyl derivative could not be obtained).



(I.)

When 2 : 3 : 4-trinitrotoluene is treated with a solution of sodium methoxide in methyl alcohol, it yields 2 : 4-*dinitro*-3-*methoxytoluene*, m. p. 86°, which condenses with cotarnine, yielding *anhydrocotarnine*-2 : 4-*dinitro*-3-*methoxytoluene*, m. p. 136° (*hydrochloride* described). Hydrastinine condenses readily with 2 : 4 : 6-trinitrotoluene, yielding *anhydrohydrastinine*-2 : 4 : 6-*trinitrotoluene*, m. p. 143° (decomp.) (*hydrochloride* described).

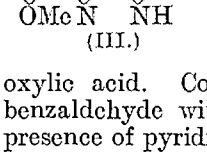
R. W. WEST.

Manufacture of derivatives [saturated or unsaturated dialkylamides] of pyridine-3-carboxylic acid. SOC. OF CHEM. IND. IN BASLE.—See B., 1926, 720.

Tryptophan–aldehyde reaction. III. Reaction of tryptophan with formaldehyde and with *p*-dimethylaminobenzaldehyde. E. KOMM (Z. physiol. Chem., 1926, **156**, 35—60; cf. A., 1923, ii, 194; 1925, ii, 164; this vol., 959).—Optimum conditions for detection and determination of tryptophan by means of formaldehyde and *p*-dimethylaminobenzaldehyde are investigated. To 5 c.c. of the tryptophan solution are added 5 c.c. of 10% hydrochloric acid containing 0·1065 mg. of formaldehyde; 10 c.c. of concentrated sulphuric acid are run in below the mixture, and on cautiously mixing the two layers, a bluish to reddish-violet coloration results, reaching a maximum intensity after 5 days or on adding a trace of an oxidant. Reduction or further oxidation destroys the colour, which is also very sensitive to variations in the proportion of formaldehyde. More stable is the deep blue coloration given by *p*-dimethylaminobenzaldehyde (2 c.c. of tryptophan solution; 2 c.c. of 0·25% *p*-dimethylaminobenzaldehyde in 10% hydrochloric acid; 6 c.c. of 10% hydrochloric acid; 10 c.c. of concentrated sulphuric acid), which is equally specific for tryptophan, though less sensitive (detecting 1 in 125,000). The single tone of the coloration is an advantage. The colour is destroyed by reduction or further oxidation. Certain proline derivatives accelerate the development of the colour in both cases.

C. HOLLINS.

[Quinoline derivatives from] 2-amino-3-methoxybenzaldehyde. J. TRÖGER and S. GËRO (J. pr. Chem., 1926, [ii], **113**, 293—308; cf. this vol., 68).—When treated with excess of acetone in alcoholic solution in presence of a trace of alkali, 2-amino-3-methoxybenzaldehyde affords 8-methoxy-2-methylquinoline (cf. Doebner and Miller, A., 1884, 1373) [*chloroaurate*, brown, m. p. 153° (decomp.)]. Acetophenone affords similarly 8-methoxy-2-phenylquinoline [*chloroplatinate* (+2H$_2$O), decomp. 195—197°], which, on reduction with tin and hydrochloric acid, yields 8-*methoxy*-2-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, m. p. 58° (*benzoyl* derivative, m. p. 104°). 2-Amino-3-methoxybenzaldehyde and phenylacetonitrile afford analogously 2-*amino*-8-*methoxy*-3-*phenylquinoline*, m. p. 222° (I) [*hydrochloride*, m. p. 238° (decomp.); *mercuric chloride* double salt, decomp. when heated; *chloroaurate*, cherry-red], which, on reduction, yields 8-*methoxy*-3-*phenyl*-1 : 2 : 3 : 4-*tetrahydroquinoline*, (II), m. p. 61° (*benzoyl* derivative, m. p. 100°) (cf. Tröger and Ungar, this vol., 524). Condensation of (I) with benzyl chloride in presence of alcoholic sodium ethoxide affords 2-*dibenzylamino*-8-*methoxy*-3-*phenylquinoline*, m. p. 183°, which also yields (II) on reduction, together with dibenzylamine. Treatment of (I) with nitrous acid affords 2-*hydroxy*-8-*methoxy*-3-*phenylquinoline*, m. p. 191°. 2-Amino-3-methoxybenzaldehyde condenses with ethyl cyanoacetate in presence of pyridine, with formation of 3-*cyano*-2-*hydroxy*-8-*methoxyquinoline*, m. p. 252—253° (decomp.). The latter appears to be reduced without the cyano-group being affected, but a reduction product could not be identified. Hydrolysis of the cyano-derivative with alkali affords 2-*hydroxy*-8-*methoxyquinoline*-3-*carboxylic acid*, m. p. not below 295° (*disilver* salt). Condensation of 2-amino-3-methoxybenzaldehyde with barbituric acid in aqueous alcoholic solution affords 9-*methoxy*-2 : 4-*diketo*-1 : 2 : 3 : 4-*tetrahydro*-1 : 3 : 10-*naphthtriazine* [2 : 4-*dihydroxy*-9-*methoxy*-1 : 3 : 10-*naphthtriazine*] (III), m. p. 273—276°, which yields *monosodium* and *monosilver* salts, and a *monobenzoyl* derivative, m. p. 242—243°. When heated with aqueous sodium hydroxide at 200°, (III) yields the above 2-hydroxy-8-methoxyquinoline-3-carboxylic acid. Condensation of 2-amino-3-methoxybenzaldehyde with malonic acid (more rapidly in presence of pyridine) also yields this carboxylic acid.



(III.)

F. G. WILLSON.

Preparation of hydantoins. H. BILTZ and K. SLOTTA (J. pr. Chem., 1926, [ii], **113**, 233—267).—Hydantoin, and its 1- and 5-derivatives, can be

conveniently prepared by the action of potassium cyanate on aminoacetonitriles (hydrochlorides or sulphates) (cf. Zelinsky and Stadnikov, A., 1908, i, 607) with subsequent ring closure from the resulting hydantoic acid nitrile by hydrolysis with concentrated hydrochloric acid, the complete synthesis being represented by the scheme

$RR'CO+NH_2R''+NaCN \longrightarrow CRR'(CN)\cdot NHR'' \longrightarrow CRR'(CN)\cdot NR''\cdot CO\cdot NH_2 \longrightarrow \begin{matrix} CRR'-NR'' \\ | \\ CO\cdot NH\cdot CO \end{matrix}$. Methylencaminoacetonitrile is converted by alcohol and sulphuric acid into aminoacetonitrile sulphate. The latter, when treated with aqueous potassium cyanate after half-neutralising with aqueous sodium carbonate, strong illumination being avoided, with subsequent hydrolysis with hydrochloric acid, affords 175 g. of hydantoin (m. p. 207—210°) per kg. of formalin. 3-Alkylhydantoins can be readily prepared by direct alkylation. Syntheses of a number of typical hydantoins are described, in the course of which the following compounds were prepared: α-amino*iso*butyronitrile, b. p. 55—60°/20 mm. (hydrochloride, decomp. 175°) (cf. Gulewitsch and Wasmus, A., 1906, i, 409); α-amino*iso*butyric acid hydrochloride, decomp. 236—237° (cf. Tiemann and Friedländer, A., 1882, 56); *α-cyano*iso*propylcarbamide*, m. p. 157°; *α-aminomethylethylacetonitrile*, b. p. 68°/14 mm., 72°/20 mm., *d* 0·9 (*hydrochloride*, decomp. 110—115°); *ureidomethylethylacetonitrile*, m. p. 142—143°; 5-methyl-5-ethylhydantoin, m. p. 149° (cf. Einhorn, D.R.-P. 289248); *α-aminodiethylacetonitrile*, b. p. 78°/12 mm., 81°/15 mm. (*hydrochloride*, decomp. 155° after sintering at 140°); *ureidodiethylacetonitrile*, m. p. 255° (decomp.); *α-methylaminoacetonitrile hydrochloride*, m. p. 104° (cf. Heimrod, A., 1914, i, 327); N-*α-cyanomethyl*-N-*methylcarbamide*, decomp. 212° after becoming brown at 180°; *α-methylamino*iso*butyronitrile*, b. p. 59°/20 mm. (*hydrochloride*, decomp. 196°); N-*α-cyano*iso*propyl*-N-*methylcarbamide*, decomp. 305°; 1 : 5 : 5-*trimethylhydantoin*; 1 : 3 : 5 : 5-*tetramethylhydantoin*, m. p. 85°; *α-ethylaminoacetonitrile hydrochloride*, decomp. 150—160° after sintering at 125° (cf. Knoevenagel and Mercklin, A., 1904, i, 981); N-*cyanomethyl*-N-*ethylcarbamide*, decomp. 208° after darkening from 175°; 1-ethylhydantoin, m. p. 103—104° (cf. Biltz, Marwitzky, and Heyn, A., 1921, i, 607); 3-*methyl*-1-*ethylhydantoin*, m. p. 93°, b. p. 278°; *α-ethylamino*iso*butyronitrile*, b. p. 70—80°/20 mm. (*hydrochloride*, decomp. 110°); N-*α-cyano*iso*propyl*-N-*ethylcarbamide*, decomp. 295—297°; and 5 : 5-*dimethyl*-1-*ethylhydantoin*, m. p. 138—139°. When boiled with acetic anhydride, 5 : 5-dimethylhydantoin affords 1-*acetyl*-5 : 5-*dimethylhydantoin*, m. p. 192°, which, on treatment with diazomethane, yields 1-*acetyl*-3 : 5 : 5-*trimethylhydantoin*, m. p. 99—100°. 1-*Nitro*-3 : 5 : 5-*trimethylhydantoin*, m. p. 115—116°, is obtained by nitrating trimethylhydantoin or methylation of 1-nitro-5 : 5-dimethylhydantoin (cf. Franchimont and Klobbie, A., 1889, 125). Chlorination of 5 : 5-dimethylhydantoin in aqueous solution affords 1 : 3-*dichloro*-5 : 5-*dimethylhydantoin*, m. p. 132°, which loses chlorine on treatment with alcohol or aqueous potassium iodide. 3-Phenylhydantoins are obtained by treating nitriles of α-amino-acids with phenylcarbimide in anhydrous benzene, with subsequent hydrolysis of the resulting *N'*-phenyl-*N*-cyanoalkylcarbamides. N'-*Phenyl*-N-*methyl*-N-*α-cyano*iso*propylcarbamide*, m. p. 118—120°, and 3-*phenyl*-1 : 5 : 5-*trimethylhydantoin*, m. p. 98—100°, are described. 1-Arylhydantoins are obtained by treating arylaminoacetic acids (cf. Hausdörfer, A., 1889, 1013) with potassium cyanate, and subsequent ring closure with hydrochloric acid. 1-Phenylhydantoin (*potassium* salt, decomp. 370—378°) (cf. Schwebel, A., 1878, 301) affords, on treatment with diazomethane and acetic anhydride, respectively, 1-*phenyl*-3-*methylhydantoin*, m. p. 185°, and 1-*phenyl*-3-*acetylhydantoin*, m. p. 145—146°. 1-Anisylhydantoin, m. p. 201° (cf. Frerichs and Breustedt, A., 1903, i, 16), 1-*anisyl*-3-*acetylhydantoin*, m. p. 172°, and 1-*anisyl*-3-*methylhydantoin*, m. p. 194°, are described. Treatment of aminoacetonitrile sulphate with phenylcarbimide affords phenylhydantoic acid, which, on treatment with hydrochloric acid, yields 3-phenylhydantoin, m. p. 168° (cf. Mouneyrat, A., 1900, i, 644).

F. G. Willson.

Alloxanic acid. H. Biltz and F. Lachmann (J. pr. Chem., 1926, [ii], **113**, 309—332; cf. A., 1921, i, 617).—Esters of alloxanic acid are conveniently prepared by saturating a paste of barium alloxanate in the appropriate anhydrous alcohol with hydrogen chloride, air being excluded and vigorous agitation applied. By prolonging the time of reaction, adding fresh alcohol and re-saturating with hydrogen chloride, and finally raising the temperature to 30—40°, ether-esters can be obtained. *Ethyl* 5-*ethoxyhydantoin*-5-*carboxylate* has m. p. 84—86°. Alloxanic amides are readily obtained by treatment of ethyl alloxanate with amines at low temperatures. 5-*Hydroxyhydantoylmethylamide* is stable only as the *monoalcoholate*, decomp. 145—146°, or the *monohydrate*, decomp. 162—163°. The corresponding *ethylamide*, decomp. 136°, and *anilide*, m. p. 99—105°, are described. Treatment of methyl alloxanate with ethereal diazomethane affords methyl 5-methoxy-1 : 3-dimethylhydantoin-5-carboxylate, m. p. 72° (cf. Biltz and Bülow, A., 1921, i, 609). Amides of 5-ethoxyhydantoic acid are obtained from the esters as above. 5-*Ethoxyhydantoyl-methylamide*, m. p. 111°, and *-ethylamide*, decomp. 136—137°, are described. When boiled with water, ethyl 5-ethoxyhydantoin-5-carboxylate yields 5-*ethoxyhydantoin*-5-*carboxylic acid*, stable only as the *dihydrate*, m. p. 54°, or *monohydrate*, m. p. 90—91°. 5-*Methoxyhydantoylanilide* has m. p. 134°. Treatment of ethyl 4-methylimino-5-ethoxy-1-methylhydantoylcarbamate (cf. Biltz and Damm, A., 1914, i, 1095) with hot aqueous methylamine affords 4-*methylimino*-5-*ethoxy*-1-*methylhydantoylmethylamide*, m. p. 257—258° (*acetyl* derivative, m. p. 168°). The corresponding *ethylamide*, m. p. 224—225° (*acetyl* derivative, m. p. 163—164°), is described. Treatment of ethyl 5-ethoxy-1-methylhydantoylcarbamate with aqueous ethylamine or methylamine affords 5-ethoxy-1-methylhydantoin-carboxylamide (cf. Biltz and Damm, *loc. cit.*), whilst alcoholic hydrogen chloride yields similarly *ethyl* 5-*ethoxy*-1-*methylhydantoincarboxylate*, m. p. 82—83°. Methyl alcohol and hydrogen chloride yield similarly methyl 5-methoxy-1-methylhydantoin-

carboxylate. 5-*Ethoxy*-1-*methylhydantoyl-amide*, m. p. 206—207° (3-*acetyl* derivative, m. p. 136—137°), -methylamide (cf. Biltz, A., 1910, i, 523) (3-*acetyl* derivative, m. p. 111—112°), and -*ethylamide*, m. p. 131—132° (+1H_2O), or m. p. 101—102° (anhydrous), were prepared from the corresponding ethyl ester.

F. G. Willson.

Salts of alloxanic acid. Systematic study of hydrates. H. Biltz and F. Lachmann (J. pr. Chem., 1926, [ii], **113**, 333—347).—Barium alloxanate crystallises from aqueous solution at below 35° as the *pentahydrate* (cf. Liebig and Wöhler, Annalen, 1838, **26**, 296). Under reduced pressure, this rapidly loses water at 80°, with formation of a *hemihydrate*, which is then dehydrated more slowly. A *tetrahydrate* is obtained by drying the pentahydrate over calcium chloride. Strontium alloxanate forms a *pentahydrate*, and also a *sesquihydrate*, whilst normal calcium alloxanate forms a pentahydrate (cf. Schlieper, *ibid.*, 1845, **55**, 275) and a *hemihydrate*. Calcium hydrogen alloxanate forms a hexahydrate (cf. Staedeler, *ibid.*, 1856, **97**, 120) and a *monohydrate*. Normal potassium alloxanate crystallises only with 2·5H_2O, whilst potassium hydrogen alloxanate is anhydrous. It is pointed out that dehydration of the most highly hydrated salt in a vacuum, and subsequent plotting of a time–dehydration curve, will not necessarily give evidence of the existence of intermediate hydrates, for the identification of which exhaustive equilibrium measurements in salt–hydrate–water–vapour systems are required.

F. G. Willson.

Compounds of amino-acids with piperazines. E. Abderhalden and Kohl-Egger (Z. physiol. Chem., 1926, **156**, 128—143).—2 : 5-Dimethylpiperazine is obtained from its tartrate (Bayer's "Lycetol") by shaking with chloroform and alkali. Peptides are prepared from it by condensation with suitable halogenated acid halides, followed by treatment with alcoholic ammonia etc.

1 : 4-*Di*-dl-α-*bromo*isocapronyl-2 : 5-*dimethylpiperazine* (1 : 4-*di*-dl-α-*bromo*-γ-*methylvaleroyl*-2 : 5-*dimethylpiperazine*), m. p. 186°; 1 : 4-*di*-dl-*leucyl*-2 : 5-*dimethylpiperazine*, m. p. 134—135° [*hydrobromide*, m. p. 298—299° (decomp.)]; 1 : 4-*di*(*chloroacetyl*)-*dileucyl*-2 : 5-*dimethylpiperazine*, m. p. 243—244° (decomp.); 1 : 4-*diglycyldileucyl*-2 : 5-*dimethylpiperazine*, m. p. 205° [*hydrochloride*, m. p. 235—237° (decomp.)]; 1 : 4-*di*-(α-*bromopropionyl*)*dileucyl*-2 : 5-*dimethylpiperazine*, m. p. 260° (decomp.); 1 : 4-*dialanyldileucyl*-2 : 5-*dimethylpiperazine*, m. p. 215—216° (*hydrobromide*, m. p. 255—256°).

1 : 4-*Di*(*chloroacetyl*)-2 : 5-*dimethylpiperazine*, m. p. 148°; 1 : 4-*diglycyl*-2 : 5-*dimethylpiperazine*, oily [*hydrochloride*, m. p. 282° (decomp.)]; 1 : 4-*di*-(α-*bromopropionyl*)*diglycyl*-2 : 5-*dimethylpiperazine*, m. p. 180—182° (decomp.); 1 : 4-*dialanyldiglycyl*-2 : 5-*dimethylpiperazine*, oily [*hydrobromide*, m. p. 265—269° (decomp.)].

1 : 4-*dl*-Diglycyldileucyl-2 : 5-dimethylpiperazine is not fermented by macerated yeast-extract, whilst *dl*-leucylglycine is easily attacked under the same conditions.

C. Hollins.

Reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid leading to the preparation of phthalazine, phthalazone, and phthalimidine derivatives. F. M. Rowe, (Miss) E. Levin, A. C. Burns, J. S. H. Davies, and W. Tepper (J. Soc. Dyers Col., 1926, **42**, 242—248).—See this vol., 625.

Indigo dye. S. N. Gupta.—See B., 1926, 736.

Benz*iso*oxazole [indoxazen]. H. Lindemann and H. Thiele (Annalen, 1926, **449**, 63—81; cf. Lindemann and Mühlhaus, this vol., 80).—2-Chloro-5-nitrobenzaldoxime is converted by boiling alcoholic alkali into 5-nitro-2-hydroxybenzonitrile, m. p. 190°, which is also prepared by nitration of *o*-hydroxybenzonitrile, or by the action of alcoholic alkali on 4-nitrobenz*iso*oxazole; intermediate formation of the nitrobenz*iso*oxazole from chloronitrobenzaldoxime could not be demonstrated.

5-Nitro-2-hydroxybenzonitrile, heated at its m. p., yields 2 : 4 : 6-*tri*-(5′-*nitro*-2′-*hydroxyphenyl*)-1 : 3 : 5-*triazine*, m. p. above 340°. 2 : 4 : 6-*Tri*-(3′ : 5′-*dibromo*-2′-*hydroxyphenyl*)-1 : 3 : 5-*triazine*, m. p. above 300°, is similarly obtained from 3 : 5-dibromo-2-hydroxybenzonitrile.

3 : 5-*Dibromosalicylaldoxime*, m. p. 218—220° (*diacetyl* derivative, m. p. 150°), could not be anhydrised to dibromobenz*iso*oxazole, but when heated with acetic anhydride gave 3 : 5-*dibromo*-2-*acetoxybenzonitrile*, m. p. 85—87°, the corresponding hydroxy-compound being formed by heating the *monoacetyl* derivative, m. p. 146°, above its m. p. In the case of *salicylaldoxime monoacetate*, m. p. 75°, however, benz*iso*oxazole itself, b. p. 82—83°/14 mm., d_4^{20} 1·172, is readily obtained by distillation in a vacuum at 120—130° (oil-bath temperature). With less precaution, the isomeric *o*-hydroxybenzonitrile results. The properties of benz*iso*oxazole are in agreement with those of Conduché's product (A., 1908, i, 154). 4-*Nitrobenz*isoo*xazole*, m. p. 126°, obtained by direct nitration, is converted above its m. p. into 5-nitro-2-hydroxybenzonitrile. 2-*Methylbenz*isoo*xazole*, b. p. 92·5°/11 mm., d_4^{20} 1·1247, prepared by heating 2-*hydroxyacetophenoneoxime monoacetate*, m. p. 146°, gives on nitration 4-*nitro*-2-*methylbenz*isoo*xazole*, m. p. 128°, and an isomeric *nitro*-compound, m. p. 250°. 4-*Amino*-2-*methylbenz*isoo*xazole*, m. p. 105° (*hydrochloride*, *sulphate*, and *acetyl* derivative, m. p. 156°, described), obtained by reduction with stannous chloride, diazotised and coupled with β-naphthol, gives a *dye*. From the *monoacetate*, m. p. 114°, of 2-hydroxy-5-methylacetophenoneoxime, m. p. 145°, there is obtained 2 : 4-*dimethylbenz*isoo*xazole*, b. p. 116°/13 mm., d_4^{20} 1·0949, which gives on nitration 6-*nitro*-2 : 4-*dimethylbenz*isoo*xazole*, m. p. 72°.

C. Hollins.

Manufacturing thiazoles. L. B. Sebrell and C. W. Bedford.—See B., 1926, 771.

Quinone vat dye. R. Herz.—See B., 1926, 735.

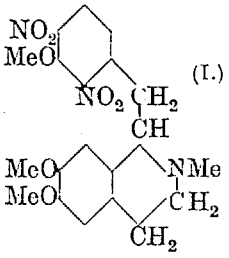
Benzoylecgonine ester. E. Poulson.—See B., 1926, 771.

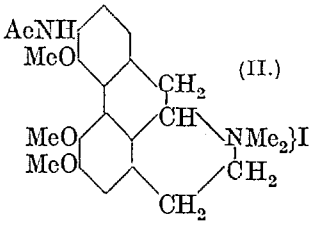
Conessine. D. D. Kanga, P. R. Ayyar, and J. L. Simonsen (J.C.S., 1926, 2123—2127).—When an aqueous solution of conessine dimethiodide is treated

with silver oxide and the solution evaporated first on the water-bath and then under diminished pressure at 200°, an oil is obtained from which apo*conessine*, $C_{22}H_{33}N$, m. p. 68·5° (*hydrochloride*, *hydrobromide*, *hydrogen sulphate*, m. p. 107—108°, *picrate*, m. p. 110—111°, *methiodide*, m. p. 283—285°), may be isolated. Conessine, m. p. 125°, reacts vigorously with methyl sulphate, yielding a dimethosulphate, m. p. 240—242°, and an oil which on treatment with aqueous potassium hydroxide yielded a *substance*, m. p. 253—254° [*picrate*, m. p. 256° (decomp.)]. When heated with aqueous potassium hydroxide, conessine dimethosulphate yields a hygroscopic *base*, $C_{26}H_{44}N_2$ [*dipicrate*, m. p. 258—259° (decomp.), and *dimethiodide* described]. Conessine reacts with mercuric acetate in acetic acid solution to give a *base* (needles).

R. W. West.

Synthetical experiments in the phenanthrene group of alkaloids. I. R. Robinson and J. Shinoda (J.C.S., 1926, 1987—1995).—The authors give the name "laudaline" to 1-hydroxy-6 : 7-dimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (cf. Pyman, *ibid.*, 1909, **95**, 1266).


(I.)


(II.)

Laudalinium chloride condenses with 2 : 4-dinitro-3-methoxytoluene in the presence of sodium methoxide, yielding *anhydrolaudaline*-2 : 4-*dinitro*-3-*methoxytoluene* (I), m. p. 111—112° (*hydrochloride* described), which can be reduced to either *anhydrolaudaline*-2 : 4-*diamino*-3-*methoxytoluene* (*dihydrochloride*, m. p. 236—237°) or *anhydrolaudaline*-2-*nitro*-4-*amino*-3-*methoxytoluene*, m. p. 145°. Acetic anhydride converts the nitro-amine into the *acetyl* derivative, m. p. 151°, and a *substance*, $C_{26}H_{33}O_9N_3$, m. p. 194°. The acetyl derivative is reduced by hydrogen and palladous chloride to *anhydrolaudaline*-2-*amino*-4-*acetamido*-3-*methoxytoluene*, m. p. 110° (picrate, m. p. 168—169°), which after diazotisation and treatment with copper powder yields *dehydroanhydrolaudaline*-4-*acetamido*-3-*methoxytoluene methiodide* (II), m. p. 210° (decomp.).

The structure of the nitro-amine (see above) is brought out by its conversion into (II) and further by analogy from the following experiments: Anhydrocotarnine-2 : 4-dinitro-3-methoxytoluene is reduced by stannous chloride, yielding *anhydrocotarnine*-2-*nitro*-4-*amino*-3-*methoxytoluene*, m. p. 184° (*acetyl* derivative, m. p. 134°), which is oxidised by potassium permanganate to 2-*nitro*-4-*acetamido*-3-*methoxybenzoic acid*, m. p. 228—229°. This acid is also obtained by the oxidation of 2-*nitro*-3-*methoxy*-p-*acetotoluidide*, m. p. 108—109°, prepared from 2-*nitro*-3-*methoxy*-p-*toluidine* (*hydrochloride*, m. p. 205°), which is obtained by the action of hydrogen sulphide on 2 : 4-dinitro-3-methoxytoluene and yields 2-nitro-*m*-tolyl methyl ether on deamination.

*iso*apoMorphine dimethyl ether (cf. Robinson and Robinson, *ibid.*, 1914, **105**, 1456) combines readily with methyl sulphate to give isoapo*morphine dimethyl ether methosulphate*, m. p. 246°, which is converted by boiling aqueous sodium hydroxide into 6 : 7-*dimethoxy*-1-(β-*dimethylaminoethyl*)*phenanthrene*, $C_{14}H_7(OMe)_2 \cdot CH_2 \cdot CH_2 \cdot NMe_2$, m. p. 111° (*hydrochloride* and *methiodide* described). R. W. West.

Ferricyanide reaction of potassium morphine. R. A. Beretevide (Rev. Fac. Cien. Quím., 1925, **3**, 89—123).—In the oxidation of morphine by potassium ferricyanide in the presence of potassium hydroxide, time of contact has only a slight effect. The amount of potassium ferricyanide reduced is, however, increased by heating, and also by increasing the proportion of potassium ferricyanide to morphine. Reduction is greater in alkaline than in neutral solution. The reaction does not appear to take place in definite molecular proportions.

G. W. Robinson.

Reactions of certain nitroso-derivatives with alkaloids. E. Navarro (Anal. Fís. Quím., 1926, **24**, 413—419).—The author has studied the reactions of the principal alkaloids with nitrosoresorcinol, nitrosophloroglucinol, nitrosopyrogallol, and sodium dihydroxynaphthalenedisulphonate. The colorations and precipitates obtained are not sufficiently distinctive for these reactions to be used for the characterisation of alkaloids. G. W. Robinson.

Manufacture of salts of cinchona alkaloids.—See B., 1926, 769.

Preparation of derivatives of aromatic arseno-compounds and their complex metal compounds. Farbw. vorm. Meister, Lucius, und Brüning.—See B., 1926, 769.

Derivatives of ethyl β-aceto-α-methylsuccinate; constitution of hæmatoporphyrin. W. Küster, H. Maurer, and A. Palm.—See this vol., 1024.

Coproporphyrin synthesis by means of yeast. O. Schumm (Z. physiol. Chem., 1926, **156**, 159—160).—Polemical against Fischer and Hilger (this vol., 189, 324, 544). C. Hollins.

Occurrence and detection of copratin and copratoporphyrin. IV. O. Schumm and E. Mertens (Z. physiol. Chem., 1926, **156**, 61—67; cf. this vol., 87, 538, 751).—The non-identity of coproporphyrin, copratoporphyrin, and hæmateric acid (α-hæmatoporphyroidin) is established by spectroscopic examination in dilute ether–acetic acid solution, in 25% hydrochloric acid, in 98% sulphuric acid, and in the presence of bromine, by the hydrochloric acid number, and by spectra of the methyl esters, and of complex iron and copper compounds. During flesh-free dieting, copratin predominates over hæmatin. C. Hollins.

Decomposition of soya-bean protein. I. Decomposition by hydrochloric acid. II. Decomposition by sulphuric acid. M. Mashino (J. Soc. Chem. Ind. Japan, 1926, **29**, 179—186, **187**—190).—I. Soya beans from four different sources were treated with light petroleum and the resulting proteins decomposed by hydrochloric acid. With 38·5% acid at 100°

9·1—9·7% of ammoniacal nitrogen (calculated on total nitrogen) was obtained after 30 min. treatment and 67·4—68·9% of amino-nitrogen after 12 hrs.; 20% acid yielded at 100° about 10% of ammoniacal nitrogen after 30 min. and about 62% of amino-nitrogen after 12 hrs., and at 40° 9·4% of ammoniacal nitrogen after 38—48 hrs. and 9·7% of amino-nitrogen after 48 hrs. About 1% of ammoniacal nitrogen and 4·3% of amino-nitrogen were formed by 0·4% acid at 40° after 48 hrs.

II. Sulphuric acid (20%) yielded 8—9% of ammoniacal nitrogen after ½—1 hr. and 9—10% after 2—12 hrs., and 52—54% of amino-nitrogen.

K. KASHIMA.

Heat coagulation of egg-albumin. H. MASTIN and H. G. REES (Biochem. J., 1926, **20**, 759—762).—Wu and Wu's observation (A., 1925, i, 1110) that tyrosine is eliminated when albumin is coagulated by heat is not confirmed. A reducing substance, probably containing a thiol group, is liberated in the filtrate when an albumin is precipitated by sodium tungstate or colloidal ferric hydroxide.

S. S. ZILVA.

Isolation of some hitherto undescribed products of hydrolysis of proteins. III. S. B. SCHRYVER and H. W. BUSTON (Proc. Roy. Soc., 1926, **B**, **100**, 360—367).—A re-examination of the basic fraction obtained by the hydrolysis of the proteins of the castor bean and of oats, using the technique previously described (cf. A., 1925, i, 794), showed that the cold-water-soluble carbamates on decomposition yield a solution which contains a fraction precipitable with phosphotungstic acid. This fraction on purification yields a *base*, $C_8H_5O_3N_3$, which has been named "protoctine" ("C_8-base"). It chars at 220°, is very soluble in water (*M* found, 192), readily soluble in alcohol (wherein it differs from all other known basic hydrolysis products), and insoluble in ether. It is precipitated from solution by mercuric chloride and barium hydroxide, but not by silver nitrate and alkali. Its solutions decolorise acid permanganate and give a series of colour reactions with diazobenzenesulphonic acid differing rather in degree than in kind from those obtainable with histidine. With bromine water, a flocculent yellow precipitate is obtained, which is destroyed on warming, the solution becoming colourless. The *hydrochloride*; *nitrate* (amorphous); *chloroaurate*, golden-brown needles; *chloroplatinate*, yellow needles; *picrate*, decomp. 205—210°; *dibenzoyl* derivative, m. p. 109°; *phenylcarbimide* derivative, $C_{15}H_{20}O_4N_4$, m. p. 130°; and the phenylhydantoin, m. p. 148°, are described. Beyond the fact that the molecule contains one amino-, one carboxyl, and one hydroxyl group, its constitution is unknown. It is suggested, however, that the other two nitrogen atoms are in the form of some basic functioning group similar to the glyoxaline ring. W. ROBSON.

Enzymic proteolysis. I. Structure of clupein. E. WALDSCHMIDT-LEITZ, A. SCHÄFFNER, and W. GRASSMANN (Z. physiol. Chem., 1926, **156**, 68—98).—An improved method for the separation of the pancreatic proteases has yielded erepsin, trypsin, and "trypsin-kinase" (*i.e.*, trypsin activated by the presence of enterokinase). These individual enzymes, and also papain in the form of its hydrogen cyanide compound, are employed for the fractional hydrolysis of clupein, the progress being followed by determinations of carboxyl and amino-groups. Throughout the hydrolysis sensibly equivalent amounts of carboxyl and amino-groups are liberated; hence the process consists essentially in the fission of amide (peptide) linkings. It follows further that in clupein the NH group of proline (not determinable by the method adopted) is not set free during this fission, and that the guanidine group of arginine is not concerned in the peptide linkings. C. HOLLINS.

Enzymic proteolysis. II. Enzymic hydrolysis of casein. E. WALDSCHMIDT-LEITZ and E. SIMONS (Z. physiol. Chem., 1926, **156**, 99—113; cf. preceding abstract).—The products of peptic hydrolysis of casein are further hydrolysed by trypsin-kinase, and these again by intestinal erepsin. Trypsin alone is only half as effective, and further hydrolysis is produced on addition of enterokinase or of yeast-erepsin. The pepsin-peptone from casein, unlike that from egg-albumin, is hydrolysed to some extent by erepsin. The product of exhaustive hydrolysis of casein by trypsin-kinase is still not completely hydrolysed after successive treatment with pepsin, trypsin-kinase, and erepsin, or with erepsin and pepsin. The method used in following these hydrolyses is determination of carboxylic acidity by titration in alcoholic solution with 0·2*N*-potassium hydroxide.

C. HOLLINS.

Potentiometric determination of aromatic nitroso- and nitro-compounds by means of titanous chloride. E. DACHSELT (Z. anal. Chem., 1926, **68**, 404—410).—The determination is carried out by direct titration at 50—80°, compounds insoluble in water being dissolved in alcohol. The break in the curve is satisfactory, but is much more pronounced in presence of sodium potassium tartrate, which also renders the colour change sharp.

S. I. LEVY.

Use of acetic anhydride in Zeisel's method for the determination of methoxyl groups. M. NIERENSTEIN (Analyst, 1926, **51**, 456).—The use of acetic anhydride in connexion with Zeisel's method is again deprecated, since besides formation of some acetyl iodide which distils into the silver nitrate solution, acetic anhydride and hydriodic acid by themselves yield weighable quantities of silver iodide (confirmed by their nearly quantitative conversion on keeping for 10—11 years).

D. G. HEWER.

Gasometric determination of primary aromatic amines. P. GRIGORJEV (Z. anal. Chem., 1926, **69**, 47—50).—The aqueous solution of the amine sulphate containing 0·1—0·2 g. of amine is mixed with a slight excess of dilute sulphuric acid, cooled in ice-water, and treated with a solution of sodium nitrite added slowly from a burette until the solution turns iodide-starch paper blue. The liquid is transferred to a nitrometer and a solution of ferrous sulphate in sulphuric acid is added, whereby the diazo-compound is decomposed with evolution of

nitrogen. After 2—3 min., the contents of the tube are agitated to complete the reaction and to absorb the greater part of the nitric oxide, formed simultaneously, in the ferrous sulphate solution. The gas is measured after cooling and finally transferred to a gas burette filled with sodium sulphite solution, whereby the last traces of nitric oxide are removed. The volume of the nitrogen remaining, after correction, indicates the amount of amine present. A. R. POWELL.

Gravimetric determination of benzidine and its analogues and new complex salts of these bases. W. HERZOG (Chem.-Ztg., 1926, **50**, 642—643).—Benzidine mercurichloride (cf. Spacu, Bul. Soc. Stiinte Cluj, **2**, 137 etc.) is so insoluble in water or dilute acetic acid that benzidine can be gravimetrically determined by precipitation with mercuric chloride. The solution must contain no free mineral acid. The precipitate is dried to constant weight without heat. *Benzidine mercuribromide*, $C_{12}H_{12}N_2,HgBr_2$, the *iodide*, and *o-tolidine mercurichloride, bromide*, and *iodide* are described. Mercury is quantitatively precipitated by excess of benzidine acetate. W. A. SILVESTER.

Colorimetric determination of tyrosine, tryptophan, and cystine in proteins. II. J. M. LOONEY (J. Biol. Chem., 1926, **69**, 519—538).—A reply is made to the criticisms of Fürth (A., 1924, ii, 575) and Kraus (*ibid.*, 1925, ii, 448) of the method of Folin and Looney (*ibid.*, 1922, ii, 539) for the determination of the above amino-acids, and further results are brought forward in support of the latter method; it is pointed out that the results obtained by this method are in good agreement with the mol. wts. of the proteins concerned, as estimated by Cohn (*ibid.*, 1925, ii, 641). The recent method of Hanke (this vol., 633) for the determination of tyrosine is criticised on the ground that this author has neglected the simultaneous precipitation of tryptophan and cystine under the conditions he employs. C. R. HARINGTON.

Marquis' reagent and hydroxydimorphine. A. LEULIER and R. DUBREUIL (Compt. rend. Soc. Biol., 1925, **93**, 1313—1314; from Chem. Zentr., 1926, I, 1865).—Addition of 1 drop of Marquis' reagent (1 c.c. of concentrated sulphuric acid+1 drop of formaldehyde) to a small quantity of hydroxydimorphine previously moistened with hydrogen peroxide produces a green colour. In the absence of hydrogen peroxide, barium dioxide, etc., a dirty reddish-brown colour is obtained. Excess of hydrogen peroxide must be avoided. The reaction is specific. J. S. CARTER.

Crystallisation by inoculation in microchemistry. N. SCHOORL (Mikrochem., 1926, **4**, 103—108).—When the precipitant contains traces of the crystalline alkaloid, the precipitation of quinidine by sodium hydrogen carbonate and of atropine by sodium carbonate always leads to crystalline deposits. J. S. CARTER.

Biochemistry.

Transport of oxygen and carbon dioxide by bloods containing hæmocyanin. A. C. REDFIELD, T. COOLIDGE, and A. L. HURD (J. Biol. Chem., 1926, **69**, 475—509).—Investigation of a number of different species shows that, whilst each hæmocyanin has its own individual properties, the general physicochemical behaviour of all the blood pigments, in the transport of oxygen and carbon dioxide, is the same, and is similar to that of hæmoglobin. In the case of certain hæmocyanins, the pigment differs from hæmoglobin in having its greatest affinity for oxygen at high tensions of carbon dioxide. C. R. HARINGTON.

So-called oxygen content of methæmoglobin. J. B. CONANT and N. D. SCOTT (J. Biol. Chem., 1926, **69**, 575—587).—Whilst the experimental observations of Nicloux (this vol., 191) regarding the oxygen content of methæmoglobin are confirmed, his deductions are criticised on the ground that (1) in the titration with sodium hyposulphite he neglected the difference between the titration of oxyhæmoglobin, where, owing to the presence of free oxygen, formation of hydrogen peroxide can take place, and that of methæmoglobin, where this is not the case; (2) that under the conditions employed by him for the oxidation of carboxyhæmoglobin the reaction was incomplete; (3) that in his experiments on the oxidation of oxyhæmoglobin he used twice the amount of ferricyanide necessary to liberate the oxygen, hence obtaining a fictitious ratio. The present authors' interpretation of the results leads to the conclusion that methæmoglobin contains one fourth of the oxygen of oxyhæmoglobin. C. R. HARINGTON.

Comparison of the sensitivities of methæmoglobin and of oxyhæmoglobin to a reducing agent. M. NICLOUX and J. ROCHE (Compt. rend. Soc. Biol., 1925, **93**, 1659—1662; from Chem. Zentr., 1926, I, 2109).—In mixtures of methæmoglobin and oxyhæmoglobin in the ratios 1 : 3, 1 : 1, and 3 : 1, the latter substance is preferentially and sometimes exclusively reduced by sodium hyposulphite. J. PRYDE.

Detection of variation in acid content of blood. K. GOLLWITZER-MEIER (Deut. Archiv klin. Med., 1925, **149**, 151—156; from Chem. Zentr., 1926, I, 1678).—The determination of the ability to take up carbon dioxide furnishes no information in cases of disease regarding the quantity of abnormal acids in blood. A true estimate is obtained only when the sum of the inorganic anions and cations is determined. The excess of cations over the normal content is equivalent to the quantity of abnormal organic acids. J. S. CARTER.

Presence of combined sugar in the blood. M. BUFANO (Arch. Farm. sperim., 1925, **40**, 235—240, 241—250; from Chem. Zentr., 1926, I, 2213).—Evidence is adduced of the presence of combined sugar in the blood. W. O. KERMACK.

Irritability and blood-sugar. E. M. GREISHEIMER (Amer. J. Physiol., 1925, **72**, 213).—In experiments with decerebrate dogs, the nerve irritability increased when the blood-sugar decreased, and *vice versa*. A. A. ELDRIDGE.

Glycolysis. VI. Distribution of phosphorus in the blood. P. RONA and K. IWASAKI (Biochem. Z., 1926, **174**, 293—307).—The amount of phosphate precipitated by molybdate increases when blood is kept at 37°. This increase is due neither to glycolysis, since it is unaffected by the addition of sodium fluoride or the maintenance of a p_H unfavourable to glycolysis, nor to autolysis, since the total phosphorus of the blood-filtrate after precipitation of the proteins is unchanged. It is probably due to the liberation of phosphoric acid by the action of enzymes from compounds of the ester type. The optimum reaction of the phosphatase is in the neighbourhood of p_H 6. The esters are of two types, easily and difficultly hydrolysable by acids. E. C. SMITH.

Influence of various factors on the course of blood glycolysis. Carbohydrate metabolism. XI. S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, **93**, 1681—1683; from Chem. Zentr., 1926, I, 2113—2114).—Glycolysis does not occur in plasma, but is confined to the corpuscles. Addition of fluoride prevents glycolysis, oxalate retards it, whilst citrate and hirudin are without influence. Glycolysis is more rapid at 37° than at 20°. Slight increases in the alkalinity of the blood and variations in the initial concentration of the blood-sugar are without effect on the rate of glycolysis. J. PRYDE.

Rate of glycolysis in normal and diabetic blood. Carbohydrate metabolism. XII. S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, **93**, 1684—1686; from Chem. Zentr., 1926, I, 2114).—The rate of glycolysis is independent of the concentration of dextrose in both diabetic and normal blood. During the first 2 hrs. after collection glycolysis proceeds more rapidly in normal than in diabetic blood, but this difference disappears later. This is ascribed to the presence of less "neo-glucose" in diabetic than in normal blood. J. PRYDE.

Effect of zinc ions on glycolysis in blood. L. J. VIVIANI (Rev. Fac. Cien. Quím., 1926, **4**, 31—72).—Defibrinated blood from well-nourished dogs maintained at 39° shows a loss of dextrose in 1 hr. amounting to 20—40%. The addition of zinc as sulphate in concentrations varying from 10^{-9} to 10^{-4} g. per c.c. does not affect glycolysis. With a concentration of 0·002 g. of zinc per c.c., glycolysis is completely inhibited. The effect is attributed entirely to the zinc ions. G. W. ROBINSON.

Volume of the proteins of serum. A. NITSCHKE (Arch. exp. Path. Pharm., 1926, **115**, 134—138).—From the distribution of chlorides across a membrane separating serum and physiological saline at the isoelectric point of the serum proteins, the volume occupied by the proteins has been calculated. The mean for a serum containing 7% of protein gave a protein volume of 7·5%. Similarly, from the distribution of dextrose there was derived a protein volume of 7·1%, which was independent of temperature, dilution of the serum, and hydrogen-ion concentration. The existence of a water envelope about the protein particle is improbable. R. K. CANNAN.

Condition of calcium in serum. A. NITSCHKE and H. J. FREYSCHMIDT (Biochem. Z., 1926, **174**, 287—292).—By application of the Donnan theory to the dialysis of serum maintained at constant p_H against physiological saline containing sodium hydrogen carbonate and phosphate, it is deduced that in serum at p_H 7·4 and 20° containing 0·010% of calcium and 0·0035% of phosphate the ionised calcium in the form of a saturated solution of calcium mono- and di-hydrogen phosphate represents 80% of the total, the remainder being present in the un-ionised, non-dialysable form, half as calcium proteinate and half as an unrecognised calcium phosphate complex. The solubility of the calcium phosphate is less than half that of the hydrogen carbonate under the same conditions. The equation $[Ca^{\cdot\cdot}][HPO_4^{\prime\prime}]=K$ holds, where $K(20°)=1·8$. Addition of calcium or phosphate or decrease of p_H must lead to the separation of molecular calcium phosphate. E. C. SMITH.

Vaso-constrictor substances of blood-serum. H. BORGERT and K. KEITEL (Biochem. Z., 1926, **175**, 1—7).—The vaso-constrictor substance of blood-serum arises from the disintegration of blood-platelets. Its formation does not depend on the presence of light, heat, oxygen, or bacteria, but after 24 hrs. it wholly or partly disappears and the preparation then has a vaso-dilator action. The vaso-constrictor substance is dialysable, not extracted with ether or acetone, and cannot be distilled.
P. W. CLUTTERBUCK.

Lipolytic activity of serum and the precipitin reaction of Sachs-Georgi. D. LAPPONI (Ann. d'Igiene, 1925, **35**, 865—871; from Chem. Zentr., 1926, I, 1592).—The precipitin reaction depends on the presence of certain lipins. It comprises a number of conditions which affect the colloidal system of antigen or serum in different ways according to the precipitation intensity of the serum. The lysis of the lipins which surround the colloidal micelles of cholesterinised antigen, does not occur with sera which precipitate the colloidal suspensions of the same extract, although these sera show lipolytic activity towards lipins of other colloidal lipo-protein systems. C. RIMINGTON.

Effect of certain substances on the precipitin reaction. C. M. DOWNS and K. GOODNER (J. Infect. Dis., 1926, **38**, 240—245).—Heterologous proteins do not interfere with the precipitin reaction or intensify the prozone, but cause dissociation of the formed precipitate. Concentrated solutions of dextrose or sucrose inhibit the formation of a precipitate; the former causes true, and the latter slight, dissociation of the formed precipitate. Other carbohydrates, in less concentrated solutions, interfered little with the reaction and acted as weak dissociating agents. CHEMICAL ABSTRACTS.

Ultrafiltration through collodion membranes. A. GROLLMAN (J. Gen. Physiol., 1926, 9, 813—826).—The author has attempted to determine how far such factors as the mode of filtration, the pressure applied, the nature of the filter, and the solution being filtered affect the validity of the deductions made from ultrafiltration experiments. He concludes that such factors as these render data obtained by ultrafiltration open to criticism, unless they are checked by other methods and certain precautions taken. Considering all the factors which might modify the effective pore size, he regards the view that ultrafiltration has a sieve-like action as adequate, and argues that it is unsound to make any deductions about living tissues from the demonstration of changes produced in the behaviour of collodion membranes. W. ROBSON.

Behaviour of the vitally important amino-acids during the incubation of the hen's egg. Y. SENDJU (J. Biochem. [Japan], 1925, 5, 391—415).—Both free and bound tryptophan are significant in the synthesis of blood and bile pigments. Possibly tyrosine is a building material for inner secretions or for substances essential for the normal progress of cellular metabolism. The free and combined purine-nitrogen increase during incubation and growth of the embryo. The amount of nitrogen which is not precipitated by phosphotungstic acid remains practically constant during the development of the egg.
CHEMICAL ABSTRACTS.

Chicken embryos: p_H, chloride, carbonic acid, and protein concentration in the tissues as functions of age. H. A. MURRAY (J. Gen. Physiol., 1926, 9, 789—803).—The p_H and the chloride concentration of the tissues decrease with age, the former from 7·00 to 6·64 (8 days), the latter from 4·82 to 1·00% of dry tissue (13 days), the fall being most rapid between the 10th and the 13th day of incubation. The carbon dioxide and protein concentrations increase with age, the latter especially between the 12th and the 16th days.
W. ROBSON.

Iodine storage in individual organs. T. VON FELLENBERG (Biochem. Z., 1926, 174, 355—363).—Iodine is present in all organs of the body, the thyroid gland being usually the richest. Administration of iodine as potassium iodide increases the iodine content of most organs. In the lung, 3 hrs. after administration a considerable accumulation occurs, which disappears after 48 hrs. In skin, hair, and, especially, muscle, a more permanent increase is observed, and it is in these tissues that the iodine reserve of the body is maintained. The organs in a case of malaria treated with iodotrypaflavine were found to contain large quantities of iodine. The thyroid gland of a newly-born child contained only a very small amount of iodine. E. C. SMITH.

Carotin-like compound as eye pigment of copepod. Origin and development during ontogeny. A. LVOV (Compt. rend. Soc. Biol., 1925, 93, 1602—1604; from Chem. Zentr., 1926, I, 2212).—An orange-yellow pigment has been isolated from the eye of *Idya furcata*. W. O. KERMACK.

Human fat. O. WAGNER (Biochem. Z., 1926, 174, 412—419).—The mean iodine value of the liquid fatty acids of human depôt fat at 0° is 100. Arachidonic acid (isolated as the bromo-derivative) is present to the extent of 0·3%, linoleic acid (isolated as the hydroxy-derivative) to the extent of 0·54% of the total fat. Sativic acid, m. p. 162°, was isolated from the products of oxidation of the fat with potassium permanganate. E. C. SMITH.

Mineral composition of the skeletons of some invertebrates from Barents and Kara seas. Y. V. SAMOILOV and K. F. TERENT'EVA (Trans. Inst. Econ. Min. Petr., Pamphlet, 1925, 12, 3—32).—In the magnesium-calcareous group (*Strongylocentrotus drobachiensis*, *Ophiopleura borealis*, and *Asteria linckii robusta*) the percentage of magnesium carbonate depends on the temperature of the water in which the organism lives; the calcium carbonate is present as calcite. In *Leda pernula*, *Tellina calcarea*, and *Natica clausa* it is present as aragonite; in *Astarte borealis*, *Pecten islandicus*, and *Neptunea despecta* the outer portion is calcite and the inner aragonite.
CHEMICAL ABSTRACTS.

Iodine content of the thyroid. E. HERGLOZ (Biochem. Z., 1926, 175, 175—180).—The iodine of the thyroid gland was determined in a number of animals by Winkler's method. The central part of the gland contains more iodine than the peripheral part. P. W. CLUTTERBUCK.

Lactic acid content of cerebrospinal fluid. J. GLASER (J. Biol. Chem., 1926, 69, 539—547).—Normal cerebrospinal fluid contains 0·011—0·027% of lactic acid, the figures amounting to 60—100% of those for the corresponding blood. The lactic acid content of the cerebrospinal fluid tends to be diminished in cerebrospinal syphilis and to be increased in meningitis and in cases of brain tumour when the sample is taken from the part of the spinal cord which is in contact with the tumour.
C. R. HARINGTON.

Relation of blood- to cerebrospinal fluid-sugar and the diagnostic value of sugar determinations in cerebrospinal fluid. F. G. DIETEL (Z. ges. Neurol. Psychat., 1925, 95, 563—587; from Chem. Zentr., 1926, I, 1593).—Normal cerebrospinal fluid contains about 44·2 mg. of sugar %, and the ratio of blood-sugar to this is 2 : 1. There is a rise in the sugar of cerebrospinal fluid after dextrose injection which follows that of the blood-sugar.
C. RIMINGTON.

Gastric juice of the pregnant woman. T. NAKAI (J. Biochem. [Japan], 1925, 5, 465—477).—The following minimum, maximum, and average values were obtained: total acidity 2·0, 14·4, 6·4 c.c.; pepsin action (by Mett's tube) 0·2, 2, 0·97; lactic acid 0; free hydrochloric acid present in 2 of 14 cases. CHEMICAL ABSTRACTS.

Sputum. H. REINWEIN (Z. physiol. Chem., 1926, 156, 144—152).—Four litres of sputum were collected from a bronchitic patient. After removal of mucus, the total nitrogen (11 g.) was distributed as follows: purine bases, 0·102 g. (no uric acid);

histidine fraction, 6·104 g. (histidine picrolonate, m. p. 220°, isolated); arginine fraction, 0·142 g.; lysine fraction, 2·9 g., divided into α-fraction, 2·04 g. of nitrogen, in which neosine is identified by its chloroaurate, m. p. 207°, and β-fraction, consisting of putrescine (chloroaurate, m. p. 210°). Histamine was probably present. C. HOLLINS.

Basal urea excretion. C. RICHET, jun., and MINET (Compt. rend. Soc. Biol., 1925, **93**, 1270—1271; from Chem. Zentr., 1926, **1**, 1594—1595).—The results are expressed in terms of urea excretion per square metre per day. The surface is calculated from the formula $10{\cdot}7\sqrt[3]{p^2}$. For dogs, the mean value is 7·5, but individual variations were great. The diet supplied consisted of ample nitrogen-free food. C. RIMINGTON.

Excretion of uric acid by the kidney. H. GREMELS and R. BODO (Proc. Roy. Soc., 1926, **B**, **100**, 336—359).—The behaviour of the isolated perfused kidney towards uric acid has been studied in relation to the various theories of kidney excretion. The technique employed involved Starling's heart–lung–kidney preparation using dogs, with, in some cases, the introduction of the liver into the circuit. The toxic effect on the kidney observed with defibrinated blood was avoided by the use of hirudinised blood. Lithium urate was injected in a solution made isotonic by the addition of dextrose. Using the above preparation, all the uric acid disappearing from the blood was recoverable from the urine, whilst the rate of fall of the blood uric acid depended on the rate of urinary flow. The urinary percentage is at least two or three times as great as that of blood. The suppression, by the use of cyanide, of the glomerular and tubular functions of the kidney leads to the secretion of uric acid into the glomerular filtrate by the tubular cells. Only when the liver is included in the heart–lung–kidney preparation is there a marked and rapid oxidation of the blood uric acid, confirming the conclusions of Mann and Magath (cf. Ergeb. Physiol., 1924, **23**, I, 250). No evidence was found for Folin's statement that the kidney removes uric acid from the blood only to return it there for oxidation. Its initial rapid disappearance is due, not to its destruction, but to the establishment of an equilibrium between its concentration in the blood and in the tissues.

W. ROBSON.

Site of ammonia formation and rôle of vomiting in ammonia formation. S. R. BENEDICT and T. P. NASH, jun. (J. Biol. Chem., 1926, **69**, 381—396).—The conclusions of Bliss (this vol., 428) are criticised in detail and further arguments are brought forward in support of the theory previously advanced by the present authors (A., 1922, i, 191).

C. R. HARINGTON.

Origin of urinary ammonia. III. I. M. RABINOWITCH (J. Biol. Chem., 1926, **69**, 283—288).—In cases of severe diabetes the urinary excretion of ammonia is much greater than the total amount of ammonia which can be brought to the kidneys by the blood-stream; this fact supports the theory of Nash and Benedict (A., 1922, i, 191) that the greater part of the urinary ammonia is formed in the kidneys.

C. R. HARINGTON.

Excretion of chlorine by the kidneys after exposure to *X*-rays. A. ENGELHARD and H. SIELMANN (Deut. Archiv klin. Med., 1925, **149**, 168—176; from Chem. Zentr., 1926, I, 1671).—Persons who are in sodium chloride equilibrium show a retention of chlorine for some days after exposure of any part of the body to *X*-rays. There is no increase of chlorine in the blood. Irradiation of single cells (goose-blood corpuscles) in serum causes no uptake of chlorine by the cells. H. I. COOMBS.

Composition of glomerular urine. J. T. WEARN and A. N. RICHARDS (Amer. J. Physiol., 1924—1925, **71**, 209—227).—The glomerular fluid of the frog is free from protein when the blood flow through the glomerular capillaries is rapid. Sugar was absent from the blood of starving frogs in winter. Glomerular urine contains sugar (when the blood-sugar concentration, obtained by subcutaneous injection of dextrose, is less than 0·05%) and chlorides; bladder urine contains neither. Preliminary investigations of the urea content and reaction of the glomerular urine were made. A. A. ELDRIDGE.

Excreta of *Tinecola crinella*. A. C. HOLLANDE and H. CORDEBARD (Bull. Soc. Chim. biol., 1926, **8**, 631—635).—The excreta of the caterpillar of *Tinecola crinella* are strongly acid, contain soluble urates, ammonium salts, and a very small quantity of urea; alkali and alkaline-earth chlorides, phosphates, and sulphates are present. Intraperitoneal and subcutaneous injections of solutions into rabbits and guinea-pigs had no harmful effects.

H. J. CHANNON.

Catalase activity of the oral mucous membrane. T. SOLLMANN and R. L. HOWARD (J. Lab. Clin. Med., 1925, **11**, 130—139).—The median value (c.c. of 0·1*N*-hydrogen peroxide decomposed per min.) is 3·3 for the first and 2·3 for the second determination, the value varying from day to day. Very bad clinical conditions were associated with values of 6·0 and 5·0, respectively.

CHEMICAL ABSTRACTS.

Potassium and calcium content and ratio in blood-serum in physiological and pathological conditions. X. The adrenaline reaction. E. KYLIN (Deut. Archiv klin. Med., 1925, **149**, 354—365; from Chem. Zentr., 1926, I, 1670).—The ratio K : Ca in serum, which is normally 1·7—2·15, is changed in diseases. When the quotient is high, adrenaline produces a vagotonic effect and lower blood pressure; when low, it produces a sympathicotonic effect and higher blood pressure. The relation between this phenomenon and the causes of the diseases with the changed K : Ca ratio is discussed.

H. I. COOMBS.

Effect of excretion of acids and bases on development of acidosis in experimental diabetes. B. M. HENDRIX, M. FAY, D. B. CALVIN, and M. BODANSKY (J. Biol. Chem., 1926, **69**, 449—473).—In depancreatised dogs, acidosis developed only when there was marked diuresis. The total

organic acids of the urine were greater in amount than the ketonic acids. The acidosis was not necessarily accompanied by diminution in the total base of the blood. C. R. HARINGTON.

Influence of dihydroxyacetone on the blood-sugar and glycosuria. E. H. MASON (Canad. Med. Assoc. J., 1926, **16**, 367—374).—Ingestion of dihydroxyacetone in 25—50 g. doses by persons with normal carbohydrate tolerance causes a slight transitory rise in the blood-sugar; with small interrupted doses there is a progressive fall. Diabetics who have a fair carbohydrate tolerance show very little rise in blood-sugar following a 25 g. intravenous dose. It appears that in certain cases the ingested dihydroxyacetone is not converted quantitatively into dextrose. CHEMICAL ABSTRACTS.

Insulin content of pancreas of diabetics. L. POLLAK (Arch. exp. Path. Pharm., 1926, **116**, 15—34).—The pancreas of human diabetics contains insulin, but much less than the pancreas of normal individuals. W. O. KERMACK.

Appearance of phenol in the blood during kidney inefficiency. E. BECHER and S. LITZNER (Klin. Woch., 1926, **5**, 147; from Chem. Zentr., 1926, I, 2015).—Free phenol may appear in the blood in moderate as well as in extreme cases of kidney inefficiency, and is separated by distillation with sodium hydrogen carbonate or dilute acetic acid. Its appearance may be transitory and dependent on the diet, and the amount is small in comparison with the large increase of bound phenol in the blood. W. O. KERMACK.

Amino-acid content of blood in melano-dermatitis. M. LOEPER, J. OLLIVIER, and A. LESURE (Compt. rend. Soc. Biol., 1925, **93**, 1290—1291; from Chem. Zentr., 1926, I, 1591).—The increase in total sulphur which accompanies melano-dermatitis bears no constant relation to the amino-acid content of the blood. C. RIMINGTON.

Significance of cholesterol in bile and serum. III. The equilibrium between cholesterol and its esters in disordered liver function. R. STERN and G. SUCHANTKE (Arch. exp. Path. Pharm., 1926, **115**, 221—231).—Although disorders of liver function and experimental poisoning of the liver are accompanied by changes in the concentration of cholesterol in the blood, the ratio of free cholesterol to its esters is not consistently modified. It is not considered that the liver function is the sole factor in the control of these substances in the blood. R. K. CANNAN.

Blood in leprosy. I. Non-protein nitrogenous substances, sugar, and chlorine. E. M. PARAS (Philippine J. Sci., 1926, **30**, 219—234).—In cases of leprosy, the non-protein nitrogenous substances, sugar, and chlorine of the blood are essentially normal. In cases of leprosy with nephritis, the findings are typical of nephritis. In cases with lepra reaction, the total non-protein nitrogen and urea is high, but the chlorides remain normal. C. P. STEWART.

Blood in pneumonia. I. Method of constructing an alinement diagram to represent changes in gaseous composition of blood and in electrolyte concentration of plasma. T. E. BUCKMAN, F. D. ADAMS, M. SMITH, and H. T. EDWARDS (Boston Med. Surg. J., 1925, **193**, 997—1020).—A nomogram shows quantitatively the association of changes in the carbon dioxide and oxygen percentage saturation with oxygen tension, hydrogen carbonate content of whole blood and plasma, hydrogen-ion concentration, and sodium chloride content of plasma. Two methods are described for the construction of diagrams in which the following factors are alined: carbon dioxide tension and hydrogen carbonate content of whole blood and plasma, oxygen tension and oxygen percentage saturation of the whole blood, sodium chloride content of the plasma, and hydrogen-ion concentration of the whole blood and plasma. CHEMICAL ABSTRACTS.

***Post mortem* blood chemical determinations.** J. R. PAUL (Bull. Ayer Clin. Lab. Pennsylvania Hosp., 1925, **9**, 51—62).—During the first 24 hrs. after death, the dextrose fell to insignificant values; the total non-protein nitrogen increased, urea-nitrogen and creatinine were unchanged, whilst the chlorides and uric acid changed irregularly. In blood taken within 24 hrs. after death, the average values of urea-nitrogen (mg. per 100 c.c.) were: lobar pneumonia, 88; advanced renal lesions, 197; cardio-vascular-renal cases, 22; heterogeneous cases, 27. A marked terminal increase apparently occurred in the blood urea-nitrogen. CHEMICAL ABSTRACTS.

Detection of guanidine substances in the blood in parathyroid tetany and their simultaneous appearance in the urine. J. KÜHNAU (Arch. exp. Path. Pharm., 1926, **115**, 75—87).—A gravimetric method, requiring only 20 c.c. of blood, is described for the determination of guanidine bases in the blood. The method takes advantage of the solubility of the phosphotungstates of the guanidine bases in methyl alcohol. In cases of post-operative and idiopathic tetany and in parathyroidectomised dogs, the concentration of guanidine substances in the blood and urine was several times as great as normal. The view that parathyroid tetany is a condition of guanidine poisoning is supported. R. K. CANNAN.

Guanidine hypoglycæmia. E. FRANK, M. NOTHMANN, and A. WAGNER (Arch. exp. Path. Pharm., 1926, **115**, 55—63).—Hypoglycæmia accompanies the tetany which follows the administration of toxic doses of guanidine to rabbits. Rabbits which had been fed survived longer than starved animals. Both dextrose and adrenaline delayed convulsions and prolonged life. Moreover, simultaneous administration of guanidine and adrenaline resulted in less hyperglycæmia than that produced by adrenaline alone, and the effect of guanidine was, like that of insulin, shown to be peripheral in origin. Nevertheless, the contention of Collip that insulin is a guanidine-like body does not find support in some important differences between the behaviour of the two substances and also of the methylated guanidines. R. K. CANNAN.

Determination of protein in cerebrospinal fluid. Increase of protein in typhus fever. S. M. LING (J. Biol. Chem., 1926, 69, 397—401).—By simultaneous determinations of total nitrogen and of tyrosine in the precipitate obtained by treating cerebrospinal fluid with tungstic acid, the relation between the amount of tyrosine and that of protein was established. The concentration of protein could then be determined rapidly by the use of the colorimetric method of Folin and Looney for the determination of tyrosine (A., 1922, ii, 539). In most cases of typhus fever the proteins of the cerebrospinal fluid are much increased. C. R. HARINGTON.

Animal calorimetry. XXXIV. Influence of glycylglycine on respiratory metabolism of the dog. N. H. PLUMMER, H. J. DEUEL, jun., and G. LUSK (J. Biol. Chem., 1926, 69, 339—348).—The increase in the basal heat-production of dogs following administration of glycylglycine is exactly the same as that following administration of equivalent amounts of glycine itself. C. R. HARINGTON.

Oxidation potential of the cell and oxidation–reduction phenomena. R. WURMSER (Compt. rend. Soc. Biol., 1925, 93, 1478—1479; from Chem. Zentr., 1926, I, 2109).—A consideration of the energetics of the intracellular oxidation and reduction of dextrose. J. PRYDE.

Decomposition of sugar in the central nervous system of man. J. WOHLGEMUTH and Y. NAKAMURA (Biochem. Z., 1926, 175, 233—240).—Brain attacks dextrose, glycogen, lactose, and galactose yielding aldehyde, the substances being placed in the order of their ease of oxidation. Lævulose, lactic acid, and amino-acids, however, are not attacked. Grey matter is much less active than white matter. In contrast with the liver, insulin does not increase, but often reduces aldehyde formation.

P. W. CLUTTERBUCK.

Intermediate carbohydrate metabolism. XVI. Glycolysis and glycometamorphosis with special reference to insulin. XVII. Myophosphate. XVIII. Hydrolysis of zymohexosediphosphoric acid by muscle and its product of fission, monohexosephosphoric acid. XIX. Mechanism of insulin action. XX. p_H of whole blood after injection of insulin into rabbits. T. BRUGSCH and H. HORSTERS (Biochem. Z., 1926, 175, 90—114, 115—119, 120—126, 127—129, 130—134).—XVI. "Glycolysis" is limited to mean the decomposition of dextrose to lactic acid, "glycometamorphosis," the esterification of dextrose with phosphoric acid. Glycolysis occurs only in presence of phosphate, the optimum conditions being: dextrose, 0·3—0·4%, phosphate, 3%, p_H, 6·3—6·4. αβ-, α-, and β-Glucose are subject alike to glycolysis. Higher concentrations than 0·3% of potassium chloride and 0·4% of calcium chloride inhibit glycolysis, and sodium fluoride does not appear to be more powerfully inhibiting. Glycometamorphosis is favoured by higher concentrations of sugar, and the concentration of phosphate must be above 3%. Glycometamorphosis involves the conversion of αβ-glucose by an isomerase into an active γ-glucose which becomes stabilised by esterification with phosphoric acid. This hexosephosphoric acid arising in the muscle is called myophosphate, to distinguish it from zymophosphate, with which it is not identical. The esterification process depends on a phosphatese which is active in presence of sugar, phosphoric acid, and a co-enzyme which is contained in the muscle, and can be replaced by insulin. Glycometamorphosis takes place independently of glycolysis, not only in muscle, but also in liver and in kidney. In the liver, myophosphate is then built up into the hexosan complex, glycogen (cf. A., 1925, i, 208, 483; this vol., 197, 198).

XVII. Using the neutral brucine salt for identification and purification, the authors show that lactacidogen is identical with the fermentation hexosediphosphoric acid $[\alpha]_D$ +3·2. Myophosphate, however, is strongly lævorotatory, is a hexosediphosphoric acid, and gives rise on treatment with acid or alkali to a monophosphoric ester, probably identical with Robison's zymohexosemonophosphoric acid, $[\alpha]_D$ +25°.

XVIII. [With M. CAHEN.]—Zymophosphate, zymodiphosphate, or yeast hexosediphosphoric acid is hydrolysed by a phosphatase of the liver and muscle of warm-blooded animals, first into hexosemonophosphoric acid and phosphoric acid and then into lævulose and phosphoric acid. The hexosemonophosphoric acid is identical with Robison's acid ($[\alpha]_D$ +25°). The optima for the action of phosphatase, zymodiphosphatase, and zymomonophosphatase are identical. Zymophosphate is not identical with myophosphate.

XIX. A discussion of Virtanen's results (see A., 1925, i, 753, 866; this vol., 95, 435, 760).

XX. After intravenous injection of fairly large doses of insulin into starving rabbits, the acidity of the blood is usually increased, but in well-fed animals the glycogen supply appears to ensure the maintenance of p_H almost unchanged.

P. W. CLUTTERBUCK.

Production of sugar in the perfused liver from non-protein sources. J. H. BURN and H. P. MARKS (J. Physiol., 1926, 61, 497—517).—When the liver taken from a cat or dog fed on a fat diet is perfused with blood from the same species, there is a production of reducing sugar at a rate of from 2 to 4 mg. per g. of liver per hr. A small formation of glycogen is demonstrable. The sugar production is not obviously influenced by insulin, adrenaline, or pituitrin. The sugar does not come from lactic acid or from any diffusible constituent of the liver and, from the concurrent formation of urea and ammonia, only a small fraction can come from protein. R. K. CANNAN.

Assimilation of lævulose, galactose, and dextrose in fasting and on a protein–fat diet. S. NAGASAYE (J. Biochem. [Japan], 1925, 5, 449—463).—The rise in blood-sugar following the ingestion of lævulose is less, and after that of galactose much greater, than that after administration of dextrose. Except with lævulose, the blood-sugar level rises much higher in fasting or on a protein–fat diet than on a normal mixed diet. The ingestion of either

dextrose or galactose in the fasting condition causes only a slight increase in the liver glycogen, whilst lævulose contributes considerably to raising the glycogen content of the liver both in fasting and on a protein-fat diet. CHEMICAL ABSTRACTS.

Content of lactic acid and development of tension in cardiac muscle. A. C. REDFIELD and D. N. MEDEARIS (Amer. J. Physiol., 1926, 77, 662—668).—From measurements of the tension developed in strips of the ventricle of the turtle and the lactic acid content, it is suggested that the stress developed at any beat varies with the difference between the lactic acid concentration of complete fatigue and the concentration at the time of the beat. R. K. CANNAN.

Mineral metabolism of horses fed solely on bran. O. BANG (Kong. Vet.- og Landsbehejskole Aarskrift, 1925, 383—404; from Chem. Zentr., 1926, I, 2016).—Analysis of the urine and fæces of a horse fed on white or red bran which contains an excess of acid over basic constituents shows that there is a negative calcium balance due to the excretion of calcium phosphate. Addition of calcium carbonate to the diet restores the calcium balance. W. O. KERMACK.

Disturbance of the mineral metabolism and its effect on the action of white phosphorus. H. BERNHARDT and C. R. H. RABL (Z. klin. Med., 1925, 102, 147—173; from Chem. Zentr., 1926, I, 1595).—Addition of 2% of ammonium chloride to a diet rich in vitamins, but as low as possible in phosphorus and calcium without being rachitic, interferes with calcification. The action of white phosphorus is dependent upon the mineral content of the diet. Fall in calcium content of the bones and appearance of rachitic symptoms do not run parallel. Many other organs were also investigated. C. RIMINGTON.

Effect of white phosphorus on calcium metabolism. H. BERNHARDT (Z. klin. Med., 1925, 102, 174—181; from Chem. Zentr., 1926, I, 1595).—In dogs fed on a diet poor in calcium, white phosphorus causes a retention of calcium and phosphorus. In three adults taking ammonium chloride, white phosphorus improved the calcium balance, but its effect on young animals is in many respects different. The action is very prompt and disappears again when the phosphorus is withdrawn from the diet. C. RIMINGTON.

Effect of ovariectomy on calcium and phosphorus metabolism. J. DALSACE and C. O. GUILLAUMIN (Compt. rend. Soc. Biol., 1925, 93, 1209—1210; from Chem. Zentr., 1926, I, 1595).—In the majority of cases a fall in blood calcium was observed and also in phosphorus where a previous hyperphosphatæmia existed. C. RIMINGTON.

Iodine metabolism. II. T. VON FELLENBERG (Biochem. Z., 1926, 174, 341—354).—The urinary iodine excretion is greater in the inhabitants of non-goiterous than in those of goiterous districts. In adults, the excretion is constant, in children less at night, and increased by psychic stimuli. Administration of potassium iodide results in the retention of about half the amount administered. The iodine excreted is mainly in organic form. Feeding with thyroid gland hinders resorption. The iodine of plants is only partly present in assimilable form. The inorganic iodine of hay is largely removed by watering. E. C. SMITH.

β-*d*-Glycuronic acid monobenzoate (benzoylglycuronic acid). A. J. QUICK (J. Biol. Chem., 1926, 69, 549—563).—Urine obtained from dogs after oral administration of large amounts of benzoic acid was cleared by addition of lead acetate; the filtrate, after neutralisation, was treated with basic lead acetate and the precipitate decomposed with hydrogen sulphide at a low temperature; the filtrate from the lead sulphide was concentrated in a vacuum until most of the hippuric acid crystallised out, and the filtrate from the latter, on keeping in the cold, deposited d-*glycuronic acid monobenzoate* contaminated with some hippuric acid which could be removed by extraction with ether; the pure substance had m. p. 170—172° (decomp.), k $1{\cdot}4\times10^{-3}$, $[\alpha]_D^{20}$ −25·2° in water or dilute acid. In alkaline solution, it exhibited mutarotation, the equilibrium value being $[\alpha]_D^{20}$ +50·0°; the *methyl* ester had m. p. 178—180°, $[\alpha]_D^{23}$ −25·0°, after mutarotation $[\alpha]_D^{20}$ +35—37°; the *lactone* had $[\alpha]_D^{20}$ +48°. The compound reacted with hydrogen cyanide and reduced Fehling's solution readily; it must therefore be regarded as a benzoic ester of glycuronic acid and not as a glucoside (cf. Magnus-Levy, A., 1907, ii, 979). C. R. HARINGTON.

Metabolism of sulphur. XI. Can taurine replace cystine in the diet of the young rat? G. T. LEWIS and H. B. LEWIS (J. Biol. Chem., 1926, 69, 589—598).—Neither taurine nor cysteinic acid, when added to a basal diet lacking cystine, could produce normal growth in young white rats. C. R. HARINGTON.

Availability of taurine as a supplementing agent in diets deficient in cystine. W. C. ROSE and B. T. HUDDLESTUN (J. Biol. Chem., 1926, 69, 599—605).—Deficiency of cystine in the diet of young rats cannot be made good by addition of taurine (cf. preceding abstract). C. R. HARINGTON.

Catabolism of uric acid in vertebrates. I and II. S. J. PRZYLECKI (Arch. int. Physiol., 1924, 24, 238—263, 317—355).—On subcutaneous injection of various purines in frogs, or incubation with extracts of frog tissues, the uric acid was catabolised by means of enzymes by way of allantoin and other intermediate products to ammonia, oxalic acid, and urea. Since amphibia and fish catabolise uric acid through allantoin and are probably unable to synthesise it except from purine bases, whilst birds synthesise it (not through allantoin) and cannot destroy it, these processes are presumably irreversible in the vertebrates. CHEMICAL ABSTRACTS.

Behaviour and action of bile acids in the organism. E. NEUBAUER (Deut. med. Woch., 1925, 51, 2150; from Chem. Zentr., 1926, I, 2017).—After intravenous injection of sodium dehydrocholate, the amount of bilirubin in the bile of rabbits, dogs,

and men was decreased, but an increase in the bile pigments was observed after the injection of more poisonous bile acids, such as cholic acid or deoxycholic acid. W. O. KERMACK.

Behaviour and action of bile acids. A. ADLER (Deut. med. Woch., 1925, **51**, 2150—2151; from Chem. Zentr., 1926, I, 2017).—A reply to Neubauer (cf. preceding abstract). W. O. KERMACK.

Comparative physiological action of guanidine derivatives. G. A. ALLES (J. Pharm. Exp. Ther., 1926, **28**, 251—276).—The effects of guanidine and its alkyl, acetyl, and amino-derivatives on blood pressure and respiration have been studied; these substances have no hypoglycæmic properties; minimum lethal doses are given. H. J. CHANNON.

Reaction between acetylcholine and muscle cells. A. J. CLARK (J. Physiol., 1926, **61**, 530—546).—Acetylcholine produces a graded action on the ventricle and the Rectus abdominis of the frog over a 100,000-fold range of concentration. The relation between the concentration of the drug and the action produced may be expressed by $K.x = y/(100-y)$, where x is the concentration of drug, y the action produced as a percentage of the maximum possible action, and K is a constant. This suggests a reversible unimolecular reaction between the drug and some substance in the cell or on its surface. The quantity of drug fixed by the cell is very small and sufficient to cover only a small fraction of the surface. There is no direct relation between the amount of drug entering the cells and the action produced. R. K. CANNAN.

Pentamethylenetetrazole (cardiazol). I. F. HILDEBRANDT (Arch. exp. Path. Pharm., 1926, **116**, 100—109).—The pharmacological action of pentamethylenetetrazole on the central nervous system and the heart is described. It does not act on plain muscle. W. O. KERMACK.

Pentamethylenetetrazole (cardiazol). II. O. EICHLER and F. HILDEBRANDT (Arch. exp. Path. Pharm., 1926, **116**, 110—116).—The pharmacological action of pentamethylenetetrazole on the circulation and blood pressure is described. Pentamethylenetetrazole counteracts the harmful effects of chloroform and chloral hydrate on the circulation.
W. O. KERMACK.

Action of quinine and its derivatives on metabolism and heat regulation. B. ROSENTHAL and W. LIPSCHITZ (Arch. exp. Path. Pharm., 1926, **116**, 39—66).—Quinine, hydroquinine, optoquin, eucupin, and vuzin have been investigated as to their effect on the autolysis of macerated guinea-pig or dog liver, and on nitrogen metabolism, and as to their pyretic or antipyretic action. Eucupin and vuzin are peculiar in increasing the excretion of nitrogen and in causing a marked rise in body temperature. W. O. KERMACK.

Influence of administration of active and inactive iron oxide on the C : N urinary quotient in rabbits. H. WADA (Biochem. Z., 1926, **175**, 62—67).—Whereas administration of "active" (magnetic) iron oxide caused the urinary C : N ratio to increase considerably, inactive oxide had only a slight delayed effect. P. W. CLUTTERBUCK.

Composition of blood-serum and its significance in the action of poisons. I. Introduction. H. HANDOVSKY. **II. Characterisation of the protein fractions of normal serum by viscosity.** P. BOSSE and H. HANDOVSKY. **III. Action of ether on serum.** P. BOSSE. **IV. Determination of cholesterol in blood-serum.** H. HANDOVSKY and K. LOHMANN. **V. State of cholesterol in blood-serum.** H. HANDOVSKY, K. LOHMANN, and P. BOSSE (Pflüger's Archiv, 1925, 35—49, 50—55, 56—58, 59—62, 63—69; from Chem. Zentr., 1926, I, 1669—1670).—I. Normal ox-serum contains on the average 6·68% of protein and 0·123% of cholesterol. The average distribution of the protein is 59% of albumin, 23% of pseudoglobulin, and 18% of euglobulin. The author assigns to the cholesterol—as a constituent of the cell walls—a share in the action of poisons on the cell.

II. For the determination of the different protein fractions in normal ox-serum, the refractometric method of Robertson was found to be satisfactory. In viscosimetric and refractometric determinations it was found that the viscosity of normal serum is an additive property of the protein fractions, and this can serve for their characterisation. One % of euglobulin raises the viscosity of water by 0·21, 1% of pseudoglobulin by 0·12, 1% of albumin by 0·08%. Sera of tuberculous humans and oxen always show a viscosity higher than normal.

III. Ether, as alcohol and chloroform, precipitates globulins first. It also denatures the albumin.

IV. For the determination of total cholesterol in serum 1 c.c. of serum is boiled with 1 c.c. of saturated sodium hydroxide on the water-bath; the neutralised —preferably slightly alkaline—liquid is shaken three times with ether and the cholesterol determined colorimetrically in the extract by the method of Liebermann and Burchardt. The cholesterol which can be shaken out directly from serum is determined colorimetrically in the extract made by shaking 2—10 c.c. of the serum with twice the amount of ether for 6 hrs. The extract contains cholesterol in the free and ester form in about the ratio 1 : 1.

V. In experiments on the precipitation of the protein fractions and determination of the phosphorus and cholesterol of serum, it was found that after the proteins were precipitated by acetic acid or ammonium sulphate the phosphatides and the greater part of the cholesterol remain in the aqueous solution. Only 22—25% of the cholesterol was found in the protein precipitate, and this exclusively with the globulin. To determine the intensity of the cholesterol linking, the serum was shaken with ether. On the average, 16—50% of the total cholesterol was extracted. The amount thus extracted does not depend on the cholesterol content of the serum. It is raised by increased albumin content. From sera poor in euglobulin large amounts, from sera rich in euglobulin small amounts of cholesterol can be extracted. It is further influenced by the salt and water content of the serum; small additions (0·1%) of potassium, sodium, and calcium chlorides and

dextrose raise the amount which can be extracted, but two or three times this quantity lowers it; dilution with Ringer or Tyrode solution does not change it; on the other hand, dilution with water lowers it and concentration strongly raises it.

H. I. COOMBS.

Effect of carbon tetrachloride and of alcohol on acid–base balance of the blood. P. D. LAMSON and R. WING (J. Biol. Chem., 1926, **69**, 349—355).—No significant changes in the acid–base balance of the dog's blood were observed after oral administration of carbon tetrachloride and alcohol, separately or together, or after inhalation for 30 min. of carbon tetrachloride in sufficient concentration to produce deep anæsthesia. C. R. HARINGTON.

Action of ethyl alcohol on the sensitivity of proteins towards electrolytes. P. WELS (Arch. exp. Path. Pharm., 1926, **116**, 67—99).—0·25% Ethyl alcohol increases the sensitiveness of proteins towards electrolytes, whilst 0·5% decreases it. The bearing of these results on the physico-chemical condition of cells, more particularly in relation to the effects of alcoholic poisoning, is discussed. W. O. KERMACK.

Ethylene narcosis. I. Behaviour of the narcotic in blood. II. Distribution of ethylene between blood corpuscles and plasma *in vitro* and during narcosis. M. NICLOUX and A. YOVANOVITCH (Comp. rend. Soc. Biol., 1925, **93**, 1653—1656, 1657—1658; from Chem. Zentr., 1926, I, 2217).—The concentration of ethylene in the blood of a dog is dependent on its concentration in the inhaled gas and amounts to 8—10 c.c. per 100 c.c. of blood, when there is 66—77·5% in the gas. *In vitro* as *in vivo*, 70—80% of the ethylene in the blood is in the corpuscles and 20—30% in the plasma.

W. O. KERMACK.

Determination of ethylene in blood. M. NICLOUX (Compt. rend. Soc. Biol., 1925, **93**, 1650—1653; from Chem. Zentr., 1926, I, 2217).—The blood is extracted in an apparatus previously described by the author for the determination of carbon monoxide and analysed eudiometrically (cf. "L'oxyde de carbone et l'intoxication oxycarbonique," 1925, Paris). W. O. KERMACK.

Influence of experimental poisoning by acids and of excision of the suprarenals on the inorganic cation content of blood-serum. K. KEITEL (Biochem. Z., 1926, **175**, 86—89).—The inorganic cation (especially sodium ion) content of dog's serum falls after intravenous injection of hydrogen chloride, but rises after extirpation of the suprarenals. P. W. CLUTTERBUCK.

Toxicity of arsinetri-*N*-piperidinium chloride. C. S. LEONARD (J. Pharm. Exp. Ther., 1926, **28**, 233—239).—The effects of the drug injected into rabbits and dogs were those characteristic, not of organic arsenic compounds, but of substituted ammonium salts. H. J. CHANNON.

Toxic action of copper on *Nitella*. S. F. COOK (J. Gen. Physiol., 1926, **9**, 735—754).—Using the loss of turgidity of the cells as a criterion, it is found that the toxicity curve of copper chloride with *Nitella* is sigmoid. When the concentration of the copper chloride is varied, the toxic effect varies as a constant, fractional power of the concentration. This relation holds when the concentration is plotted against either (1) the time necessary to reach a given point on the ordinate of the survivor curve, (2) the maximum speed of toxic action as shown by the tangent to the survivor curve, or (3) the first derivative of the equation which fits the survivor curve. When the temperature is varied, and the logarithm of the reciprocal of the time necessary to reach a given point on the survivor curves is plotted against the reciprocal of the absolute temperature, the resulting figure consists of curves intersecting at 16°, 27°, and 32°. W. ROBSON.

Toxicological considerations on the production of hydrocyanic and thiocyanic acids in the putrefying animal organism. I and II. G. SENSI and M. REVELLO (Annali Chim. Appl., 1926, **16**, 268—275, 275—280; cf. A., 1925, ii, 607).—I. Hydrocyanic acid disappears rapidly from the body after poisoning. It is transformed into thiocyanic acid, but this conversion is not quantitative and varies according to conditions. In the putrefaction of animal tissues thiocyanic acid is sometimes formed, and this can lead to wrong deductions as to hydrocyanic acid poisoning.

II. A description of a case of fatal poisoning by hydrocyanic acid in which the dose was small and the acid could not be detected in the body with certainty. S. B. TALLANTYRE.

Purification of enzymes by electrodialysis and electro-osmosis. R. FRICKE, F. A. FISCHER, and H. BORCHERS (Kolloid-Z., 1926, **39**, 371—372).—Addenda to a previous paper (this vol., 791).

N. H. HARTSHORNE.

Biochemistry of electrolytes. L. HUGOUNENQ and J. LOISELEUR (Bull. Soc. Chim. biol., 1926, **8**, 610—620).—Enzyme activity is considered to be due to catalytically active ions adsorbed on protein, and will in consequence be a function of the selective adsorption by the protein and the p_H. The existence within the cells of proteins with different isoelectric points and the selective adsorption of ions allows control of wide variations in enzyme activity by small changes in the hydrogen-ion concentration. It is suggested that the nucleoproteins may be the colloidal support for more than one catalytically active ion.

H. J. CHANNON.

Hydrogen cyanide in the metallic poisoning of enzymes. M. JACOBY (Biochem. Z., 1926, **175**, 79—85).—Papain is inactivated by zinc only when the metal, in presence of excess of potassium cyanide, is brought into contact with the enzyme. The inactivation is similar to that of pepsin, but different from that of urease. P. W. CLUTTERBUCK.

Effect of potassium thiocyanate on diastatic action. A. BITTORF and VON FALKENHAUSEN (Arch. exp. Path. Pharm., 1926, **115**, 9—17).—The amylolytic activity of saliva is notably increased by addition of potassium thiocyanate. The optimum concentration of the latter increases with the dilution of the enzyme. Experiments with dialysed saliva

show that the effect is not merely that of neutral salts activating the amylase, since the presence of sodium chloride is also necessary for the full effect to be observed. The diastase of the submaxillary gland, the pancreas, and the liver are similarly activated by thiocyanate. R. K. CANNAN.

Supposed hydrolysis of starch by salts and protein degradation products. K. TAKANE (Biochem. Z., 1926, **175**, 241—252).—The view that starch can be hydrolysed by solutions of salts, amino-acids, and peptones, advocated by Iljin (A., 1923, i, 172), Biedermann (*ibid.*, 655), Haehn (*ibid.*, 443), and by Haehn and Berentzen (Chem. Zelle Gewebe, 1925, **12**, 286) is shown to be erroneous. When starch was carefully purified and when the solutions both of starch and of salts etc. were boiled sufficiently and the apparatus was carefully sterilised, no evidence of hydrolysis could be obtained. P. W. CLUTTERBUCK.

[Alleged] artificial glycolytic enzyme. H. KÖCHLING (Chem. Zelle Gewebe, 1925, 247—285; from Chem. Zentr., 1926, I, 1587).—So far, all attempts to prepare an agent capable of degrading dextrose under aseptic conditions have failed. The activity of the peptone–dextrose–hydrogen carbonate system of Schlatter, as also of the oleate–fibrin–dextrose–buffer system of Warden, was due to bacteria, whilst the fibrin-containing preparations of Schroeders and of Sieber are not active if cell-free plasma is used. C. RIMINGTON.

Retardation of invertase action by dextrose and lævulose. J. M. NELSON and R. S. ANDERSON (J. Biol. Chem., 1926, 69, 443—448).—Curves obtained by plotting the retarding effect on inversion of sucrose exerted by β-glucose, αβ-fructose, and β-fructose against the concentration of sucrose are all of the same shape; with α-glucose curves of another type were obtained, the retardation due to this substance being greater at 2% and less at 20% sucrose concentration than that of the other hexoses mentioned above. C. R. HARINGTON.

Effect of esterifying carbocyclic acids on their action in preventing the development of micro-organisms. T. SABALITSCHKA, K. R. DIETRICH, and E. BÖHM (Pharm. Ztg., 1926, **53**, 834—836).—*Penicillium glaucum* was added to a suitable nutrient medium to different portions of which the substance under investigation had been added in varying amounts. Phenol was used as a standard for comparison. Of the free acids used, benzoic acid was found the most active, its activity being one-third that of phenol. Then came in descending order of activity, anisic, salicylic, and cinnamic acids, whilst *m*- and *p*-hydroxybenzoic acids were the least active. Benzoic and salicylic acids show a stronger activity than their methyl esters, a behaviour, however, which is reversed in the case of the other acids and esters. Esterification leads to similar results, whilst the introduction of chlorine further increases the activity, so that methyl *m*-chloro-*p*-hydroxybenzoate has an activity comparable with that of phenol. The action of this ester (a commercial preservative) was tested, in comparison with the commoner preservatives, against various fungi and bacteria and was found to be superior to them. The conclusion is reached that whilst the salts of the acids act only in an acid medium, the free acids only in acid or non-acid-binding medium, the activities of the esters remain unchanged whether the medium is acid, neutral, or alkaline. W. ROBSON.

Formation of lactic acid from methylglyoxal by ketone-aldehyde mutase of animal and vegetable origin. G. GORR and G. PERLMANN (Biochem. Z., 1926, **174**, 433—439).—Methylglyoxal is converted into lactic acid by aqueous extracts of muscle to the extent of 77—90%, of liver to the extent of 64% in 15 hrs. at 37°, and by *Bacterium pasteurianum*, under anaërobic conditions, to the extent of 90% in 26 hrs. E. C. SMITH.

Conversion of phenylglyoxal into mandelic acid by the ketone-aldehyde mutase of green plants. G. BINDER-KOTRBA (Biochem. Z., 1926, **174**, 443—447).—Phenylglyoxal is converted into *l*-mandelic acid by the action of pea-meal, aqueous extract of peas, the alcohol–ether precipitate from the latter, and the acetone-dried pea-meal preparation. The presence of the ketone–aldehyde mutase inhibits the spontaneous formation of *dl*-mandelic acid, the product after 6 days' action of bean-meal being 90% *l*-mandelic acid. E. C. SMITH.

Determination of lipase in germinating pine-seeds. H. W. NICOLAI (Biochem. Z., 1926, **174**, 373—383).—Lipase is determined by a modification of the method of Rona and Lasnitzki (A., 1925, i, 471). The lipase content of pine seeds increases up to the fifth day of germination. The amount of fat hydrolysed during the first 7 days, calculated from the lipase action, corresponds with that determined by analysis. The seeds contain maltase, but no glycolytic enzymes. E. C. SMITH.

Behaviour of lipase during autolysis of the liver. H. KOSTERLITZ and H. PETOW (Biochem. Z., 1926, **175**, 31—45).—Solutions obtained by extraction at 2° of liver pulp after autolysis have much greater lipolytic power than extracts made before autolysis. The lipolytic power of extracts obtained by combining autolysis with dialysis is at first still greater and then falls away. P. W. CLUTTERBUCK.

Specificity of luciferin and luciferinase. E. N. HARVEY (Amer. J. Physiol., 1926, **77**, 548—554).—Among 41 different genera of luminous animals, only *Pholas dactylus*, ostracods, fire-flies, and *Odontosyllis* give the luciferin–luciferinase reaction. *Cypridina* luciferin (or luciferinase) will react with the luciferinase (or luciferin) of two other genera of ostracods with luminescence, but with none of the other luminous animals. The oxyluciferin of *Cypridina* and *Pholas*, but not of *Pelagia* or *Chætopterus*, can be reduced again with hydrogen and platinised asbestos. It is suggested that the absence of the luciferin–luciferinase reaction is in many cases due to the fact that just enough luciferinase is present to be completely used up by the luciferin during the attempted preparation of the former. R. K. CANNAN

Bioluminescence and fluorescence in the living world. E. N. HARVEY (Amer. J. Physiol., 1926, **77**, 555—561).—A survey has been made of the fluorescence in near ultra-violet light of the tissues and photogenic material of luminescent animals. In general, the luminous organs show a marked fluorescence, the colour of which is the same as that of the luminescence, although there are exceptions to both of these statements. Dried fire-flies and some fish preserved in formalin show this fluorescence, which, in some cases, seems definitely to be associated with the oxidation product of the luminous material. R. K. CANNAN.

Regeneration of enzymes made inactive by heating. A. N. BAKH and A. I. OPARIN (Trans. Karpov Inst. Chem., 1925, [4], 217—231).—The properties of peroxydase, inactivated by heating, are restored to a noticeable extent only in presence of atmospheric oxygen; the conditions are most favourable in slightly alkaline solutions. The absorption of oxygen by slightly alkaline solutions of vegetable extracts is due to the presence of " breathing chromogens " which unite with oxygen and thereby become coloured. If such chromogens and pigments are removed from vegetable extracts containing enzymes, regeneration of the activity of the latter does not take place. Isolated crystalline pigment (chlorogenic acid) regenerates enzymes in solutions which otherwise exhibit no regeneration. The process is therefore one of oxidation of the zymogen.

CHEMICAL ABSTRACTS.

Specificity of animal proteases. VI. Mode of action of pepsin. E. WALDSCHMIDT-LEITZ and E. SIMONS (Z. physiol. Chem., 1926, **156**, 114—127).—The equivalence of carboxyl and amino-groups liberated by the hydrolysis of various proteins by pepsin suggests that the peptolysis consists in the fission of carboxylamides. Exceptions in which the ratio $NH_2 : CO_2H$ varies from unity are probably due to the presence of such compounds as glutamic and pyrrolidinecarboxylic acids in the products. The peptolysis of caseinogen, egg-albumin, globulin from ricinus seeds, gliadin, zein, and gelatin is described, and the $NH_2 : CO_2H$ ratios are determined.

C. HOLLINS.

Determination of pepsin using Congo-red. M. KAWAHARA and O. PECZENIK (Wien. med. Woch., 1926, **76**, 129—130; from Chem. Zentr., 1926, I, 1865).—A modification of the Congo red-albumin method previously described (Pflüger's Archiv, 1924, **206**, 360). Using the easily digestible and completely soluble caseinogen, 2—4 hrs. is a sufficient time for digestion. J. S. CARTER.

Pancreatic protein digestion. R. WILLSTÄTTER (Deut. med. Woch., 1926, **52**, 1—2; from Chem. Zentr., 1926, I, 1672).—The pancreatic enzyme mixture is separated into its components—lipase, trypsin, and amylase—by separating the lipase and trypsin from the amylase by adsorption on alumina and kaolin, respectively. The pure trypsin is not able to act on simple peptides, but is able to hydrolyse peptones (also thymus histone and clupein). The recent view of the predominantly disintegrating action of trypsin and pepsin is not borne out by quantitative experiments. It appears more likely that the breakdown of protein compounds in the animal body is essentially by hydrolytic reactions which convert protein through peptones and peptides into amino-acids. H. I. COOMBS.

Digestibility of deaminated proteins by proteolytic enzymes. R. NAKASHIMA (J. Biochem. [Japan], 1925, **5**, 293—310).—Caseinogen, edestin, and zein (5—10 g.) were deaminated with a cold mixture of 50 c.c. of glacial acetic acid and 100 c.c. of 30% sodium nitrite solution, the yellow mass being collected after 4—6 hrs., and washed successively with cold urea solution, water, alcohol (unless the protein is soluble), and ether. The products, which were practically free from amino-nitrogen, were dried in a vacuum. The reactions given by the deaminated proteins are detailed. The optimum acidity for peptic and tryptic digestion differs from that for the natural protein, but (except for zein) at that optimum acidity there is no difference in digestibility between the natural and deaminated proteins.

CHEMICAL ABSTRACTS.

Enzymes of the skin. J. WOHLGEMUTH. V. Respiration and glycolysis of the skin and the influence of hormones. E. KLOPSTOCK. **VI. Behaviour of lipase and presence of phosphatase, sulphatase, and carboxylase in the skin.** Y. NAKAMURA (Biochem. Z., 1926, **175**, 202—215, 216—232).—V. Respiration and glycolysis are determined by Warburg's method. The mean values for human skin are, for respiration $Q_{O_2}=-2{\cdot}1$ and for anaërobic glycolysis $Q^{N_2}_{CO_2}=+6$. The corresponding values for the skin of a cadaver are $Q_{O_2}=-2{\cdot}0$ and for $Q^{N_2}_{CO_2}=+3{\cdot}4$. These values refer only to superficial layers of skin, the deeper layers giving lower values. Aërobic glycolysis of skin gave only very small values. Adrenaline causes a slight increase in respiration of the skin. The active principles of the thyroid, ovaries, and testis increase the respiration to 300, 220, and 170%, respectively, whilst insulin and hypophysin decrease respiration to 65 and 30% of the original value. Glycolysis is reduced by the active substances of the thyroid, testis, and hypophysis to 40, 60, 70%, but is slightly increased by that of the ovaries and is scarcely at all affected by insulin (cf. A., 1925, ii, 203, 472; this vol., 93, 864).

VI. Lipase of the skin has its optimum action at p_H 7·1—7·5, and is activated by the phosphate ion. The resistance of this lipase to quinine and atoxyl depends, not on any specific property of the enzyme, but on the presence of certain dialysable substances. In the skin and in the subcutaneous fat a phosphatase is present and in the skin a sulphatase. Since the skin can also break down pyruvic acid to aldehyde, a carboxylase is probably present.

P. W. CLUTTERBUCK.

Sulphatase. VIII. Difference between sulphatase and myrosinase. C. NEUBERG and J. WAGNER (Biochem. Z., 1926, **174**, 457—463).—Sinigrin is resistant to plant sulphatase, whilst myrosinase from *Sinapis alba* is without action on the substrates normally used for determining sulphatase action. E. C. SMITH.

Isolation and crystallisation of urease. J. B. SUMNER (J. Biol. Chem., 1926, **69**, 435—441).—Jack-bean meal is extracted at the ordinary temperature with 5 parts of 31·6% acetone; on keeping the filtrate over-night at 2—2·5° a crystalline deposit is obtained, which is soluble in water and dilute alkalis, gives the reactions for protein, but no reactions for carbohydrate; 1 mg. will produce 100 mg. of ammonia nitrogen from urea in 5 min. at 20°. The substance is denatured on keeping in the dry state and on treatment with acid; it is regarded as a globulin and as being identical with urease.

C. R. HARINGTON.

Fermentation. S. N. CAGAN (Z. angew. Chem., 1926, **39**, 951—952).—Pyruvic acid, one of the intermediate products of the fermentation of sucrose with yeast, yields α-*iso*butyl-β-naphthocinchoninic acid with an ethereal solution of *iso*valeraldehyde and β-naphthylamine, and this acid is readily purified by recrystallisation from ethyl acetate. An attempt to obtain a large yield of the pyruvic acid derivative by shaking a dilute sugar solution containing yeast with an ethereal solution of the above aldehyde and amine failed, however, only 0·85 g. of the cinchoninic acid being obtained from 90 g. of sucrose owing to the phytochemical reduction of the aldehyde to *iso*amyl alcohol. At the same time, it appeared that pyruvic acid must undergo fermentation at an extraordinarily rapid rate to account for such a poor yield.

A. R. POWELL.

Carbohydrate metabolism. XIV. Presence of "neo-glucose" in the course of fermentation of αβ-glucose. C. LUNDSGAARD and S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, **93**, 1688—1690; from Chem. Zentr., 1926, I, 2114).—Aqueous and ethereal extracts of various yeasts are mixed with αβ-glucose and subjected to dialysis. Good correspondence between reduction and polarimetric values for glucose is found in the dialysates. It is concluded that "neo-glucose" is not formed during the fermentation of sugar by yeast. J. PRYDE.

Action of oxygen on the alcoholic fermentation of sugar. G. GORR and G. PERLMANN (Biochem. Z., 1926, **174**, 425—432).—The combined ethyl alcohol and acetaldehyde formation during the fermentation of sucrose by yeast is only very slightly less in the presence of air than under anaërobic conditions. The yield of butylene glycol is in each case minute, and acetylmethylcarbinol and diacetyl cannot be detected.

E. C. SMITH.

Action of ammonium salts on yeast fermentation. IV. H. ZELLER (Biochem. Z., 1926, **175**, 135—161).—The fermenting power of pressed yeast is increased by 80—140% by addition of ammonium phosphate, carbonate, oxalate, citrate, tartrate, and formate and by 20—30% by ammonium chloride, sulphate, bromide, iodide, nitrate, benzoate, molybdate, thiocyanate, and ammonium magnesium sulphate. The fermenting power of brewers' yeast is also increased by these salts with the following exceptions: ammonium benzoate inhibits fermentation strongly, and ammonium citrate, which assists fermentation with pressed yeast only when in small concentration and inhibits in more concentrated solution, increases fermentation with brewers' yeast both in concentrated and dilute solution. The permeability of ammonium salts is approximately proportional to the increase in fermenting power with the exception of ammonium phosphate. The increased fermentation is probably related to the formation of complex sugar–ammonium salt compounds. Ammonium salts do not increase the action of Lebedev's extract. Insulin, which cannot replace the enzyme, partly inhibits the action of ammonium salts.

P. W. CLUTTERBUCK.

Fermentation of hexosediphosphoric acid, dextrose, lævulose, sucrose, and invert-sugar by yeast juice and fresh yeast. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **174**, 480—492).—At the commencement of the fermentation of sodium or magnesium hexosediphosphate in the presence of arsenate, fermentation is more rapid than is the case with the simple sugars. This supports the hypothesis that the breakdown of the ester results in the liberation of a more readily fermentable sugar, but later in the course of fermentation the breakdown of the simple sugars is the more rapid, and preliminary treatment of the hexosediphosphate with tissue phosphatase does not result in a more rapid fermentation than that of dextrose or lævulose. The fermentation of the hexosediphosphate is accelerated by the addition of toluene, bile salts, and other substances which affect the permeability of the cell.

E. C. SMITH.

Fermentation of phenylglyoxylic acid. G. BINDER-KOTRBA (Biochem. Z., 1926, **174**, 440—442).—Phenylglyoxylic acid is converted by yeast in the presence of sodium hydrogen sulphite into benzaldehyde, which separates as the hydrogen sulphite compound. E. C. SMITH.

Reaction between sugars and amino-acids. Fermentation of mixtures of amino-acids and sugars. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **174**, 464—479).—It is shown by means of the alteration of rotation of solutions of the sugars and amino-acids on admixture that reactions take place between the following: lævulose, dextrose, maltose, and magnesium hexosediphosphate with urea, asparagine, and glutamic acid; lævulose and dextrose with *l*-alanine, thiourea, acetamide, and arginine. The fact that amino-acids are fermented only in the presence of carbohydrate is considered to be explained by the necessity for this combination to occur.

E. C. SMITH.

Zymophosphate formation and biochemical transformation of sugar. H. VON EULER and E. BRUNIUS (Svensk Kem. Tidskr., 1925, **37**, 301—307; from Chem. Zentr., 1926, I, 2013).—The formation of zymophosphate by yeast is inhibited by phenol at approximately the same concentration at which it retards fermentation. W. O. KERMACK.

Separation of the oxidoreductase from the zymase complex. I. A. LEBEDEV (Z. physiol. Chem., 1926, **156**, 153—158).—The filtrate from macerated yeast-extract which has been coagulated at 60—65° does not ferment sucrose, but decolorises

methylene-blue. The oxidoreductase, precipitated from the filtrate by ammonium sulphate, has no action on methylene-blue, and the residual liquor, after boiling, is also without action. The latter, however, contains a co-enzyme, for a mixture of the boiled liquor and the precipitated oxidoreductase decolorises methylene-blue. C. HOLLINS.

Bacterial filters. S. P. KRAMER (J. Gen. Physiol., 1926, 9, 811—812).—Regarding a filter in action as a suspension of the material composing the filter in the fluid which is being filtered, it is found that colloids or micro-organisms which pass filters of silica (electronegative charge) will not pass filters of plaster of Paris or of pure calcium sulphate to which calcium carbonate has been added (electropositive charge) and *vice versa*. Filters of pure calcium sulphate (no electrical charge) have no action on the dyes or organisms used. W. ROBSON.

Dismutation of aldol by *Bacterium ascendens*. G. BINDER-KOTRBA (Biochem. Z., 1926, **174**, 448—451).—Aldol is converted by *Bacterium ascendens* into *d*-β-butylene glycol, $[\alpha]_D$ +14·6°, and into β-hydroxybutyric acid of only very small dextrorotation, $[\alpha]_D$ +1·0°. E. C. SMITH.

Biochemistry of the asymmetry problem. P. MAYER (Biochem. Z., 1926, **174**, 420—424).—Phenylglyoxal is quantitatively converted into *d*-mandelic acid by treatment with *Bacterium ascendens*, and into *l*-mandelic acid with lactic acid bacteria or an acetone-dried preparation of the latter. The two bacteria contain therefore a ketone–aldehyde mutase. E. C. SMITH.

Behaviour of pyrimidine derivatives in organisms. II. Action of *Bacillus coli* on uracil and cytosine. A. HAHN and L. SCHÄFER (Z. Biol., 1925, **83**, 511—514; from Chem. Zentr., 1926, I, 1666).—Cytosine can be hydrolytically deaminated to uracil by means of an enzyme found in yeast. *B. coli* can also convert cytosine into uracil. Uracil is not attacked by *B. coli*. H. I. COOMBS.

Bacterial metabolism. LXXVI. Soluble proteolytic enzyme of *Bacillus proteus*. LXXVII. Intestinal flora of nurslings. LXXVIII. Intestinal bacteria of artifically fed infants. LXXIX. Intestinal flora of normal adults. LXXX. Intestinal flora of man containing abnormal numbers of gas bacilli. A. J. KENDALL, A. A. DAY, and A. W. WALKER (J. Infect. Dis., 1926, **38**, 193—199, 200—204, 205—210, 211—216, 217—221).—The soluble proteolytic enzyme of *Bacillus proteus* effects a rapid change, tryptic rather than peptic, in the gelatin molecule. Bacteria from nurslings induce but small nitrogenous changes, but effect pronounced fermentation of dextrose and lactose, with formation of acid. Bacteria from artificially fed infants cause putrefaction in sugar-free media, and fermentation in similar media containing carbohydrates. Moderate proteolysis and some putrefaction, caused by bacteria from normal adults in media containing no utilisable carbohydrate, are suppressed when utilisable carbohydrates are present. Rapid degradation of protein and extensive deamination, caused by bacteria from subjects containing abnormal numbers of gas bacilli in solutions free from utilisable carbohydrate, are also suppressed in presence of carbohydrate. CHEMICAL ABSTRACTS.

Pyorubrin, a red, water-soluble pigment characteristic of *Bacillus pyocyaneus*. P. D. MEADER, G. H. ROBINSON, and V. LEONARD (Amer. J. Hyg., 1925, **5**, 682—708).—Like the fluorescent pigment and pyocyanin, pyorubrin yields its specific leuco-base on reduction with zinc and hydrochloric acid, and is regenerated therefrom on oxidation; unlike the first two substances, it is not an indicator. CHEMICAL ABSTRACTS.

Carbamide [formed] by bacteria. N. N. IVANOV (Biochem. Z., 1926, **175**, 181—184).—Cultures of *Bacillus megatherium* and *B. tumescens* form from peptone containing gelatin and from amino-acids containing arginine, considerable amounts of carbamide which is derived from the arginine (cf. A., 1925, i, 344, 746). P. W. CLUTTERBUCK.

Dismutation of α-methylbutaldehyde. C. NEUBERG and E. SIMON (Biochem. Z., 1926, **174**, 452—456).—*dl*-α-Methyl-*n*-butaldehyde is quantitatively converted by *Bacterium xylinum* into the corresponding *dl*-amyl alcohol and *dl*-valeric acid. Suspensions of horse-liver act very slowly and incompletely, the amyl alcohol obtained being inactive. E. C. SMITH.

Attenuation and antigenic power of diphtheria toxin after treatment with various substances. P. NELIS (Ann. Inst. Pasteur, 1926, **40**, 666—696). The removal of dialysable substances from diphtheria toxin (which itself dialyses slowly) causes it to lose rapidly much of its toxic power. The dialysed toxin is the more rapidly acted on by ozone. In the preparation of the anatoxin, most of the formaldehyde is taken up by the dialysable substances. Sodium oleate solution at 37° destroys the toxin completely. Quinine salts destroy it in part. The antigenic power of the toxins treated by these methods is given. H. J. CHANNON.

Peptone culture medium for *Bacillus tuberculosis*. L. BOEZ (Ann. Inst. Pasteur, 1926, **40**, 746—754).—The use of a medium consisting of the product of pancreatic digestion of beef, together with glycerol, dextrose, and salts, is advocated. H. J. CHANNON.

Isolation of a crystalline protein with tuberculin activity. F. E. SEIBERT (Science, 1926, **63**, 619—620).—The protein was completely precipitated from tuberculin by saturation with ammonium sulphate; the product consisted of a water-soluble, non-coagulable protein, a water-soluble, heat-coagulable protein, and a water-insoluble protein, the first two containing most of the tuberculin activity. When the water-soluble, non-coagulable dialysed fraction was treated by Hopkins' method for isolating crystalline ovalbumin, needles were obtained which gave the biuret, Millon, and Molisch reactions, together with a marked skin reaction in tuberculous guinea-pigs. A. A. ELDRIDGE.

Isolation of insulin. C. FUNK (Science, 1926, **63**, 401—402).—Insulin, purified by way of its com-

pound with flavianic acid, yields analytical results corresponding with the formula $C_{69}H_{102}O_{22}N_{18}S$ or $C_{74}H_{114}O_{24}N_{20}S$. The structure may be that of a polypeptide composed of about 15 amino-acids.

A. A. ELDRIDGE.

Crystalline insulin. J. J. ABEL (Proc. Nat. Acad. Sci., 1926, **12**, 132—136).—A purified preparation of insulin is dissolved in weak acetic acid. Contaminating substances are precipitated by addition of a solution of brucine in acetic aeid and removed in the centrifuge. On adding *N*/6-pyridine to the clear solution, crystalline insulin together with some amorphous insulin separate from the liquid. This crystalline insulin has m. p. 233°, and gives biuret, Millon's, Pauly's, and the ninhydrin reactions.

H. W. DUDLEY.

Biuret-free insulin. R. S. ALLEN and J. R. MURLIN (Amer. J. Physiol., 1925, **75**, 131—139).—Perfusion is followed by salting out with sodium chloride (35 g. per 100 c.c. of solution); the dry substance is then extracted with 70% alcohol, the residue after evaporation of the filtrate being extracted with 80% alcohol, and the process repeated several times. The product is insoluble in acid solutions and in water, but is readily soluble in dilute alkali. It is unstable, but gives none of the colour reactions for proteins.

A. A. ELDRIDGE.

Mechanism of the action of insulin. G. VIALE (Arch. ital. Biol., 1924, **74**, 131—140; from Chem. Zentr., 1926, I, 2112).—The observations of Stosse (Compt. rend. Soc. Biol., 1924, **89**, 98) and of Winter and Smith (J. Physiol., 1923, **57**, 100) are not confirmed. An ultra-filtrate from blood concentrated in a stream of warm air gives the same reduction and polarimetric value for dextrose. A mixture of liver extract, insulin, and dextrose after keeping at 38° for 5 hrs., also shows, when deproteinised, identical reduction and polarimetric values. Insulin does not increase glycolysis in normal or diabetic blood, nor does it alter the blood reaction. Formic acid in the blood is increased after insulin and diminished by extirpation of the pancreas.

J. PRYDE.

Action of insulin on the disappearance of dextrose and oxidations in blood *in vitro*. O. KAUFFMANN-COSLA and J. ROCHE (Bull. Soc. Chim. biol., 1926, **8**, 636—654).—Addition of insulin to defibrinated blood increases glycolysis and carbon dioxide production, but the latter is usually less than that which would account for all the dextrose disappearing. The increased carbon dioxide production is not affected by cyanide. Glycolysis and carbon dioxide production decrease in blood kept at 0°, but are restored by the addition of insulin. Insulin added to a suspension of washed corpuscles in dextrose–Ringer solution causes disappearance of sugar, but has no effect on carbon dioxide production.

H. J. CHANNON.

Action of insulin and pituitary extract on constituents of blood. A. GIGON (Biochem. Z., 1926, **174**, 257—261).—The injection of insulin into rabbits causes a decrease in the total carbon and nitrogen of the blood and an increase in the water content. With pituitrin, the same changes occur, but the blood-sugar increases slightly. When insulin and pituitrin are injected simultaneously, the effect is that of insulin alone, except that the effect on the blood-sugar is weakened, but insulin injected 48 hrs. after the injection of pituitrin causes a rise in the total carbon and nitrogen of the blood and a fall in the water content, with very little effect on the blood-sugar. In mild cases of diabetes, in which insulin has a similar action on the blood constituents, disturbance of the pituitary gland may be the primary cause. The action of adrenaline on animals in insulin hypoglycæmia is also reversed by previous treatment with pituitrin. The imbibition of frog's muscle in Ringer's solution is increased 50% by previous treatment of the animal with pituitrin.

E. C. SMITH.

Influence of insulin on liver glycogen. D. BINDI (Arch. ital. Biol., 1924, **74**, 141—145; from Chem. Zentr., 1926, I, 2113).—The amount of glycogen in the fluid from a perfused liver is diminished when insulin is present. On perfusing one half of the liver with insulin, the other without, the former always shows a higher glycogen content.

J. PRYDE.

Supposed influence of insulin on sugar formation in the liver. I. L. CHAIKOFF (Trans. Roy. Soc. Canada, 1926, [iii], 20, [V], 27—31).—Repeating part of the work of Brugsch and his co-workers (cf. A., 1924, i, 1017), the author concludes that, contrary to their findings, insulin has no influence on the rate of appearance of dextrose or phosphoric acid in incubated suspensions of liver-tissue.

W. ROBSON.

Influence of glucosamine on insulin hypoglycæmia. Possible change of glucosamine into dextrose in the organism. A. MOSCHINI (Arch. ital. Biol., 1924, **74**, 117—125; from Chem. Zentr., 1926, I, 2113).—Hypoglycæmic symptoms in rabbits are not relieved either by subcutaneous or oral administration of glucosamine hydrochloride. The symptoms are less marked and are later in appearing when 8—10 g. of glucosamine are given along with, or previous to, the insulin injection. It is concluded that glucosamine is transformed but slowly into dextrose *in vivo*.

J. PRYDE.

Action of mono- and di-saccharides administered orally on insulin hypoglycæmia. A. MOSCHINI (Arch. ital. Biol., 1924, **74**, 126—130; from Chem. Zentr., 1926, I, 2113).—To relieve hypoglycæmic symptoms 10 g. of dextrose, administered *per os*, are necessary, or 5 g. if given simultaneously with the insulin injection. Lævulose must be administered half an hour before the insulin injection. Galactose is practically inactive. Sucrose behaves like dextrose, maltose is intermediate in its action between those of sucrose and lævulose, whilst lactose is inactive.

J. PRYDE.

Effect of glyceraldehyde and dihydroxyacetone on insulin hypoglycæmia. H. G. REEVES and J. A. HEWITT (J. Physiol., 1926, **61**, Proc. xxxv).—Dihydroxyacetone proved as efficient as dextrose in allaying the symptoms of insulin hypoglycæmia in mice and rabbits. Glyceraldehyde had no beneficial action.

R. K. CANNAN.

Presence of an insulin complement in the muscles of warm and cold-blooded animals. Carbohydrate metabolism. XIII. C. LUNDSGAARD and S. A. HOLBØLL (Compt. rend. Soc. Biol., 1925, **93**, 1687—1688; from Chem. Zentr., 1926, I, 2114).—As in the muscles of warm-blooded animals, so in those of cold-blooded animals, a substance is present which, with insulin, converts αβ-glucose into "neo-glucose." Minced frog muscle is placed in an isotonic solution of αβ-glucose containing insulin. On subjecting a sample taken after 2 hrs. to dialysis, differences between polarimetric and reduction values are found. Later samples show an increased polarimetric value, rising until the equilibrium value for dextrose is reached. This so-called "insulin complement" has a temperature optimum of 20° for cold-blooded animals and 37° for warm-blooded animals.
J. PRYDE.

Extraction of ovarian hormone and some chemical properties of the product. J. O. RALLS, C. N. JORDAN, and E. A. DOISY (J. Biol. Chem., 1926, **69**, 357—380; cf. A., 1924, i, 1387).—Liquor folliculi is treated with alcohol to remove proteins and the filtrate evaporated to dryness in a vacuum; the aqueous solution of the residue in made alkaline to phenolphthalein and extracted with ether; the residue obtained on evaporation of the ether is dissolved in 70% alcohol and the solution repeatedly extracted with light petroleum; evaporation in a vacuum of the aqueous-alcoholic solution then yields a preparation, free from cholesterol, of which 0·03—0·04 mg. is 1 rat unit. The purest preparations so far obtained, by further fractionation with light petroleum, have 1 rat unit per 0·015 mg. Further purification cannot be effected by vacuum distillation, which always involves the loss of at least 50% of the active material. The product having 1 rat unit per 0·04 mg. had C 80·5, H 10·7, N 0·93%; *M* was, however, 418—458, so that the nitrogen may have been due to impurity. The activity of this product was lost on acylation in pyridine and on bromination, but was scarcely affected by hydrogenation, hydrolysis, or treatment with *p*-nitrophenylhydrazine; it is therefore suggested that the hormone may contain a hydroxyl group and a double linking, but no carbonyl group.
C. R. HARINGTON.

Ovarian hormone. M. HARTMANN and H. ISLER (Biochem. Z., 1926, **175**, 46—61).—Using a new method of purification and after preliminary treatment with acetic anhydride, the active substance of the ovaries and placenta may be readily distilled in a high vacuum. The active fraction consists of esters of higher unsaturated acids and is of approximately constant composition. On saponification, it yields an active *substance*, b. p. 145°/0·02 mm., of average composition, C 81·83, H 11·43%.
P. W. CLUTTERBUCK.

Effect of spaying, pregnancy, and administration of ovarian extracts on the urinary quotient C : N. H. WADA (Biochem. Z., 1926, **174**, 400—411).—Spaying had no effect on the urinary quotient of two bitches, apart from an exaggeration of the daily variation. Subcutaneous and oral administration of oophorin had no effect on the spayed animals, apart from a further increase in the daily variation in one case, but in a normal female rabbit the injection brought about a decrease in carbon and an increase in nitrogen, indicating increased oxidation in intermediate metabolism. No effect was observed on a male rabbit. Pregnancy and parturition had no effect on the quotient.
E. C. SMITH.

Effect of administration of thyroid and pituitary gland preparations on the urinary quotient C : N. H. WADA (Biochem. Z., 1926, **174**, 392—399).—The urinary quotient C : N is lowered by feeding with thyroid gland owing to an increase in nitrogen excretion. Pituitary extract has the reverse effect. Considerable changes may occur in the urinary nitrogen without any corresponding effect on the dysoxidisable carbon.
E. C. SMITH.

Active substances of the posterior lobe of the hypophysis present in the cerebrospinal fluid. P. TREDELENBERG (Arch. exp. Path. Pharm., 1926, **114**, 255—261).—Whilst an extract of the posterior lobes of the hypophysis has a strong action on the frog's melanophores, solutions of various alkaloidal salts produce no darkening in them; 0·01% solutions of quinine hydrochloride and curarine produced a slight darkening, but 0·001% solutions had no effect. Extracts from lung, liver, kidneys, spleen, heart, brain, suprarenal capsule, guinea-pig muscle, and blood were inactive. The conclusion is reached that the substance of the posterior lobe of the hypophysis which acts on the melanophores is also present in the cerebrospinal fluid.
W. ROBSON.

Distribution of the active substance of the hypophysis in its different parts. H. B. VAN DYKE (Arch. exp. Path. Pharm., 1926, **114**, 262—274).—The *pars nervosa* is much richer than the *pars intermedia* in the substance which stimulates the uterus, raises the blood pressure, and acts as an antidiuretic. The stem and particularly the *tuber cinereum* are very poor in the uterus-stimulating substance. On the other hand, the substance responsible for expanding the melanophores is present particularly in the *pars intermedia*. After injecting extracts of *pars intermedia* and of *pars nervosa* into rabbits, the author was unable to detect the changes in fatty-acid content of the liver reported by Coope and Chamberlain (cf. J. Physiol., 1925, **60**, 69).
W. ROBSON.

Isolation of secretin. J. MELLANBY (J. Physiol., 1926, **61**, Proc. xxxvii).—The method depends on the extraction of the secretin from the mucous membrane by alcohol, its removal from aqueous solution by adsorption to a precipitate of bile acids induced in the solution, and its precipitation from alcoholic solution containing bile acids by means of acetone. Secretin is destroyed by pepsin, trypsin, and by boiling acid or alkali (0·1*N*). It is probably a polypeptide.
R. K. CANNAN.

Vitamin content of human milk. L. F. MEYER and E. NASSAU (Klin. Woch., 1925, **4**, 2380—2383; from Chem. Zentr., 1926, I, 2117).—The failure of guinea-pigs to grow on oats and human milk is ascribed, not to vitamin deficiency, but to a deficiency

of protein. Guinea-pig milk and cow's milk contain about three times as much protein as human milk.
J. PRYDE.

Metabolism and vitamin-*A*. V. E. NELSON and C. M. MCCAY (Proc. Iowa Acad. Sci., 1924, **31**, 286).—With rats, lack of vitamin-*A* led to an unusually large percentage of the nitrogen being excreted as urea; uric acid, creatine, and creatinine were unchanged. Albumin is apparently a normal constituent of the urine of the rat.
CHEMICAL ABSTRACTS.

Spectroscopic observations on cod-liver oil. II. Absorption bands of cholesterol. F. W. SCHLUTZ and M. R. ZIEGLER (J. Biol. Chem., 1926, **69**, 415—419).—The spectrum of cholesterol ($+1H_2O$) shows two absorption bands; that of anhydrous cholesterol shows greater general absorption, but no bands; irradiation of an ethereal solution of cholesterol with ultra-violet light increases the general absorption to a greater extent in the case of hydrated than in that of anhydrous cholesterol.
C. R. HARINGTON.

Vitamins. XIV. Influence of ultra-violet light on purified rations used in study of vitamin-*A*. R. A. DUTCHER and J. H. KRUGER (J. Biol. Chem., 1926, **69**, 277—282).—A basal diet of caseinogen, agar, dextrin, and salts, such as is customarily employed in investigations of vitamin-*A*, has no antirachitic properties; after irradiation with ultra-violet light such a diet becomes antirachitic, owing, exclusively, to the activation of the dextrin; the degree of activation of the dextrin is, however, slight in comparison with that induced in maize oil or olive oil by similar treatment. C. R. HARINGTON.

Photo-activation of vitamin-*A*, cholesterol, fats, and other substances by ultra-violet rays. S. HAMANO (Proc. Imp. Acad. Japan, 1926, **2**, 53—55, 56—57).—See this vol., 98, 546.

Water-soluble growth-promoting and anti-neuritic substances. S. M. HAUGE and C. W. CARRICK (J. Biol. Chem., 1926, **69**, 403—413).—Addition of yeast to a basal diet, lacking water-soluble vitamins, permitted normal growth in chickens, but did not protect against polyneuritis, whereas addition of maize protected against polyneuritis, but did not yield good growth. It is therefore concluded that, in addition to the water-soluble antineuritic substance (vitamin-*B*), there exists a separate water-soluble growth-promoting vitamin.
C. R. HARINGTON.

Preservation of vitamin-*C* in dried orange juice. G. J. HUMPHREY (J. Biol. Chem., 1926, **69**, 511—512).—Orange juice, treated with 25% of sugar and dried in a vacuum, retained its antiscorbutic potency when kept for 5 years under reduced pressure.
C. R. HARINGTON.

Chemical nature of the cell membrane. F. M. WOOD (Ann. Bot., 1926, **40**, 547—570).—The liberation of iodine from potassium iodide after treatment of sections with chlorine followed by sodium hydrogen phosphate solution has been used for the detection of protein in cell-wall. Not more than 0·001% of protein occurs in the cellulose cell-wall of any of the plants examined; tests for oxycellulose before and after chlorination were made. The tests have been applied to the leaves, petioles, aërial and underground stems and roots of a number of plants.
H. J. CHANNON.

Kinetics of carbon dioxide assimilation. J. HOLLUTA.—See this vol., 1011.

Reciprocal relationship between carbohydrates in foliage leaves and water content. W. AHRNS (Bot. Arch., 1924, **5**, 234—259).—Only sucrose and hexoses take part in the production of sugar through starch hydrolysis in the wilting leaf. In the presence of starch, the sucrose content rises (independently of light) with falling, and falls with rising, water content. The hexose content rises in starch-containing leaves kept in the dark; the maltose content decreases during darkness. In *Tropæolum* and *Helianthus*, the hexoses alone are transported.
CHEMICAL ABSTRACTS.

Chemical constituents of fruit spurs associated with blossom bud formation in the apple. H. R. KRAYBILL, G. F. POTTER, S. W. WENTWORTH, P. T. BLOOD, and J. T. SULLIVAN (New Hampshire Agric. Exp. Sta., Tech. Bull., 1925, **29**, 1—40).—At various dates during the growing season, the carbohydrate, nitrogen, phosphorus, ash, and dry matter content of bearing and non-bearing spurs of Baldwin apple trees, growing in sod or in a highly nitrogen-fertilised plot, were determined. Significant differences were observed. CHEMICAL ABSTRACTS.

Normal variation in the chemical composition of fruit spurs and the relation of composition to fruit-bud formation. C. P. HARLEY (Proc. Amer. Soc. Hort. Sci., 1925, 134—146).—The trustworthiness of results may largely depend on the uniformity of spurs selected for analysis. Indication is afforded of the importance of sugar and starch in relation to fruit-bud formation. A high percentage of nitrogen, especially of soluble nitrogen, is present in new growths of bearing spurs immediately following fruit setting. CHEMICAL ABSTRACTS.

Ripening of tomatoes. J. T. ROSA (Proc. Amer. Soc. Hort. Sci., 1925, 315—322).—The hydrogen-ion concentration and total acidity are maximal at the turning stage and minimal in the ripe fruit. Sugars (chiefly dextrose) and nitrogen increase from the green-mature to the ripe condition; starch practically disappears in the earliest stages of ripening. The proportions of total soluble nitrogen and soluble solids increase, the insoluble solids decreasing. Ethylene acts as a stimulus to normal oxidative processes in the fruit. CHEMICAL ABSTRACTS.

Influence of fertilising ingredients on the hydrogen-ion concentration of the juice of the rice plant. K. MIYAKE and M. ADACHI (J. Biochem. [Japan], 1925, **5**, 321—326).—Nitrogen lowers the hydrogen-ion concentration of the juice of the rice plant, the effect being greater when applied in conjunction with phosphate and potassium. Phosphate increases the hydrogen-ion concentration, the effect being weakened by potassium or nitrogen. In the first period of plant growth, potassium decreases,

and in the second period increases, the hydrogen-ion concentration of the juice. The rise in the p_H value caused by lime is not influenced by the amount used, or by the application of phosphate, nitrogen, or potassium. CHEMICAL ABSTRACTS.

Effect of soil reaction on germination of meadow grasses and clovers. L. MÜLLER (Fortschr. Landw., 1926, 1, 52—57; Chem. Zentr., 1926, I., 1698).—Meadow grasses and clovers prefer a slightly acid reaction for germination. Grasses tolerate an alkaline reaction better than clovers. The anions present, as well as the hydrogen-ion concentration of the soil solution, have an influence on germination. C. T. GIMINGHAM.

Influence of potassium chlorate on germination of rye, wheat, barley, and oats. A. STROBEL and K. SCHARRER (Fortschr. Landw., 1926, 1, 62—63; Chem. Zentr., 1926, I, 1697—1698).—In small amounts, potassium chlorate does not injure germination of winter rye and wheat; higher doses produce a morbid light green colour in the seedlings. Barley is most sensitive; oats were not injured by the highest doses used. C. T. GIMINGHAM.

Toxicity and antagonism in salt solutions as indicated by growth of wheat roots. S. F. TRELEASE and H. M. TRELEASE (Bull. Torrey Bot. Club, 1926, 53, 136—156).—A study of the rates of elongation of wheat roots in 0·0006—0·36*M*-potassium, calcium, or magnesium nitrate solutions, and in 0·06*M*-solutions of pairs of these salts in varied proportions. No stimulation was observed; magnesium was more toxic than potassium or calcium. Antagonistic effects were marked with potassium and calcium, less marked with calcium and magnesium, and only slight with potassium and magnesium.
CHEMICAL ABSTRACTS.

Action of sodium carbonate on germination and growth in plants. II. D. FEHÉR and S. VÁGI (Biochem. Z., 1926, 175, 172—174).—With increasing amounts of carbonate, the growth of plants is considerably inhibited, more especially in regard to the root development (cf. A., 1925, i, 1023).
P. W. CLUTTERBUCK.

Action of nitrites on the growth of plants. D. FEHÉR and S. VÁGI (Biochem. Z., 1926, 174, 262—270).—The lethal concentration of nitrites in the soil varies from 0·09 to 0·10% of N_2O_3, whereas the concentration in the Hungarian alkaline soils is only 0·000027—0·000114%, which has no action on the growth of the plant. The lethal concentration for cultures in water is much higher, 0·125—0·372% of N_2O_3. The percentage absorption of nitrites diminishes with the concentration. When the nitrites are present in sufficient concentration to cause injury, the effect is most apparent on the root.
E. C. SMITH.

Nitrogen and dry matter content of sweet clover tops and roots at various stages of growth. H. J. SNIDER and M. A. HEIN (J. Amer. Soc. Agron., 1926, 18, 273—280).—In the autumn and winter, the roots, and in the spring and summer the tops, contained the highest percentage of nitrogen.
CHEMICAL ABSTRACTS.

Latex. A. J. ULTEE (Pharm. Tijdschr. Nederl.-Indie, 1925, 2, 515—528; from Chem. Zentr., 1926, I, 2110).—The dry alcohol coagulum from the latex of *Ficus elastica* yielded 96·2% of caoutchouc; latex from *Castilloa elastica* yielded 84·9%; from *F. Vogelii* 72·9%; from *F. glomerata* 16·6%; from *F. procera* 12·1%; from *F. fulva* 1·1%; from *F. alba* a trace; from *Atrocarpus elastica* and *Broussonetia papyrifera* nil. Latex is classified in groups according to its richness in: (1) caoutchouc, (2) phytosterols (containing principally lupeol and α- and β-amyrol), (3) protein, (4) tannins, *e.g.*, latex of *Jatropha curcas*, (5) salts, *e.g.*, latex of *Plumiera acutifolia* yielded a coagulum containing 46·42% of salts, chiefly calcium plumierate, and 44·6% of sterols, (6) alkaloids.
J. PRYDE.

Oxidation and reducing properties of hermidin, the chromogen of *Mercurialis*. P. HAAS and T. G. HILL (Ann. Bot., 1926, 40, 709; cf. this vol., 99).—Chrysohermidin can be reduced to cyanohermidin by hermidin and by sodium hyposulphite only in freshly-prepared solutions. H. J. CHANNON.

Lævulosans of the *Gramineæ*; graminin and tricitin. H. COLIN and A. DE CUGNAC (Bull. Soc. Chim. biol., 1926, 8, 621—630).—Preparations of graminin from *Arrhenatherum bulbosum*, Presl., and of tricitin from *Triticum repens*, L., have been made. Graminin has m. p. 199°, $[\alpha]_D$ −44°, $[\alpha]_{Hg\ green}$ −54°; tricitin m. p. 198°, $[\alpha]_D$ −47°, $[\alpha]_{Hg\ green}$ −57°; after inversion both substances have $[\alpha]_D^{15}$ −93°. Triticin is more soluble in water at 15° and in alcohol at 60° than is graminin. These substances are not precipitated from neutral or acid solutions by salts of heavy metals; they yield insoluble compounds with barium hydroxide, whilst the corresponding compounds with the hydroxides of calcium and strontium are soluble. They have no reducing action and on hydrolysis yield lævulose only. The plants from which they are prepared contain enzymes which hydrolyse them. Graminin is readily hydrolysed by top yeast and triticin less readily. H. J. CHANNON.

Proteins of the Adzuki bean (*Adzukia subtrilobata*). E. TAKAHASHI and T. ITAGAKI (J. Biochem. [Japan], 1925, 5, 311—319).—The bean contains about 25·7% of protein, of which 15% is albumin and globulin. Two globulins (β_1 and β_2), resembling the β-globulin of *Phaseolus angularis*, were isolated, the respective contents of lysine being 10·2 and 5·8%, and of amino-nitrogen, 55·2 and 61·2%. The arginine and histidine content is lower in β_2 than in β_1; the former is the principal protein in the Adzuki bean. CHEMICAL ABSTRACTS.

Differences in the physico-chemical properties of the protein, oryzanin, as found in glutinous and in common rice. T. TADOKORO, Y. NAKAMURA, and S. WATANABE (J. Coll. Agric. Hokkaido Imp. Univ., 1925, 14, 129—169).—The differences in the starches of glutinous and common rices are attributed on biochemical grounds to differences in the chief protein of rice, oryzanin. Preparations of oryzanin from the two varieties show that the protein from common rice, which is less soluble in alkali and has a higher acid-binding capacity, con-

tains a higher proportion of nitrogen and of ash; it contains relatively fewer carboxyl groups, and more free amino-, ammonia-, arginine-, and lysine-nitrogen, but less monoamino-, histidine-, and cystine-nitrogen. The acetyl derivative of common rice oryzanin contains more nitrogen, and its hydrolysis produces the more basic substances. The amount of tyrosine and tryptophan is the same in both proteins. Pancreatin decomposes glutinous rice oryzanin more rapidly than the compound from common rice, indicating a higher molecular complexity for the latter. The rotatory power of the alkali solution of common rice protein is the higher. Exposure of the alkali solutions of the oryzanins to ultra-violet light increases the free amino-nitrogen, the velocity of increase being greater for the compound from glutinous rice.

CHEMICAL ABSTRACTS.

Electrodialysis in biochemistry. C. DHÉRÉ (Bull. Soc. Chim. biol., 1926, 8, 604—610).—Extension of the review already published (cf. this vol., 762).

H. J. CHANNON.

Open gas analytical method for metabolic measurements. L. CAPPELLEN and A. K. NOYONS (Compt. rend. Soc. Biol., 1925, 93, 1530—1533; from Chem. Zentr., 1926, I, 1864).—An apparatus designed to avoid working in closed systems is described.

J. S. CARTER.

Apparatus for graphical registration of oxygen-consumption and carbon dioxide production. H. DETHLOFF (Klin. Woch., 1925, 4, 2440—2441; from Chem. Zentr., 1926, I, 2223).—An apparatus is described which allows the oxygen consumed and the carbon dioxide produced by a person under examination to be recorded graphically in a continuous manner. Air is circulated through the system; the oxygen consumed is given by the total diminution in volume of the system as recorded by a spirometer; the carbon dioxide formed is given by the difference between the readings of meters, placed one on each side of an absorption apparatus containing soda-lime.

J. S. CARTER.

Portable calorimeter for determination of oxygen and carbon dioxide. J. F. MCCLENDON, G. J. HUMPHREY, and M. M. LOUCKS (J. Biol. Chem., 1926, 69, 513—517).—In a closed circuit respiration apparatus the expired air is passed through a chamber containing a known amount of barium hydroxide solution in rapid agitation and containing phenolphthalein. As soon as the latter is decolorised, the total volume of gas in the apparatus is measured; the difference between this and the initial volume gives the oxygen utilised, whilst the carbon dioxide produced can be calculated from the amount of barium hydroxide neutralised, a correction being applied for incomplete absorption.

C. R. HARINGTON.

Determination of p_H of blood. New hydrogen electrode. G. ETIENNE, M. VERAIN, and M. BOURGEAUD (Compt. rend. Soc. Biol., 1925, 93, 765—766; from Chem. Zentr., 1926, I, 1866—1867).—A modified Michaelis electrode is described.

J. S. CARTER.

Modification of Widmark's microchemical method for the determination of blood-alcohol. M. AOKI (J. Biochem. [Japan], 1925, 5, 327—331).—A weighed quantity of blood is distilled at 100° in a Gréhaut micro-distillation apparatus, the receiver containing a solution of potassium dichromate and sulphuric acid. The contents are finally heated for 1—2 min. on the water-bath, washings from the apparatus being added, and the unreduced dichromate is titrated using thiosulphate. The average alcohol content of rabbit's blood is 0·0025%.

CHEMICAL ABSTRACTS.

Determination of sugar in blood. A. D. STAMMERS (S. Afric. Med. Record, 1925, 23, 426—427).—The blood-proteins are precipitated by heating with sodium hydrogen sulphate and treatment with "dialysed iron," an aliquot part of the filtrate being then boiled for 2·5 min. with 1 c.c. of 0·0075% methylene-blue in alkaline solution. Quantities of sugar between 0·075 and 0·3% are determined by means of a graph if the time taken for the blue colour to disappear is observed.

CHEMICAL ABSTRACTS.

Micro-determination of blood-sugar. S. L. WRIGHT, jun. (Bull. Ayer Clin. Lab. Pennsylvania Hosp., 1925, 9, 65).—A modification of the Folin–Wu method.

CHEMICAL ABSTRACTS.

Effect of potassium oxalate on blood-sugar determinations. H. J. JOHN (J. Lab. Clin. Med., 1925, 10, 1000—1004).—When 10 c.c. or less of blood are used, 15 mg. of potassium oxalate are sufficient to prevent clotting; low values are obtained if more than 30 mg. are employed.

CHEMICAL ABSTRACTS.

Determination of hydrogen carbonate in small amounts of serum. J. P. BOUCKAERT (Compt. rend. Soc. Biol., 1925, 93, 841—843; from Chem. Zentr., 1926, I, 1867).—0·5—1·0 C.c. of serum is dialysed, the dialysate decomposed with 0·01*N*-hydrochloric acid, and titrated back, using 0·01*N*-barium hydroxide, to p_H 7·4.

J. S. CARTER.

Mendel–Goldscheider method for the determination of lactic acid in blood. M. VAS and A. LÁNG (Biochem. Z., 1926, 172, 428—431).—The Mendel–Goldscheider method (this vol., 212) is adaptable to clinical requirements, being rapid and requiring not more than 1 c.c. of blood. The accuracy is within 5—10%.

C. RIMINGTON.

Micro-determination of the blood urea. A. BOIVIN (Bull. Soc. Chim. biol., 1926, 8, 456—461).—After removal of protein, urea is precipitated by xanthhydrol and the nitrogen content of the precipitate is determined by the micro-Kjeldahl method. The results are claimed to be more exact than the higher values obtained by the urease or hypobromite methods.

C. P. STEWART.

Contributing cause of turbidity of nesslerised solutions in the determination of urea in the whole blood. F. B. COOPER (J. Lab. Clin. Med., 1925, 10, 1012).—A mixture of 1 c.c. of toluene and 0·02 c.c. of octyl alcohol, which prevents foaming for 45 min. and gives clear solutions for 1 hr., is used in the aëration tubes in the Gradwohl–Blaivas method.

CHEMICAL ABSTRACTS.

Micro-determination of phosphorus in blood. M. MÂCHEBOEUF (Bull. Soc. Chim. biol., 1926, 8, 464—468).—The blood (1 c.c.) is ashed with a mixture of sulphuric and nitric acids, and the phosphorus precipitated as phosphomolybdate. The precipitate is

separated by means of a Pregl micro-filter, washed, and dissolved in ammonia. Standard sodium hydroxide is added, the ammonia boiled off, excess of standard acid added, carbon dioxide boiled off, and the excess acid titrated with sodium hydroxide.
C. P. STEWART.

Determination of calcium, magnesium, phosphate, and carbonate in bone. B. KRAMER and J. HOWLAND (J. Biol. Chem., 1926, **68**, 711—719).—The bone is dried and pulverised; in the resulting powder the carbonate is determined gasometrically by shaking with hydrochloric acid; the remaining acid solution is made up to known volume and aliquot portions are used for determinations of calcium, magnesium, and phosphorus by standard methods. C. R. HARINGTON.

Nephelometric determination of phosphoric acid. H. KLEINMANN (Biochem. Z., 1926, **174**, 43—52).—A modification of the author's original method (*ibid.*, 1919, **99**, 134) capable of the determination of 0·001 mg. of phosphoric acid (as P_2O_5) with an error of $\pm 2\%$. E. C. SMITH.

Detection of traces of fluorine in organic material. H. LÜHRIG (Pharm. Zentr., 1926, **67**, 465—474).—0·2 Mg. of fluorine may be detected in solid organic material by mixing with milk of lime, drying the mixture, igniting at a fairly low temperature, carefully adding sulphuric acid, and observing the etching of a cooled glass surface by the hydrogen fluoride liberated. Fluorides may first be precipitated by lanthanum acetate. No fluorine could be detected in 100 c.c. of cow's milk or in hen's eggs, but a trace was found in 25 g. of milk powder. Normal urine and human liver did not contain fluorine except after administration of fluosilicates etc. No fluorine could be detected in the urine 4 days after oral administration of fluosilicates. L. F. HEWITT.

Biochemistry of strontium. Determination of strontium in the presence of calcium. O. ARND and E. A. HAFNER (Biochem. Z., 1926, **174**, 182—187).—The determination of strontium in the presence of calcium is most accurately carried out by precipitation and weighing together as oxalate, followed by titration of the oxalate (cf. Hodel, A., 1925, i, 1496). The titration of strontium oxalate in quantities greater than 0·1 mg. is accurate to 3·3%. The determination in serum can be carried out without ashing, and is accurate to 5%.
E. C. SMITH.

Micro-determination of potassium in pure solutions and in biological media. M. DELAVILLE and P. CARLIER (Bull. Soc. Chim. biol., 1926, **8**, 481—488).—See this vol., 491. The application of the process to small volumes of serum, plasma, etc. is described.

Sampling and analysis of stomach gas. A. D. DUNN and F. L. DUNN (J. Lab. Clin. Med., 1925, **10**, 769—776).—An apparatus is described. In air of known composition, introduced into the stomach of a normal individual, the carbon dioxide and oxygen tend to reach equilibrium at relatively constant values. CHEMICAL ABSTRACTS.

Determination of free hydrochloric acid in gastric contents. E. HALLANDER (J. Lab. Clin. Med., 1925, **10**, 935—937).—Paper impregnated with dimethylaminoazobenzene (0·25% alcoholic solution) is treated with solutions containing, respectively, 10, 20, 30, 40, or 50 c.c. of 0·1*N*-hydrochloric acid per 100 c.c. of water, and with the gastric contents, the resulting colours being compared.
CHEMICAL ABSTRACTS.

Comparison of electrometric and colorimetric methods for determination of p_H of gastric contents. G. KAHN and J. STOKES, JUN. (J. Biol. Chem., 1926, **69**, 75—84).—Good agreement between the results of electrometric and direct colorimetric determinations of the p_H of gastric content is obtained only at reactions more acid than p_H 2·1; on the alkaline side of this point, moderate agreement between the two methods can be obtained if the fluid be dialysed against physiological salt solution and the colorimetric method applied to the dialysate.
C. R. HARINGTON.

Metabolism of sulphur. X. Determination of cystine in urine. H. B. LEWIS and R. H. WILSON (J. Biol. Chem., 1926, **69**, 125—131).—It has been shown that, when the concentration of cystine is low, the precipitation methods of Gaskell (A., 1908, ii, 75) and of Magnus Levy (A., 1925, i, 610) may involve losses of as much as 50% of the cystine present, although, owing to precipitation of impurities, the actual weight of the precipitate may be as great as, or greater than, that of the cystine; it is therefore concluded that the best available method for the determination of cystine in urine is the direct colorimetric method of Looney (A., 1923, ii, 195).
C. R. HARINGTON.

Solubility of some picrates and determination of guanidines in urine. I. GREENWALD (Biochem. J., 1926, **20**, 665—667).—Sharpe's method (A., 1925, i, 722) for the detection and determination of guanidines in urine is criticised mainly on the basis that other picrates, such as creatinine picrate, might separate with guanidine picrate and especially with the picrates of methyl- and dimethyl-guanidine. There is also a possibility of ammonium salts dissolving in the alcoholic extract of the treated urine.
S. S. ZILVA.

Determination of total nitrogen in plants and plant solutions. E. R. RANKER (Ann. Mo. Bot. Garden, 1926, **12**, 367—380).—Since 75% of the total nitrogen may fail to be recovered by means of the "salicylic-thiosulphate" method, a modification is proposed which is accurate for the determination of amino-, amido-, ammonia- nitrate-nitrogen and of total plant nitrogen in the presence of nitrate-nitrogen. In the presence of water, methods dependent on the reduction of nitrates in an acid medium are inaccurate; much sugar causes a slight loss of nitrate-nitrogen. CHEMICAL ABSTRACTS.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1926.

General, Physical, and Inorganic Chemistry.

Spectra of metals excited by means of high tension and heavy current. H. NAGAOKA, T. FUTAGAMI, and H. OBATA (Proc. Imp. Acad. Tokyo, 1926, **2**, 161—162).—The metal under examination is placed between the ends of two purified carbon rods and a heavy discharge from a condenser passed through it, the light emitted being caused to fall on the slit of a quartz spectrograph. Very minute samples of metal and even of glass can be analysed in this way. R. CUTHILL.

Form and structure of long sparks. T. TERADA and U. NAKAYA (Proc. Imp. Acad. Tokyo, 1926, **2**, 258—260).—The sparks obtained by condenser discharge in air, nitrogen, oxygen, hydrogen, and coal gas have been photographed. The structure and form of the sparks appear to depend largely on the manner in which the *P.D.* is established and falls off during the discharge. R. CUTHILL.

Occurrence of harmonics in spectral lines. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 153—155).—In the spectra of the elements, particularly in the ultra-violet, the wave-lengths of numerous lines manifest harmonic relations similar to those which prevail for sound waves. Thus in the hydrogen spectrum there are many pairs of lines of which the wave-lengths are in the ratio of 1 : 2, or 1 : 3, or 1 : 4. R. CUTHILL.

Autoelectronic discharge. K. CUNRADI (Ann. Physik, 1926, [iv], **81**, 155—172).—When a discharge in high vacuum is running from a sharp point, the point electrode becomes slightly heated. The magnitude of the heating effect varies with the vacuum and the electrical conditions; its cause may be ionisation due to secondary electrons or to the pulling of electrons out of the metal by the field and the generation of *X*-rays by collision of these electrons with the cathode. The autoelectronic discharge is a pure electron discharge; its characteristics are discussed.
R. A. MORTON.

Time interval between the appearance of spectrum lines in spark and in condensed discharges. J. W. BEAMS (Physical Rev., 1926, [ii], **28**, 475—480).—Measurements of the time intervals between the appearance of the bright visible spectrum lines of cadmium, magnesium, and zinc in the spark in air and nitrogen and hydrogen in condensed discharges at various pressures indicate that the intervals are due to atomic phenomena. The appearance of the lines is not in the order of increasing wave-lengths, or in that of integrated intensities. For magnesium, cadmium, and zinc, the spark lines appear before the arc lines. In the sharp arc triplet of zinc, but not in that of cadmium, the members appear in the order of increasing wave-lengths. A. A. ELDRIDGE.

Fine structures in non-hydrogenic atoms. A. E. RUARK, F. L. MOHLER, and R. L. CHENAULT (Physical Rev., 1925, [ii], **25**, 241).—Fine structures of spectral lines of non-hydrogenic atoms often arise from transitions between the components of complex spectral levels. It is believed that slight quantised variations in the configuration of underlying electron shells suffice to explain the existence of all the fine structures examined. A. A. ELDRIDGE.

High-vacuum arc in hydrogen. F. H. NEWMAN (Phil. Mag., 1926, [vii], **2**, 796—799).—When impure hydrogen at a pressure of 10^{-4} mm. was activated by a momentary coil discharge, an arc could be struck between iron electrodes by an applied *E.M.F.* of 80 volts. The arc persisted for about 1 min. after the electric discharge had ceased. The radiation from the arc was nearly white and consisted chiefly of the Balmer and secondary hydrogen lines, together with a continuous spectrum over the range 6000—2000 Å. The nitrogen bands were faint, but those of ammonia at 3360 and 3371 Å. were prominent. The current could be varied between 6 and 10 ampères, and although the cathode became very hot, no iron lines were obtained. Occasionally while the arc electrodes were still cold a white glow was formed between them, the spectrum of which was similar to the arc spectrum. With very pure hydrogen, containing only water vapour, at a pressure of 10^{-2} mm., the arc could be started and maintained with a *P.D.* of 40 volts. With very clean electrodes, it could be started at a pressure of 10^{-1} mm. Both the arc and glow could be obtained at pressures less than 10^{-3} mm. The arc spectra were more continuous than those of the glow, whilst the water bands in the ultra-violet were more predominant in the glow radiation. A mechanism to explain the starting and the persistence of the arc is suggested. A. E. MITCHELL.

Self-reversal of the red hydrogen line. R. W. WOOD (Phil. Mag., 1926, [vii], **2**, 876—880).—When the spectrum from a long end-on spectrum tube containing hydrogen was examined by means of a twenty-plate echelon grating, it was found that by sufficiently increasing the current in the tube a self-

reversal of both components of the H_α line could be obtained. Examination of the spectrum with Lummer-Gehrcke plates has so far failed to reveal this phenomenon. Thus, contrary to expectation, self-reversal has been obtained, by using a long end-on spectrum tube, under conditions precluding the existence of an absorbing layer under physical conditions different from those of the emitting layer. Hydrogen is apparently peculiar in that under the conditions of the experiment it is impossible to reduce the intensity of the lines by passing the light through a layer of less powerfully excited gas, the latter contributing always more light than it absorbs. It is suggested that this behaviour is characteristic of working with the gas under molecular and not under atomic conditions. A. E. MITCHELL.

Observed relative intensities of Stark components in hydrogen. J. S. FOSTER and M. L. CHALK (Nature, 1926, **118**, 592).—For the p components of H_β, $\Delta=\pm8/\Delta=\pm10$, the observed, calculated, and estimated ratios of intensities are 1·00, 1·06, 0·40, respectively; values for the s components of H_β, $\Delta=\pm4/\Delta=\pm6$, are 1·59, 1·55, and 0·54.
A. A. ELDRIDGE.

Origin of spectral doublets. W. V. HOUSTON (Physical Rev., 1925, [ii], **25**, 884).—Bowen and Millikan's data for stripped atoms from lithium to nitrogen are in accord with the relativity law; from sodium to chlorine, the data accord more closely with a third power law. With increasing atomic number, the power of the effective nuclear charge decreases, being between the first and second for silver and cadmium. It is concluded that optical doublets are not due to relativity, but that the magnetic and other interactions of the electrons must be taken into account. A. A. ELDRIDGE.

Vacuum spark spectrum of carbon, 2200—6600 Å. R. A. SAWYER and E. J. MARTIN (Physical Rev., 1925, [ii], **25**, 110).—The vacuum spark spectrum of carbon, using coconut charcoal electrodes, contained practically all the lines recorded by Eder and Valenta, all those assigned by Fowler to C^+, and a large number of new lines (chiefly close doublets) of which 30 are of an intensity comparable with that of previously known lines. A. A. ELDRIDGE.

Wave-length standards in the extreme ultra-violet spectra of carbon, nitrogen, oxygen, and aluminium. I. S. BOWEN and S. B. INGRAM (Physical Rev., 1926, [ii], **28**, 444—448).—The wave-lengths of the aluminium lines used by Bowen and Millikan as primary standards (A., 1924, ii, 638) were inconsistent with themselves. The wave-lengths in the spectra indicated in the title have therefore been directly compared with iron standards, to an accuracy of 0·01—0·04 Å. The pp' groups of C III and N IV have been resolved into their six components, the ratios p_1p_2/p_2p_3 being 2·47 and 2·33, respectively.
A. A. ELDRIDGE.

Spectrum of argon. F. A. SAUNDERS (Proc. Nat. Acad. Sci., 1926, **12**, 556—560; cf. Physical Rev., 1926, [ii] **27**, 799; Meissner, this vol., 766).—Further progress in the analysis of the structure of the spectrum of the normal argon atom is described. In general plan, the spectrum is similar to that of neon. The $1s_2$, $1s_3$, $1s_4$, and $1s_5$ terms are, respectively, 31,713·9, 32,560·1, 33,363·1, and 33,970·0. These combine with a large number of $2p$ terms, the values of which are tabulated. The $1s$—mp_4 and $1s$—mp_5 series run to limits which appear to lie about 1400 units higher than the normal values; this number has therefore to be added to these series to make them Ritzian. More than 80 combinations of the $2p$—md and $2p$—ms classes have been found. Several lines in the extreme ultra-violet appear to be combinations between $1p$ and various $2p$ terms, which violate the rules of selection. Some faint lines have been discovered in the neon spectrum, however, which seem to have the same cause. A. B. MANNING.

Intensities of absorption lines in alkali metal vapours. G. R. HARRISON (Physical Rev., 1925, [ii], **25**, 238).—The relative areas, depths, and widths of the first 15 absorption lines in the principal series of sodium, and the first 12 lines of potassium, have been measured precisely. Approximate atomic absorption coefficients are calculated, and the results are applied to certain atomic models of the alkali metals. A. A. ELDRIDGE.

Yellowish-green discharge in potassium vapour. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 711—712).—If a bulb containing an electrodeless discharge in potassium is heated for a long time, and the length of the spark then diminished, the bright blue ring changes suddenly to a diffuse yellowish-green discharge, having a very simple spectrum. A. GEAKE.

Spectrum of ionised potassium. I. T. L. DE BRUIN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 713—729).—The spectrum of ionised potassium, obtained with an electrodeless discharge, has been photographed over the range 2000—8000 Å. About 150 of the lines are recorded and classified according to a scheme similar to that for neon. A. GEAKE.

Characteristics of the spectrum of the high-current arc. A. S. KING (Physical Rev., 1925, [ii], **25**, 237—238).—The spectra of iron and titanium arcs carrying 1000 ampères at 100 volts are mainly those of the neutral atoms, with a higher excitation stage than usual. The cooler envelope of vapour emitting oxide bands is apparently forced so far out by the large mass of highly heated vapour that these bands are absent in photographs of the line spectrum.
A. A. ELDRIDGE.

Regularities in the arc spectrum of cobalt. F. M. WALTERS, jun. (Physical Rev., 1925, [ii], **25**, 238).—Multiplets found in the arc spectrum of cobalt result from combinations of terms the maximum multiplicities of which are even, thus verifying the alternation law. Six of the multiple levels occur in pairs separated by rather small wave-number intervals: P'—P=1300; D'—D=2700; F'—F=3800.
A. A. ELDRIDGE.

Absorption and series spectra of nickel. A. L. NARAYAN and K. R. RAO (Proc. Physical Soc., 1926, **38**, 354—362).—The absorption spectrum of nickel was investigated by the under-water spark from 6000 to 2000, and 180 lines are recorded in the range

3800—2100 Å. The intensity rule and the selection rule for inner quantum numbers are accurately fulfilled, and the classification of Bechert and Sommer is confirmed. A. GEAKE.

Arc spectrum of copper. A. G. SHENSTONE (Physical Rev., 1926, [ii], **28**, 449—474).—A large part of the spectrum has been analysed, with results in agreement with the theory of Heisenberg and Hund; it is partly an ordinary doublet spectrum with lowest term ^2S=62308·0, and partly a complicated spectrum with lowest term m^2D_3=51105·5 and m^2D_2=49062·6. Most of the lines are due to the combinations of the quartets and doublets with a set of terms having negative wave-numbers extending from −95·2 to −14772·4. The two types of spectra are connected by combinations of the lowest terms of each with higher terms of the other. All the classified lines of the copper arc spectrum (about 350) are tabulated with wave-lengths, intensities, and designations. The results are at variance with those of Stücklen (this vol., 1). A. A. ELDRIDGE.

Spectrum of zinc. D. M. SMITH (Nature, 1926, **118**, 592).—A new zinc line was observed at 2147·36 (±0·02) Å. Of the zinc lines at 2265·08 and 2265·40 Å. mentioned by Hagenbach and Schumacher (A., 1920, ii, 207), the latter was observed at 2265·35±0·02 Å., whilst the former is probably the cadmium line 2265·04 Å. A. A. ELDRIDGE.

Fine structure of xenon and krypton lines. E. GEHRCKE and L. JANICKI (Ann. Physik, 1926, [iv], **81**, 314—316).—Forty-two lines of xenon in the visible region have been examined for fine structure. With the exception of two lines, 4734·30 and 4501·13, all the lines are simple. The former has two satellites, the separations being −0·0249 and +0·0177 and the intensities, respectively, 1/10 and 1/3 of that of the principal line; the latter has satellites: 1/20, −0·043; 1/3, −0·0225; and 1/5, +0·0306. Sixteen krypton lines, including the 5871 and 5570 lines, show no evidence of fine structure and the work of Pérard (Compt. rend., 1923, **176**, 1060) is regarded as in error. R. A. MORTON.

Rubidium- and cæsium-like doublets of stripped atoms. R. C. GIBBS and H. E. WHITE (Proc. Nat. Acad. Sci., 1926, **12**, 551—555; cf. this vol., 874).—Using the method of extrapolation previously applied to stripped atoms of the potassium type, the ($5s$—$5p_2$), ($5s$—$5p_1$) doublets of Rb I, Sr II, Y III, and Zr IV, and the ($6s$—$6p_2$), ($6s$—$6p_1$) doublets of Cs I, Ba II, La III, Ce IV, and Pr V, have been identified. They conform with the regular and irregular doublet laws of stripped atoms. A. B. MANNING.

Regularities in the spectrum of ionised silver. C. S. BEALS (Phil. Mag., 1926, [vii], **2**, 770—777).—The spectrum of silver has been observed under varying conditions of excitation. Measurements of the Zeeman effect have been made on the lines between 2240 and 2940 Å. Thirty lines in the region 1850—2930 have been assigned definitely to the spectrum of Ag II. Twenty-three of these lines have been arranged in four groups, each with constant wave-number differences. The term separations are large, and it is suggested that a number of the lines in the region examined may be connected by constant difference relations with others in the Schumann region. The wave-number differences involve terms showing some evidence of analogy of these lines with those found in the arc spectrum of palladium. A. E. MITCHELL.

Fine structure of cadmium lines. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, **2**, 201—203).—The structure of the lines 3614·4, 3612·9, 3467·6, 3466·2, 3403·6, 3261·0, 3252·5, 3133·2, and 3080·9 in the cadmium spectrum has been examined. Strong reversal is indicated, especially when the vapour is dense. R. CUTHILL.

Fine structure of certain lines and energy levels of cadmium. W. A. MACNAIR (Proc. Nat. Acad. Sci., 1926, **12**, 555—556).—See this vol., 986.

Ultra-violet arc lines of iodine. R. S. MULLIKEN and L. A. TURNER (Physical Rev., 1925, [ii], **25**, 886).—The lines at 2062·25, 1876·40, 1844·39, and 1830·32 (±0·03) Å. have been produced by introducing iodine or metallic iodide vapour into active nitrogen, or by introducing metallic iodides into a carbon arc. It is suggested that these are all arc lines involving transitions to low energy levels of the iodine atom. A. A. ELDRIDGE.

Term regularities in the arc spectrum of tungsten. O. LAPORTE (Physical Rev., 1925, [ii], **25**, 886).—The lowest term is the D term (separations, 1670·25; 1655·25; 1504·50; 1389·30) with the s term lying between its levels. The interval rule is not fulfilled. So far, 200 tungsten lines have been classified as combinations of the s and D terms with higher levels. A. A. ELDRIDGE.

Coincidence of some spectral lines of gold and thallium. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 252—253).—By using very large high-tension currents for excitation, the new lines 3164·5, 2428·3, and 2409·9 have been observed in the spectrum of thallium, and the lines 3091·5, 2767·9, and 2580·1 in the spectrum of gold. Since for each element the new lines correspond very closely with lines already known in the spectrum of the other element, it seems that the experimental conditions are able to modify the atomic configuration. This is all the more likely since thallium and gold can be derived from mercury by the gain or loss, respectively, of a proton. R. CUTHILL.

Absorption of 2540 Å. by mercury vapour. J. T. TATE (Physical Rev., 1925, [ii], **25**, 110).—The age of the vapour does not appear to affect the absorption of 2540 Å. It is concluded that the entities which are responsible for the visible fluorescence in freshly distilling vapour are not the molecules which absorb 2540 Å. The latter are not heteropolar molecules formed between excited and neutral atoms. A. A. ELDRIDGE.

Absorption of the enhanced mercury line 1942·5 Å. by ionised mercury vapour. L. A. TURNER and K. T. COMPTON (Physical Rev., 1925, [ii], **25**, 238—239).—The intense light from an electrodeless discharge in mercury vapour, which gives a rich spark spectrum, was photographed after

passage through a mercury arc. The only spark line absorbed was that at 1942·5 Å., supporting the view that this is the longer wave-length member of the first pair of the principal series of ionised mercury. The Rydberg "doublet" 2847·8 and 2224·8 Å. showed no absorption, and their minimum excitation potential is greater than that of the line 1942·5 Å.

A. A. ELDRIDGE.

Fine structure of bismuth lines. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, **2**, 249—251).—The lines 3596·1, 3510·9, 3397·2, 3076·6, 3067·7, 3024·6, 2993·5, 2938·3, 2989·0, 2898·0, and 2780·5 Å. have been examined. R. CUTHILL.

***M*-Series of tungsten.** R. V. ZUMSTEIN (Physical Rev., 1925, [ii], **25**, 106).—Faint emission lines were observed at 6·948, 6·857, 6·789, and 6·720 Å. Absorption lines were observed at 6·708, 6·475, 5·418, 4·800, and 4·365 Å. A. A. ELDRIDGE.

Determination of certain outer *X*-ray energy levels. K. CHAMBERLAIN and G. A. LINDSAY (Physical Rev., 1925, [ii], **25**, 106).—Values of $(\nu/R)^{\frac{1}{2}}$ for outer levels, obtained from the differences between the three *L*-absorption edges and the corresponding adjacent emission lines, for ten elements from antimony to samarium inclusive, when plotted against atomic numbers, give curves showing a distinct change of slope at the beginning of the rare-earth group. This confirms Bohr's theory that the electrons here begin to be inserted into inner groups which were previously only partly filled. The curve representing the $O_{2,3}$ level is nearly horizontal for elements above lanthanum (57). A. A. ELDRIDGE.

Excitation of the *M*-series in iron by electronic impact. O. STUHLMAN, jun. (Physical Rev., 1925, [ii], **25**, 234—235).—The most prominent lines obtained were located at ($M\alpha$) 50, ($M\beta$) 80, ($M\gamma$) or (MA_1) 120, (MA_2) 160, and (MA_3) 171 volts. The computed convergence limit is probably at 177·4 volts.

A. A. ELDRIDGE.

Scattering power of oxygen and iron for *X*-rays. A. A. CLAASSEN (Proc. Physical Soc., 1926, **38**, 482—487).—The side of the unit cell of magnetite is 8·400 Å., and the parameter $x=0{\cdot}379$. The scattering power of oxygen and iron ions declines more strongly than the calculated value with increasing glancing angle. A. GEAKE.

Spectrographic junction between the *X*-ray region and the extreme ultra-violet. A. DAUVILLIER (Nature, 1926, **118**, 551).—The following thorium lines have been observed: $N\beta$, 45·3 Å., $O\delta$, 48·2 Å.; $N\alpha$, 51·5 Å.; $O\gamma$, 71·0 Å.; $O\beta$, 121 Å. The line $O\alpha$, not observed, would have a wave-length of about 230 Å. The very strong line at 45·3 Å. coincides with the carbon $K\alpha$ line.

A. A. ELDRIDGE.

Analysis at reduced pressure of radiation emitted by pastilles of high electrical resistance. G. REBOUL (J. Phys. Radium, 1926, [vi], **7**, 275—288).—When a substance (such as yellow mercuric oxide) possessing a high electrical resistance is traversed by a current, radiation in wave-length between *X*-rays and ultra-violet rays is emitted. By an ionisation method, it is shown that the radiation consists of (*a*) a continuous spectrum varying with the conditions of excitation and extending over a spectral region within the limits 10—1000 Å., (*b*) slow cathode rays, and (*c*) very slow anode rays.

R. A. MORTON.

True absorption of hard *X*-rays in water. H. FRICKE, O. GLASSER, and K. ROTHSTEIN (Physical Rev., 1925, [ii], **25**, 581).—The coefficient of true mass absorption for *X*-rays of wave-length 0·14 Å. is 0·0279, comprising a photo-electric absorption (0·0064) and a scattered absorption (0·0215), in accordance with Compton's theory.

A. A. ELDRIDGE.

Influence of the scattering substance on the intensity of the Compton line in scattered *X*-rays. P. A. ROSS (Physical Rev., 1925, [ii], **25**, 235).—Molybdenum $K\alpha$ lines were scattered from carbon at 30°, 60°, and 90°, and from aluminium, copper, silver, and lead at 90°. The intensity ratio of the modified to the unmodified line decreases as the atomic number of the scatterer increases. With copper *K* radiation scattered from aluminium, the modified line did not appear. The modified line is relatively stronger with tungsten *K* radiation than with molybdenum *K* radiation. When the green mercury line is scattered from paraffin, or by multiple reflexions from silver mirrors, no shifted component can be detected. A. A. ELDRIDGE.

Phenomena accompanying the Zeeman effect in weak magnetic fields and the influence on them of added gases. W. SCHÜTZ (Z. Physik, 1926, **38**, 864—886).—Observations on the double refraction of sodium vapour produced by a magnetic field transverse to the incident light (the Cotton effect) cannot be explained satisfactorily by the ordinary scheme of energy levels. The Cotton effect is reduced by the following gases at low pressures in the order argon, nitrogen, helium–neon mixture. Investigation of the Righi effect (rotation of the plane of polarisation by a magnetic field along the direction of the incident light) furnished evidence of the Zeeman effect with a field as weak as 1 gauss. The reduction in the effect is much greater for increase of pressure of the vapour itself compared with the increase produced by the addition of a foreign gas. The radius of the atoms in the excited state is discussed, together with the time of collision and duration of the excited state.

E. B. LUDLAM.

Intensities of the Zeeman components in the partial Paschen–Back effect. (FRL.) L. MENSING (Z. Physik, 1926, **39**, 24—28).—The intensities of the doublets and triplets in the intermediate stages between the Zeeman effect and the Paschen–Back effect have been calculated by the new quantum mechanics. Certain of both inner and outer components do not appear, in agreement with Back's measurements. E. B. LUDLAM.

Sparking potentials of helium, neon, and argon at reduced pressures between plane parallel electrodes of pure aluminium and of potassium-coated aluminium. C. C. VAN VOORHIS (Physical Rev., 1925, [ii], **25**, 583).—With pure aluminium electrodes, Paschen's law holds for

pressures greater than 9, 12, and 3 mm. for helium, neon, and argon, respectively, values for potassium-coated electrodes being 6, 6·5, and 1·5 mm. Corresponding values of the product of the pressure (mm.) and electrode separation (mm.) are: 35, 38, 12, and 24, 20, 5·3, respectively. A. A. ELDRIDGE.

Ionisation potential of O II. I. S. BOWEN and R. A. MILLIKAN (Nature, 1926, **118**, 410).—Fowler's study of the spectral characteristics of O II (this vol., 445) has been extended by an accurate determination of the fundamental levels. The ionisation potential is 34·88 volts. A. A. ELDRIDGE.

Ionisation potential of O II. A. FOWLER (Nature, 1926, **118**, 410).—A comment on Bowen and Millikan's results (preceding abstract). A. A. ELDRIDGE.

Low-voltage arcs in phosphorus vapour. O. S. DUFFENDACK and H. HUTHSTEINER (Physical Rev., 1925, [ii], **25**, 110—111).—The minimum arcing potential is 10·3 volts, which is also the voltage at which ionisation begins in a vapour containing a high percentage of atomic phosphorus. A new band spectrum was found in the region 2200—2600 Å.
A. A. ELDRIDGE.

Second ionising potential of argon. H. D. SMYTH and H. A. BARTON (Physical Rev., 1925, [ii], **25**, 245).—In argon, doubly charged ions can be formed from normal neutral atoms by single impacts of 45 ± 2 volts. The appearance of the blue spectrum lines at 34 volts is presumably due to cumulative effects, since a 34-volt impact would be just sufficient to give a neutral, excited atom the total 45 volts energy necessary for double ionisation. A. A. ELDRIDGE.

Critical potentials in secondary electron emission from iron. R. L. PETRY (Physical Rev., 1925, [ii], **25**, 583—584).—Critical potentials were observed at 6·7, 9·0, 13·85, 26, 34, 39, 42·8, 48·3, 54·6, 66·7, 80·5, 92·7, 740, 810, and 1010 volts, and others were indicated. A. A. ELDRIDGE.

Soft *X*-rays from metals. C. T. CHU (Physical Rev., 1925, [ii], **25**, 883).—Critical voltages (uncorrected) were observed as follows: nickel, 45, 75, 98; iron, 52, 68, 80; copper, 30, 49, 62, 79, 90.
A. A. ELDRIDGE.

Soft *X*-rays from cobalt, nickel, and copper. C. H. THOMAS (Physical Rev., 1925, [ii], **25**, 883).—Between 0 and 1500 volts, 47 critical potentials were found for nickel, 48 for cobalt, and 45 for iron, the agreement of the position of the breaks being especially good for the nine breaks resembling ionisation potentials. Agreement is less satisfactory with copper. Potentials corresponding with L series lines were found as follows: iron, L_{I} 818·5, L_{III} 704·3; cobalt, L_{I} 873·2, L_{III} 764·8; nickel, L_{I} 948, L_{III} 833·4; copper, L_{I} 1017, 929 volts. A. A. ELDRIDGE.

Excitation potentials of mercury atoms. R. G. LOYARTE (Physikal. Z., 1926, **27**, 584—588).—In the work of Franck and Einsporn (Z. Physik, 1920, **2**, 18) on voltage discontinuities for mercury, five values cannot be related with the known lines and series classifications. These critical potentials, together with others which were apparently rejected, can be obtained by the addition of 1·4 or 2·8 or 4·2 to potentials corresponding with known lines or series terms. Several other discontinuities are recorded which fit in with this scheme. It follows, therefore, that either mercury possesses a critical potential of 1·4, or some other substance is present in the tube. It is considered likely that a substance volatilised from the glowing wire is responsible. R. A. MORTON.

Photo-electric response of potassium at low temperatures. J. W. HORNBECK (Physical Rev., 1925, [ii], **25**, 113).—Potassium was illuminated with monochromatic light of constant intensity. The current–wave-length curve at −180° is reversibly shifted to shorter wave-lengths with respect to the curve for 20°. Monochromatic heating and cooling curves run approximately parallel to the temperature axis except between −80° and −100°, a region where a change of crystal structure is known to take place. A. A. ELDRIDGE.

Production and control of successive ionisation by collision in a photo-electric cell. J. T. TYKOCINER and J. KUNZ (Physical Rev., 1925, [ii], **25**, 245—246).—Helium is ionised by photo-electrons from illuminated potassium, the current produced in the circuit (the photo-electric cell, a thermionic current-limiting device, a milliammeter, and a source of *E.M.F.* 300—3000 volts) depending on the intensity of illumination, the pressure and nature of the gas, the distance between the electrodes, and the potential applied (cf. Albers, *ibid.*, 248).
A. A. ELDRIDGE.

Photo-electric thresholds and the quantum theory. R. HAMER (Physical Rev., 1925, [ii], **25**, 584).—Photo-electric thresholds are intrinsic properties of the elements. For lithium, sodium, and potassium, values of v_0 approximate to the transition energies for $1s$—$2p_{1,2}$; for copper, silver, and gold they equal the ionising energy for the $2p_1$ or $2p_2$ orbits. Values for aluminium and thallium are within 0·30 volt of the transition $2p_2$—$2s$; for lead, v_0 corresponds with the transition $2p_4$—$2s$. For bismuth, v_0 corresponds with the ionising energy for the observed resonance level or to its transition energy from the normal state. For oxygen, and probably sulphur, v_0 corresponds with the ionising energy for the $2s$ orbit.
A. A. ELDRIDGE.

Photo-electric effect in potassium vapour. E. LAWRENCE (Physical Rev., 1925, [ii], **25**, 584).—Previous results are confirmed. There is evidence of a photo-electric threshold at 2610 Å., in disagreement with the critical value 2856 Å. suggested as the threshold by the Bohr theory. A. A. ELDRIDGE.

Effect of minute surface impurities on the photo-electric long wave-length limit of mercury. H. K. DUNN (Physical Rev., 1925, [ii], **25**, 717—718).—Kazda's value of 2735 ± 10 Å. is confirmed for flowing mercury; the cleanest obtainable stationary surface gave the value 2860 Å. The effect of impurities, particularly hydrogen, has been investigated.
A. A. ELDRIDGE.

Total photo-electric emission of electrons from metals as a function of the temperature of the exciting radiation. S. C. ROY (Proc. Roy. Soc., 1926, **A**, **112**, 599—630; cf. this vol., 483).—The total photo-electric currents from aluminium,

iron, molybdenum, carbon, zinc, platinum, silver, gold, tantalum, tungsten, and nickel excited by the complete radiation from tungsten at temperatures between 1900° and 2700° Abs. have been measured, and Richardson's law is found to be obeyed. The theory that thermionic emission from hot bodies is due to the photo-electric activity of the radiation from the bodies themselves is worked out in some detail, and leads to results in fair agreement with the experimental data. R. CUTHILL.

Variation with temperature of the work-function of oxide-coated platinum. M. S. GLASS (Physical Rev., 1926, [ii], **28**, 521—523).—The experimental results support the theory that the thermionic activity of oxide-coated platinum filaments is probably due to a film of metallic barium and strontium produced by reduction of the oxides. A. A. ELDRIDGE.

Excitation of the hydrogen spectrum by electron impact. P. LOWE (Physical Rev., 1925, [ii], **25**, 885).—A study of the variation in intensity of hydrogen spectrum lines excited by electron impact in a three-electrode tube as a function of the pressure of the gas and the density of the electron current indicates that most of the radiation is due to direct electron impacts, but that at low voltages of impact some may be due to secondary effects. A. A. ELDRIDGE.

Excitation of polarised light by electron impact. H. W. B. SKINNER (Proc. Roy. Soc., 1926, **A**, **112**, 642—660).—Further details of the work previously described (this vol., 329) are now given. The results of Ellett, Foote, and Mohler (*ibid.*, 221) have been confirmed. Application of a magnetic field parallel to the electron stream does not affect the polarisation, but a field at right angles both reduces the polarisation and rotates its plane. A theoretical explanation of the observed effects is advanced. R. CUTHILL.

Scattering of electrons by ionised mercury vapour. A. F. DITTMER (Physical Rev., 1926, [ii], **28**, 507—520).—Langmuir's observation (*ibid.*, 1925, [ii], **26**, 585) that when a stream of electrons from a hot filament is projected into ionised mercury vapour with a given velocity it is scattered so that some of the electrons are accelerated and others retarded has been studied experimentally, and a theory which accounts for the effect is indicated. A. A. ELDRIDGE.

Cold electronic discharge from molybdenum. R. J. PIERSOL (Physical Rev., 1925, [ii], **25**, 112—113).—The electrodes, consisting of hemispherical molybdenum plates welded to tungsten rods, are sealed in the discharge tube, which, with the aid of charcoal, is evacuated to show a gradient of 5400 kilovolts/cm. at 20°. Increase in temperature, below thermionic range, increases the cold electronic current and lowers the breakdown gradient. A. A. ELDRIDGE.

Size-distribution of ions in gases. W. BUSSE (Ann. Physik, 1926, [iv], **81**, 262—280).—Nolan's experiments (Phil. Mag., 1926, [vii], **1**, 417) on the production of ions by waterfall electricity have been confirmed, but their interpretation is contested. Gaseous ions may vary in size from molecular to microscopic dimensions, and the results point to continuous gradation, whereas they were claimed to afford evidence of discontinuities. Experiments on the production of ions in the course of the oxidation of phosphorus indicate that the majority of the ions show continuous distribution, and that deviations occur only under favourable conditions (temperature, moisture, presence of nuclei). Nolan's interpretation is not satisfactory, even under these conditions. Radioactive ionisation also gives a symmetrical distribution for the size of ions. R. A. MORTON.

Doubly ionised atoms in mercury vapour. C. D. CHILD (Physical Rev., 1925, [ii], **25**, 111).—Mercury vapour that has been distilled past a hot cathode from which cathode rays are streaming is luminous, but the luminosity is not a continuation of the cathode rays. It is believed that in the positive column only singly ionised atoms are produced, whilst near the cathode doubly ionised atoms are produced, the latter recombining with electrons much more slowly than the former. A. A. ELDRIDGE.

Independence of the mobility and mass of an ion. H. A. ERIKSON (Physical Rev., 1925, [ii], **25**, 111).—It appears necessary to assume that all natural complex molecules which have lost or gained an electron move with the same velocity when the gaseous medium and the applied fields are the same, *i.e.*, that the mobility is determined by the charge. When, however, one molecular ion associates itself with another neutral molecule forming an artificial structure, the mobility becomes less. Hence an air ion (2 mols.) and a carbon dioxide ion (2 mols.) have the same mobility in air. A. A. ELDRIDGE.

Probabilities of ionisation by electron impacts in hydrogen and argon. K. T. COMPTON and C. C. VAN VOORHIS (Physical Rev., 1925, [ii], **25**, 245).—In hydrogen, the probability of ionisation by electron impact increases from zero at 16 volts to 0·31 at 125 volts, then decreasing to 0·25 at 325 volts. In argon, the maximum value is 0·48 at 130 volts, decreasing to 0·41 at 325 volts. A. A. ELDRIDGE.

Secondary emission from metals due to bombardment of high-speed positive ions. W. J. JACKSON (Physical Rev., 1926, [ii], **28**, 524—530).—The secondary electron emission on bombardment with potassium ions was not detected ($<0{\cdot}5\%$) at positive ion velocities less than 200 volts for aluminium, 300 volts for nickel, and 600 volts for molybdenum after heat treatment; at 1000 volts, values for the secondary emission were 7·0, 4·2, and 3·8%, respectively. Without heat treatment to exclude emission from adsorbed gases, the latter values were doubled, and the emission was detected at lower voltages. A. A. ELDRIDGE.

Ionisation in reacting gases. A. K. BREWER (Proc. Nat. Acad. Sci., 1926, **12**, 560—564; cf. A., 1925, ii, 919).—The ionic emission produced during the oxidation of hydrogen, ethyl alcohol, benzene, and other organic compounds at a heated gold or copper oxide surface has been measured. The variation of the ionisation current with temperature is expressed by Richardson's formula, $i=AT^{\frac{1}{2}}e^{-b/T}$. The values of b are regarded as a comparative measure

of the various rates of reaction. Where the rates of emission are the same for positive and negative ions, the temperatures of emission, *i.e.*, the temperatures at which the emission reaches a definite amount ($i=10^{-15}$ ampère per em.^{2}), are the same, whilst an increase in the rate of emission of the positive over the negative ions is accompanied by an increase in the difference in the emission temperatures. The bearing of the results on the theory of the mechanism of the surface reactions is discussed. It is suggested that the gas molecules are ionised at the surface by the combined image and contact forces, and that an ion with a sufficient energy component perpendicular to the surface will move out to a region of weak surface forces, where it can combine with an ion of opposite sign to form a neutral molecule, which is then able to escape from the surface region.

A. B. MANNING.

Ionisation by ultra-critical frequencies [of monochromatic ultra-violet light]. E. M. LITTLE (Physical Rev., 1925, [ii], **25**, 247—248).

Non-oscillatory abnormal low-voltage arcs with reversed electric fields caused by ion diffusion. C. ECKART and K. T. COMPTON (Physical Rev., 1925, [ii], **25**, 111).

Collisions of the second kind in monatomic iodine. H. D. SMYTH (Physical Rev., 1925, [ii], **25**, 583).—An account of preliminary experiments.

A. A. ELDRIDGE.

Optical evidence as to the orientation of atoms in a magnetic field. W. SCHÜTZ (Z. Physik, 1926, **38**, 853—863).—Experiments with sodium vapour, hydrogen, carbon dioxide, and air indicate that the atoms do not take up any oriented position in a magnetic field. E. B. LUDLAM.

Electrostatic moments of molecules. R. J. CLARK (Nature, 1926, **118**, 555).—The electrostatic moments of sodium chloride and mercuric chloride are estimated to be of the order of magnitude 10^{-18} e.s.u.em., that of arsenic trioxide being somewhat greater. That of metallic potassium was too small to detect. A. A. ELDRIDGE.

Recent determinations of the magneton. J. KUNZ (Physical Rev., 1925, [ii], **25**, 115).—The difference between experimental and calculated values is 4—6%, larger than is compatible with the accuracy of the measurements. The Bohr magneton seems not yet to be established by the determinations of paramagnetic susceptibilities. A. A. ELDRIDGE.

Magnetic moments of the alkali metal atoms. J. B. TAYLOR (Physical Rev., 1926, [ii], **28**, 576—583).—Experiments with sodium and potassium yield values for the magnetic moments of 5350 and 5380 gauss cm., respectively. Hence it is concluded that the normal atoms both possess a magnetic moment equal to one Bohr magneton (5584 gauss cm.).

A. A. ELDRIDGE.

Structure of the atomic magnet. Rotation and reversal of the multiplet. R. FORRER (Compt. rend., 1926, **183**, 559—560; cf. this vol., 878).—In an intense positive field the multiplet is closed (saturated magnetisation), but opens with decrease in intensity of the field so that the magnetisation approaches the value of the resultant. As the field approaches zero intensity, the multiplet tends to occupy the nearest normal position (residual magnetisation). Magnetisation further decreases when a weak negative field causes the multiplets to turn, but beyond the limits of stability the multiplets rapidly reverse by rotation, and negative magnetisation results. For stronger negative fields, the resultants take the direction of the field. This tendency to reversal by rotation is distinguished from reversal of one of the moments of the doublets as with nickel, and varies with the degree of annealing. It probably occurs chiefly in annealed ferromagnetic metals.

J. GRANT.

Copper oxide and the atomic weight of copper. R. RUER and K. BODE (Ber., 1926, **59**, [*B*], 1698—1703; cf. A., 1925, ii, 620).—In reply to Hönigschmid (Ber., 1926, **59**, [*A*], 11), further evidence is adduced that cupric oxide, ignited in air at 1000° and subsequently in oxygen at 700°, is a well-defined compound, free from cuprous oxide and occluded gases.

H. WREN.

Method of estimating atomic weights with the aid of the periodic law. E. W. WASHBURN (J. Amer. Chem. Soc., 1926, **48**, 2351—2352).—If the difference of the ratio of the atomic weight of each element to that of the next preceding (or following) zero-group element and the ratio of the corresponding atomic numbers is plotted against the atomic numbers of the elements, graphs are obtained which, for elements in rows 5, 7, and 8 of the table, are more or less regular. From these graphs the following atomic weights of the undiscovered or doubtful elements (all of which occur in these rows) are computed, the numbers in parentheses being atomic numbers: masurium (43), 97·5 or 98·8; illinium (61), 146·0; rhenium (75), 187·4; eka-iodine (85), 212; eka-cæsium (87), 223; actinium (89), 229; protoactinium (91), 234. S. K. TWEEDY.

Calculation of the ages of radioactive minerals. A. HOLMES and R. W. LAWSON (Nature, 1926, **118**, 478).—The age of a primary radioactive mineral is given to a first approximation in millions of years by the formula $\mathrm{Pb}\times C/(\mathrm{U}+k\times\mathrm{Th})$, where k is the amount of uranium which is equivalent in lead-producing capacity to 1 g. of thorium and $1/C$ is the amount of lead produced by 1 g. of uranium in 10^6 years. Divergences in the values of k and C which have been employed are discussed. The values $C=7400$ and $k=0{\cdot}38$ are regarded as the most trustworthy available. The relation approximate age$\times(1-x/2+x^2/3)$, where $x=1{\cdot}155\mathrm{Pb}/(\mathrm{U}+0{\cdot}38\mathrm{Th})$, gives the corrected age. A. A. ELDRIDGE.

Number of electrons and α-particles in atomic nuclei. H. NAGAOKA (Proc. Imp. Acad. Tokyo, 1926, **2**, 112—115).—If the difference between the atomic weight and the atomic number be taken as equal to the number of electrons in the nucleus, the difference between this figure and the atomic number increases with increase of the latter. If, however, the nucleus is regarded as consisting of α-particles with two positive charges as well as of hydrogen protons, this increase does not occur, but the value remains constant at 0 or 1. Elements giving the

latter value are usually those with a single outermost electron orbit, whereas the others have two such orbits. R. CUTHILL.

Nucleus of helium atom or α-particle. H. NAGAOKA (Proc. Imp. Acad. Tokyo, 1926, **2**, 204—207).—It is suggested that within the nucleus of the atom two protons may combine to produce a helium nucleus, the additional two units of mass being produced by energy absorbed in the process. This accounts for the fact that the difference in the atomic weights of the isotopes of a particular element is most usually 2. R. CUTHILL.

Mode of radioactive disintegration accompanied by secondary β-ray emission. S. KINOSHITA, S. KIKUCHI, and Y. HAGIMOTO (Proc. Imp. Acad. Tokyo, 1926, **2**, 195—197).—The emission of β-particles from radium and radium-$B+C$ has been examined by C. T. R. Wilson's cloud method. It is found that the fraction of atoms emitting secondary β-rays is about 0·8 for radium, 0·2 for radium-B, and 0·1 for radium-C. R. CUTHILL.

Range of α-particles in various media. E. Q. ADAMS (Physical Rev., 1925, [ii], **25**, 244—245).—The equation $\Lambda=\varepsilon-\log(1+\varepsilon)$, in which ε is the energy of the α-particle in terms of the energy at that velocity which makes the two work functions (primary ionisation, and kinetic energy imparted to the ions) equal, for the medium considered, and Λ is the distance in such units that the ratio Λ/ε approaches unity for high velocities, is in agreement with measurement. It leads to a modification of the Geiger and Nuttall formula from which the periods of the substances responsible for the long-range α-particles from radium-C have been calculated. A. A. ELDRIDGE.

Formation of α-ray tracks by simple means. C. T. KNIPP and N. E. SOWERS (Physical Rev., 1925, [ii], **25**, 108).—A simple apparatus is described which permits of the tracks being observed directly or projected on to a screen. A. A. ELDRIDGE.

α-Ray track projector. H. T. PYE (Physical Rev., 1925, [ii], **25**, 107).—The Shimizu apparatus is modified to permit of projection on to a screen. A. A. ELDRIDGE.

Transformation of the energy of cathode or β-rays into energy of *X*-rays. J. A. GRAY (Physical Rev., 1925, [ii], **25**, 237).—When β-rays of total energy E pass through a plate of mass dm per unit area, they excite X-rays of energy dX, and $dX=\kappa E dm$; $\kappa A/N$, where A is the at. wt., and N is Avogadro's number, is the atomic transformation coefficient α. Experimentally, κ is proportional to Z^2/A, α to Z^2, and both to $1/V$, where Z is the at. no. and V the *P.D.* in volts necessary to give the cathode or β-ray its energy. For a given material, dX depends only on n (the total number of β-rays) and dm. A. A. ELDRIDGE.

Three-dimensional reproduction of tracks of β-particles ejected by *X*-rays. O. DARBYSHIRE (Nature, 1926, **118**, 371—372).—By using a right-angle- instead of a stereo-photographic method of observation, both lateral and longitudinal types of asymmetry of the initial direction of ejection have been observed for heterogeneous X-rays in moist air. A. A. ELDRIDGE.

Measurements of the β-rays excited by hard *X*-rays. A. H. COMPTON and A. W. SIMON (Physical Rev., 1925, [ii], **25**, 107).—Two distinct types of tracks (P and R) are found in such a ratio as to indicate that just as each absorbed quantum of incident X-ray energy results in a photo-electron or P track, so each scattered quantum results in an R track. Further measurements support this view. A. A. ELDRIDGE.

Penetration of matter by corpuscular radiation. A. BECKER (Ann. Physik, 1926, [iv], **81**, 91—108).—The penetration of matter by cathode rays and by α-particles is compared. The loss of velocity for α-particles follows Geiger's equation $v^3=a(R-x)$, in which the range R is given by $v_0{}^3/a$, v_0 being the initial velocity and a a constant for the material. Correlation of the existing data on the loss of velocity of cathode particles results in a curve of the same type as that found for α-particles. The values $(dv/dx)_+ : (dv/dx)_-=0{\cdot}0014$ and $S_+/S_-=8{\cdot}9$ are given (S denotes the number of carriers per mm. path in air at 1 atm.). Within the limits of accuracy of the observations, no fundamental difference in mechanism between the two types of phenomena appears; the differences observed can be ascribed entirely to differences in mass between the carriers of energy. R. A. MORTON.

Secondary radiations produced by γ-rays and their effect on γ-ray absorption measurements. L. H. CLARK (Phil. Mag., 1926, [vii], **2**, 783—796).—Owen, Fleming, and Fage (A., 1925, ii, 84) have shown that the scattered radiation emitted by all matter when irradiated with γ-rays plays an important part in absorption measurements. Absorption measurements made with an electroscope suspended in air show the existence of a general scattered radiation from the surroundings which may contribute more to ionisation than that transmitted by very thick lead filters. This scattered radiation is softer than the primary rays causing it. Examination of the radiation scattered from different substances by the same beam of γ-rays shows that the penetrating power of the radiation scattered from layers of lead up to 0·66 cm. in thickness increases with increasing thickness of the layer and that the radiation scattered by different substances equally absorbent for the primary rays has a wave-length of about 0·063 Å., corresponding with X-rays excited by a peak potential of about $1{\cdot}96\times10^5$ volts. The radiation scattered from air by γ-rays is comparatively soft. It is suggested that errors, due to these radiations, in absorption measurements may be eliminated by encasing the electroscope in lead 1 cm. in thickness which has been shown to be capable of absorbing 99% of the hardest of the scattered radiation. A. E. MITCHELL.

Scattering and absorption of γ-rays. J. A. GRAY (Physical Rev., 1925, [ii], **25**, 236—237).—Secondary β-rays produced in light elements by the hard γ-rays of radium possess too much energy to be regarded as recoil electrons unless the γ-rays have a

much lower effective wave-length (0·008 Å.) than that usually accepted; they penetrate 3 mm. of aluminium.
A. A. ELDRIDGE.

Distribution of intensity in the spectrum of γ-rays. D. SKOBELTZYN (Nature, 1926, **118**, 553—554).

Luminescence of pure barium bromide under the action of α-, β-, and γ-rays. L. E. SMITH (Physical Rev., 1926, [ii], **28**, 431—437).—Heat-treated barium bromide was exposed to the action of α-, β-, and γ-rays from radium, the luminescent material and the exciting agent being kept apart. The brightness became maximal, and then decayed with time to a limiting value; the initial luminosity varied according to the heat-history of the sample.
A. A. ELDRIDGE.

Chemical action of gaseous ions produced by α-particles. IX. Saturated hydrocarbons. S. C. LIND and D. C. BARDWELL (J. Amer. Chem. Soc., 1926, **48**, 2335—2351).—Under the influence of α-particles from radon, ethane, propane, and butane each condenses with the elimination of hydrogen and methane (approx. 5 : 1 by vol.) with the formation of higher saturated and unsaturated hydrocarbons. The longer the carbon chain in the initial hydrocarbon the more readily the condensation occurs; methane eliminates hydrogen only. The condensation products are solid, liquid, or gaseous; unsaturated hydrocarbons are absent in the gaseous state, indicating immediate condensation of freshly-formed, unsaturated hydrocarbons. A mechanism is suggested for this, based on the assumption that the formation of a singly-charged two-molecule cluster precedes the elimination of hydrogen, at least two of the four valencies left vacant by the removal of two hydrogen molecules from the cluster remaining open, and acting as centres of attraction for other, similar, open pairs until a large chain or ring compound is condensed out. Methane and ethane are completely oxidised by oxygen in one step: $(O_2,CH_4,O_2)^+ + (O_2',CH_4,O_2)=2CO_2+4H_2O$; the ions of both reactants are equally effective with methane. Propane and butane do not oxidise completely in one step; liquid partial oxidation products are formed. Methane and carbon dioxide combine under the influence of the radiation to a wax-like solid. S. K. TWEEDY.

Chemical reactions produced by β- and γ-rays of radium on compounds in the vapour state. J. ERRERA and V. HENRI (J. Phys. Radium, 1926, [vi], **7**, 225—229).—The β- and γ-rays of radium probably produce polymerisation of the molecule of chlorobenzene. The action of the same rays on a mixture of chlorobenzene and hydrogen results in the hydrogenation of the former without the formation of benzene. A mixture of benzene and air or oxygen results in phenol when subjected to the rays, the number of molecules of phenol formed being at least sixty times that of the ions produced by the rays. The position, intensity, and fine structure of the absorption bands of the vapours of benzene, chlorobenzene, or phenol do not appear to be at all modified by the action of the rays. Neither an electric field of 10,000 volts per cm. nor a magnetic field of 20,000 gauss has any appreciable action on the absorption spectra of benzene, carbonyl chloride, or sulphur dioxide.
A. S. RUSSELL.

Lines of transformation products of uranium and thorium in the spectra of these elements. H. NAGAOKA and T. FUTAGAMI (Proc. Imp. Acad. Tokyo, 1926, **2**, 318—323).—Samples of thorium and uranium containing the products of radioactive disintegration have been examined spectrographically and the lines obtained tabulated, for comparison, with those found by other investigators for elements isotopic with the different disintegration products, and therefore having the same spectrum. The presence of a few new lines has been confirmed.
M. S. BURR.

Transformation of hydrogen into helium. F. PANETH and K. PETERS (Ber., 1926, **59**, [*B*], 2039—2048).—The methods of examination for helium have been so improved that it is possible to detect 10^{-8} to 10^{-9} c.c of the gas. The relatively condensible gases are removed by liquid air and carbon, and hydrogen is burnt with excess of oxygen at a platinum or palladium contact. Residual oxygen is absorbed by charcoal and the minimal remainder is examined spectroscopically in a glass capillary of 0·1 mm. diameter. The method is sufficiently sensitive to permit the detection of helium from active thorium precipitates and the determination of helium in small samples (a few c.c.) of natural gas. No evidence could be obtained of the production of helium by the bombardment of certain salts by cathode rays, by the subjection of hydrogen to the silent electric discharge, or by the discharge between aluminium electrodes in hydrogen. Evidence of the production of helium by passage of hydrogen over heated palladium is obtained. More definite results are produced by allowing hydrogen to remain in contact with palladium-black, spongy palladium, or palladised asbestos at the ordinary temperature, a rough proportionality being observed between the intensity of the effect and the duration of the reaction. The behaviour of the catalyst is somewhat irregular and its activity diminishes with time. The inert catalyst may frequently be revived in the usual manner. Parallelism of the active condition for union with hydrogen and for the formation of helium exists only so far that helium is not produced in the presence of a catalyst inactive to hydrogen; occasionally catalysts which readily absorb hydrogen do not yield helium. Disperse specimens of palladium which have been preserved for a period at the ordinary temperature appear invariably to retain helium, which is evolved when they are heated; the gas naturally contains also neon, but the ratio helium : neon is almost invariably much greater than that of the mixture derived from air. The hypothesis that the activity of the palladium is purely catalytic is strengthened by the observation that a similar, although weaker, effect is produced by platinum. The possible sources of error are treated in detail. Full description of the apparatus will be given later.
H. WREN.

Kaufmann's experiment and the spinning electron. L. H. THOMAS (Nature, 1926, **118**, 374).—Jackson's argument (this vol., 991) is invalidated by a mistake in the formula employed. A. A. ELDRIDGE.

Bohr's atomic model from the point of view of general relativity. M. S. VALLARTA (Physical Rev., 1925, [ii], **25**, 582).—Using Nordström's fundamental form for a static sphero-symmetrical material field and the Weyl–Eddington equation of electronic motion, it is shown that in the hydrogen atom and all hydrogenic ions (i) the curvature of the material field of the nucleus almost vanishes, (ii) its field is very nearly static, (iii) such atom and ions may be treated as a relativistic one-body problem, (iv) the general equation of the electronic orbit reduces to Sommerfeld's equation. An attempt to bring the quantum theory into relativity leads to an explanation of the existence of unmechanical orbits in atoms of more than one electron, and a unification of Bohr's frequency postulate and correspondence principle.
A. A. ELDRIDGE.

Mechanical aspects of the Bohr atom. F. S. BRACKETT and L. B. SNODDY (Physical Rev., 1925, [ii], **25**, 884).—Agreement between computed and experimental conductivities of metals supports the view that the Bohr atom may be regarded as a mechanical picture. A. A. ELDRIDGE.

Spatially extended electron in the general relativity theory. V. FRÉEDERICKSZ and A. ISAKSON (Z. Physik, 1926, **38**, 788—802).—Mathematical.
E. B. LUDLAM.

Fields of force within atoms. H. C. UREY (Physical Rev., 1925, [ii], **25**, 241).—One central static field of force, in which all the electrons of atoms of higher atomic number are assumed to move, can be chosen such that the quantum numbers assigned by Bohr are integral. Even levels could not be fitted to a similar field, or to the same field as the odd levels by using half quantum numbers.
A. A. ELDRIDGE.

Virtual oscillators and scattering in the quantum theory. J. H. VAN VLECK (Physical Rev., 1925, [ii], **25**, 242—243).—It is argued that the term $B\rho h\nu$ (Becker, Z. Physik, 1924, **27**, 173) equals the gross absorption by virtual oscillators, rather than absorption less scattering, and that the scattering by the phantom resonators is to be identified with the energy $Ah\nu$ emitted in spontaneous quantum transitions. There is then only the resonance radiation type of scattering. A. A. ELDRIDGE.

Half quanta and the specific heat of hydrogen. E. HUTCHISSON and J. H. VAN VLECK (Physical Rev., 1925, [ii], **25**, 243—244).—If half quanta are used in Kemble and Van Vleck's theory, which considers an elastic model and includes vibrational energy, the calculated specific heat curves are in fair agreement with the experimental curves at low temperatures when the probability $p_n=2n$ $(n=\frac{1}{2}, \frac{3}{2}, \ldots)$, excluding $n=\frac{1}{2}$. A. A. ELDRIDGE.

Half quanta and the stability of relativistic orbits. J. H. VAN VLECK (Physical Rev., 1925, [ii], **25**, 108).—Wilson's assumptions (Proc. Roy. Soc., 1922, **A**, **102**, 9) vitiate the contention against half quanta that owing to relativity corrections an electron of azimuthal quantum number k would spiral into the nucleus if the atomic number Z exceeded k/a, where $a=2\pi e^2/hc=1/137$. A. A. ELDRIDGE.

Atomicity of electricity as a quantum theory law. O. KLEIN (Nature, 1926, **118**, 510).

Theory of quantum mechanics. P. A. M. DIRAC (Proc. Roy. Soc., 1926, **A**, **112**, 661—677).—A mathematical treatment of the Heisenberg–Schrödinger theory of atomic mechanics. The problem of an atomic system subjected to an external perturbation is considered, and the theory is shown to account for the absorption and stimulated emission of radiation, but not for spontaneous emission.
R. CUTHILL.

Quantum mechanics of collisions. M. BORN (Z. Physik, 1926, **28**, 803—827).

Intensity of band lines and the affinity spectrum of diatomic molecules. E. FUES (Ann. Physik, 1926, [iv], **81**, 281—313).—A mathematical investigation on the lines of the newer quantum mechanics in which the relations between intensity factors and matrix elements, in the cases of band spectra, continuous spectra, and affinity spectra, are discussed. R. A. MORTON.

Nature of resonance radiation. J. C. SLATER (Physical Rev., 1925, [ii], **25**, 242).—The view that the absorption and emission of radiant energy by quantised atoms takes place continuously during the stationary states, whilst the atomic energy changes discontinuously at transition, exact conservation of energy being discarded, is developed to explain the nature of resonance radiation. On this assumption, the resonance radiation would be emitted by atoms in the normal state. A. A. ELDRIDGE.

Ionic properties and chemical facts. X. Curves of the ionic magnitudes, atomic volumes, and atomic magnitudes and the empirical facts. H. G. GRIMM (Z. physikal. Chem., 1926, **122**, 177—216).—The previously published data for ionic magnitudes (this vol., 664) are used to show that in any particular group of the periodic classification the physical properties of elements and compounds run closely parallel to the sizes of the ions. Bohr's atomic theory is shown to account in a satisfactory manner for the form of the ionic magnitude curves, also for various empirical generalisations such as the "lanthanide contraction." The physical significance of L. Meyer's atomic volume curve is discussed.
R. CUTHILL.

Physical and chemical properties of silicon and its position in the periodic classification. A. VON ANTROPOFF (Z. Elektrochem., **32**, 423—428).—A discussion of the relationship between silicon and the other elements, particularly those of group IV, as exhibited by properties such as ionic radius, ionisation potential, electron affinity, crystal structure, etc., and interpreted in terms of atomic structure. A modified form of the periodic table is used (cf. this vol., 773). H. J. T. ELLINGHAM.

Absorption spectrum of the hydrogen molecule. J. J. HOPFIELD and G. H. DIEKE (Nature, 1926, **118**, 592).—More than 20 absorption bands of molecular hydrogen were observed between 1245 and 840 Å., mostly showing the characteristic structure of the emission bands in the ultra-violet. Twelve bands of a progression beginning at 1105 Å.

were recognised. The long wave-length limit of the continuous absorption, corresponding with dissociation into a normal and an excited atom, is in agreement with the theoretical value of 14·4 volts.

A. A. ELDRIDGE.

Spectrum of lithium hydride. W. W. WATSON (Physical Rev., 1925, [ii], **25**, 887).—The complex spectrum, partly due to the LiH molecule, resembles the secondary hydrogen spectrum in that there are no apparent band heads. The moment of inertia of the LiH molecule is computed at 6×10^{-40} g.cm.^{2}

A. A. ELDRIDGE.

Relations between certain comet-tail spectra and the first negative Deslandres group. H. B. LEMON (Physical Rev., 1925, [ii], **25**, 109).—Conditions described for producing the "comet-tail" spectra with great brilliance also develop in great intensity the first negative Deslandres group.

A. A. ELDRIDGE.

Analysis of the "comet-tail" bands. C. M. BLACKBURN (Physical Rev., 1925, [ii], **25**, 888).—Each "band" consists of two strong bands, each with a satellite band, all degraded towards the red, and characterised by the absence of any Q branch. The established connexion between the system and the first negative Deslandres system is verified.

A. A. ELDRIDGE.

Band spectrum of magnesium hydride. W. W. WATSON and P. RUDNICK (Physical Rev., 1925, [ii], **25**, 887).—P, Q, and R branches of the narrow doublet character were found in which systematic departures from the combination principle appeared. Bands attributable to the two less abundant isotopes were present. The hypothesis of a dipole carrier, probably MgH, is supported. A. A. ELDRIDGE.

Excited states of the cuprous iodide molecule, and the band spectra of certain salts. R. S. MULLIKEN (Physical Rev., 1925, [ii], **25**, 887).—The cuprous iodide spectrum consists of five systems of bands, each corresponding with a transition to the normal state from excited electronic states corresponding with energies of 2·44, 2·68, 2·70, 2·83, and 2·96 volts, respectively. Similar relations probably hold in cuprous bromide and chloride. Probably the excited electron belongs to the Cu^+ ion. It is argued that the band spectra of the alkaline-earth halides may be due to diatomic molecules, MX.

A. A. ELDRIDGE.

Electronic states and band spectrum structure in diatomic molecules. I. Statement of the postulates. Interpretation of CuH, CH, and CO band-types. R. S. MULLIKEN (Physical Rev., 1926, [ii], **28**, 481—506).—The problem of the interpretation of band-structure from combination relations is considered with reference to ambiguities and the criteria for overcoming them. Recent work on the classification of electron levels in molecules in analogy with those of atoms is discussed. The NO γ-bands are classified as $^2S\rightarrow{}^2P_{1,2}$; Jevons' SnCl bands as $^2S\rightarrow{}^2P_{1,2}$ in the tin ion; the violet CN bands are ascribed to a $^2S\rightarrow{}^2S$ transition. With these bands are classed the AlO, SiN, N_2^+, BOβ, and CO^+ negative Deslandres bands. The CuH, AgH, and AuH bands and the infra-red hydrogen halide bands are ascribed to $^1S\rightarrow{}^1S$ electronic transitions.

The chief conclusions and assumptions involved in these interpretations can be stated in the form of the following three postulates, with the aid of which a systematic interpretation of most known band spectra is possible: (i) The electronic states of molecules can be characterised by a term-designation carrying implications similar to those for an atom; it is associated with an electronic quantum number j_e, the numerical value of which is substantially identical with Sommerfeld's atomic inner quantum number j for the given term-type, or each atom may possess a number j_e, when the electronic states of the hydrogen atom are to be classed with those of an alkali metal. (ii) The vector or vectors j_e set themselves nearly parallel or perpendicular to the vector m, and the rotational energy term is given in the general case substantially by a Kratzer–Kramers and Pauli formula. (iii) The molecular j has integral values for odd molecules and half-integral values for even molecules, and is subject to the selection principle $\Delta j=0,\pm1$, the relative intensities for these three transitions being governed by the correspondence principle.

The normal state of all diamagnetic gases (hydrogen, nitrogen, carbon monoxide, hydrogen chloride, etc.) is probably a ^1S state; the paramagnetism of nitric oxide is attributed to its double ^2P normal state, and that of oxygen possibly to a ^3S normal state.

A. A. ELDRIDGE.

Spectrum of the condensed spark in aqueous solution. E. O. HULBURT (Physical Rev., 1925, [ii], **25**, 888).—A study of the spectra, from 3200 to 2400 Å., of the condensed spark in 0·2% aqueous solutions of salts of aluminium, antimony, arsenic, barium, bismuth, bromine, cadmium, calcium, chromium, cobalt, copper, iodine, iron, lead, lithium, magnesium, mercury, molybdenum, nickel, potassium, sodium, strontium, tin, and zinc. A. A. ELDRIDGE.

Absorption spectrum of formic acid vapour in relation to molecular associations. L. HARRIS (Nature, 1926, **118**, 482).—The law of distribution of practically all the bands in the absorption spectrum of formic acid vapour is represented with close approximation by the formula $1/\lambda=41700+1050n+385p$, where $n=-2$, -1, 0, 1, and 2, and $p=-7$ to 7; the null-band has wave-length 2398·0 Å. The larger fundamental period, 1050, is of the same order of magnitude as is obtained for a number of molecules containing a carbonyl group; probably this corresponds with the vibration of the oxygen relative to the carbon atom. The bands are considered to be due to one molecular species only, apparently single molecules, $H{\cdot}CO_2H$. A. A. ELDRIDGE.

Absorption colours of the second order. J. PICCARD (J. Amer. Chem. Soc., 1926, **48**, 2352—2354).—In a series of compounds, in which, by progressive increase in mol. wt., the colour has passed through the usual series, yellow → violet → green, a further similar change in constitution may cause the colour to become yellow again, and subsequently pass through the same colour series (cf. Piccard, A., 1913, i, 895). These "colours of the second order" are derived, not

by disappearance of the original absorption band, but by its passage into the immediate infra-red, whilst a second absorption band, the "octave" of the first, enters the visible spectrum at the violet end. Auramine has no absorption band in the infra-red next the visible spectrum; its colour cannot therefore be of the second order, and its constitution is probably represented by the non-quinonoid formula $[Me_2N{\cdot}C_6H_4{\cdot}C(:NH_2){\cdot}C_6H_4{\cdot}NMe_2]Cl$.

F. G. Willson.

Absorption colours of the second order. J. Piccard (Ber., 1926, **59**, [*B*], 1653—1655; cf. preceding abstract).—A reply to Havas (A., 1914, ii, 319). An improved method for the preparation of *p*-nitrosotriphenylamine is incidentally described. H. Wren.

Spectrum of methæmoglobin. Spectrum of carboxyhæmoglobin. E. Dollmer and L. Fourrier (Compt. rend. Soc. Biol., 1925, **93**, 1364—1388; from Chem. Zentr., 1926, I, 1815).—Methæmoglobin was prepared by warming a solution made up of equal parts of blood and glycerol for 1 hr., carboxyhæmoglobin by bubbling illuminating gas through a blood solution. The development of the characteristic spectra and the time of appearance of the different bands, using different thicknesses of layer, were observed. M. Clark.

Absorption of light by simple amines in the ultra-violet. H. Ley and F. Volbert (Ber., 1926, **59**, [*B*], 2119—2131).—Piperidine and benzylamine show a marked influence of solvent on the course of absorption, thus probably indicating a general property of aliphatic amines. Salt formation has a strong hypsochromic effect. The spectra are arranged in the following series in order of decreasing intensity of absorption: piperidine (vapour, liquid, in hexane, in water or alcohol, in hydrochloric acid); benzylamine (liquid, in hexane and chloroform, in water and alcohol, in hydrochloric acid). In the region examined, piperidine shows mainly continuous absorption. The oscillations proper to the nitrogen or the group $N<\begin{matrix}C-C\\C-C\end{matrix}>C$ probably lie at wave-lengths shorter than 0·2 μ. With benzylamine, the initial absorption is less influenced by factors such as solvent or salt formation, the position of the maximum remaining nearly constant. The influences are more pronounced in the magnitudes of the ε values and in the end absorption. The initial absorption and maximum are ascribed to the phenyl or PhC– group, since they are common to other compounds, such as benzylaminoacetic acid, phenylaminoacetic acid, and phenylacetic acid. The analogous behaviour of the end absorption of benzylamine and of the continuous absorption of piperidine in different media and in salt formation is remarkable.

The optical behaviour of benzyl- and phenylaminoacetic acid is described in detail. H. Wren.

Absorption of linearly and circularly polarised light. E. von Angerer and G. Joos (Physikal. Z., 1926, **27**, 579—584).—The conditions under which a possibility exists of variations in the absorption of a gas with variations in the polarisation of the exciting light are discussed. For the rubidium doublet 7947·6, 7800·2 Å., the relative intensity of the components is the same for ordinary light as for either linearly or circularly polarised light. The rubidium lines can be recognised first at 18°. The vapour pressure 7×10^{-8} mm. corresponds with 3×10^{-11} g. of rubidium in a tube 1 metre long. R. A. Morton.

Transparency of the atmosphere to the visible spectrum. Molecular diffusion. Absorption by ozone. J. Cabannes and J. Dufay (J. Phys. Radium, 1926, [vi], **7**, 257—274).—The apparent coefficient of absorption of a pure gas is given by $k=8\pi^3/3\lambda^4\,.\,(\mu^2-1)^2/n\,.\,(6+3\rho)/(6-7\rho)$ (λ is the wave-length, μ the index of refraction, n the number of diffusing particles per c.c., ρ the depolarisation of light diffused at 90° to the incident beam). ρ is known experimentally, and from Rayleigh's generalised formula $n=2{\cdot}90\times10^{19}$. The optical density of the atmosphere considered as a mixture of ideal gases is $n=(2{\cdot}91\pm0{\cdot}8)\times10^{19}$, showing that concordant results are obtained from experiments on diffusion and from Fowle's measurements (Astrophys. J., 1913, **38**, 395) at the altitude of Mt. Wilson. Molecular diffusion occurs only in the blue, violet, and ultra-violet regions. The accepted value for the number of molecules per c.c. of a gas under normal conditions is $2{\cdot}70\times10^{19}$, so that Rayleigh's expression does not lead to an accurate value of the Avogadro number.

Between 4800 and 6500 Å. the optical density measured by Fowle is greater than the calculated value, owing to selective absorption, due entirely to the presence of ozone equivalent in amount to a 3 mm. layer under ordinary conditions. This conclusion is confirmed by measurements of atmospheric absorption. R. A. Morton.

Visible absorption spectra of several azoxine colouring matters. F. Kehrmann and P. Borgeaud (Helv. Chim. Acta, 1926, **9**, 881—885).—The absorption spectra of the mono-, di-, and tri-salts of the azoxine dyes described (*ibid.*, 866–880) are plotted, and the displacement caused by the various substituent groups is compared. J. W. Baker.

Colour of crushed alkaline-earth sulphur phosphors. J. Stalony-Dobrzański (Z. Physik, 1926, **38**, 841—847).—The phosphors were subjected to pressure and thin scales examined by transmitted light in a microscope and by means of a direct-vision spectroscope. The transmitted light was brilliantly coloured and the spectrum closely resembled that of the Bunsen flame coloured by the alkaline earth contained in the phosphor, the groups of lines being represented by bands, presumably due to the influence of neighbouring atoms on each other in the solid state. It is predicted that compressed radium sulphide would show a carmine-red colour and give a spectrum consisting of red and blue bands. Pure strontium sulphide showed the colour even more strongly than the phosphor containing this substance. If the pressure is excessive, the absorption, or scattering, is so great that the substance loses its transparency. E. B. Ludlam.

Colour of the tervalent titanium ion. J. Piccard (J. Amer. Chem. Soc., 1926, **48**, 2295—2297).—Since dilute titanium chloride solution event-

ually loses its violet colour on progressive addition of water or dilute acid, and since Beer's law is not followed, it is concluded that the hydrated tervalent titanium ion is colourless, but has a strong latent colour (cf. A., 1924, ii, 81), on account of which titanium trichloride is coloured. Titanium trifluoride solutions are colourless, which is in support of this statement (cf. Fajans and Joos, A., 1924, ii, 372).

S. K. TWEEDY.

Dependence of sensitised fluorescence on the added gas. S. LORIA (Z. Physik, 1926, **38**, 672—674; cf. this vol., 10).—Exception is taken to the statement by Franck and Jordan ("Anregung von Quantensprüngen durch Stösse," 1926) that the difference between the author's and Donat's results was due to impurity in the gases caused by fusing off the silica tubes of the former. E. B. LUDLAM.

Phosphorescence of nitrogen. J. C. MCLENNAN, H. J. C. IRETON, and K. THOMPSON (Nature, 1926, **118**, 408—409).—The spectrum of the light emitted when solid nitrogen is bombarded by electrons under a potential of 125,000 volts includes: (*a*) a narrow band (N_4) at 5945 Å., (*b*) three broad diffuse bands (N_1) at approximately 5554, 5617, and 5658 Å., (*c*) eight bands (N_2) at 5204·4, 5210·4, 5214·3, 5220·4, 5224·4, 5228·8, 5235, and 5240 Å., (*d*) a number of faint, diffuse bands between 4500 and 2460 Å., some of which have already been observed by Vegard, and some belong to the second positive band spectrum of nitrogen. Vegard's group N_3 was not observed. Interruption of the bombardment caused the immediate disappearance of the group N_1, the N_2 group and the N_4 band being persistent; the N_1 group almost vanished with prolonged bombardment. It is suggested that the nitrogen is first deposited in the form *A*, which is then changed by electronic bombardment or otherwise into the form *B*, which exhibits phosphorescence. Vegard's theory connecting the aurora with the presence of solid nitrogen in the upper atmosphere is untenable.

A. A. ELDRIDGE.

Phosphorescent silicon disulphide, activated by carbon. E. TIEDE and M. THIMANN (Ber., 1926, **59**, [*B*], 1706—1712).—Silicon disulphide phosphors are obtained by subliming a mixture of silicon disulphide and an organic compound at 1200—1300° in an atmosphere of nitrogen or by heating aluminium sulphide and silica in nitrogen containing the vapours of organic compounds. Substances other than carbon appear incapable of exciting the fluorescence of silicon disulphide. The phosphors exhibit a greenish- or yellowish-red fluorescence, the emission spectrum being composed mainly of three bands at 615—575, 568—540, and 536—507 μμ. They are characterised by great predominance of the shortest centres, in addition to which, centres of very long duration are present in very small proportion; centres of medium duration are almost completely absent.

H. WREN.

Energy of active nitrogen. P. D. FOOTE, A. E. RUARK, and R. L. CHENAULT (Physical Rev., 1925, [ii], **25**, 241).—Since active nitrogen is believed to consist of metastable nitrogen molecules, metallic atoms are apparently excited by collisions of the second type. Mercury lines requiring 9·52 volts for their production were readily obtained, but not lines requiring 9·66 volts. A. A. ELDRIDGE.

Active nitrogen. E. B. LUDLAM and L. H. EASSON (Nature, 1926, **118**, 590).—Although Willey and Rideal (this vol., 893) find the energy of active nitrogen to be 42,500 cal./g.-mol., Strutt observed the iodine line 2061 Å., requiring at least 150,000 cal., when active nitrogen interacts with iodine. The exchange of energy is probably direct.

A. A. ELDRIDGE.

Dependence of dielectric constant on pressure for gases and vapours at low pressures. K. WOLF (Physikal. Z., 1926, **27**, 588—591).—The dielectric constant for carbon dioxide, nitrogen, oxygen, and hydrogen varies linearly with the pressure over a range extending from 1200 mm. to very low pressures. For water and ammonia vapours, the graph shows a discontinuity (cf. Zahn, this vol., 456), but the branches on either side are straight lines.

R. A. MORTON.

Rotatory powers of borneol, *iso*borneol, and their esters. P. PEIGNIER (Bull. Soc. chim., 1926, [iv], **39**, 1235—1243).—The rotatory powers of borneol and *iso*borneol vary with the solvent employed (cf. Peacock, J.C.S., 1914, **105**, 2785), the variations being much greater in the case of *iso*borneol (cf. Haller, A., 1891, 575). Cryoscopic determinations indicate that in acetic acid or benzene solution the proportion of associated molecules of *iso*borneol is very small, and the variations are attributed to the existence of two distinct configurations of the simple molecule. In the esters of these alcohols variations are less pronounced, and in some cases the bornyl ester shows the greater variation in rotatory power with the solvent. The hydrogen phthalates, benzoates, hydrogen succinates, and *iso*valerates were examined.

R. BRIGHTMAN.

Refractive power of cellulose fibres. A. FREY (Koll.-Chem. Beih., 1926, **23**, 40—50).—The theory of the immersion method of measuring refractive indices, as applied to complex bodies such as cellulose fibres, is discussed. It is only by careful choice of the immersion fluid and sufficiently long imbibition of the fibres, so that the immersion fluid in the fibres has the same composition as that outside, that the refractive indices of the liquid coincide with the required values. The results of measurements with a number of pure cellulose plant fibres, including ramie, nettle, flax, *Callotropis*, and cotton wool, show that the refractive indices for the two rays, n_α and n_γ, are approximately constant and possess the mean values 1·533 and 1·594, respectively, which are claimed to be optical constants for the cellulose micelle. If the micelle runs at an angle to the fibre axis, in the direction of which the measurements are taken, the required values must be calculated by means of an equation for an ellipse. Deposits of lignin and pectin in the fibre alter the refractive indices of the complex body and reduce the double refraction.

L. L. BIRCUMSHAW.

Double refraction of natural cellulose fibres and of chitin. A. MÖHRING (Koll.-Chem. Beih., 1926, **23**, 162—188; cf. Ambronn, Z. wiss. Mikrosk., 1915, **32**, 43).—Wiener's formulæ for the "rod-like" double refraction of mixed bodies composed of isotropic components were assumed by Ambronn (*loc. cit.*) to hold for mixed bodies composed of anisotropic components, if the mean values of the chief refractive indices of the components are put for n_1 and n_2 in the formulæ. The possible error introduced in this way has been tested. The formulæ for the double refraction of a mixed body of anisotropic components have been derived from Wiener's theory, and calculation made with the help of these show that Ambronn's assumption was justified, the deviation from his results being extremely small. The influence of the refractive index of the imbibition fluid on the double refraction of plant membranes has been studied in the bast fibres of ramie, of *Urtica dioica*, and the collenchyma of *Sambucus nigra*. The double refraction of the investigated cellulose fibres is due to the combined effects of a strong positive specific double refraction, and a "rod-like" double refraction. The fibres are assumed to be composed of elongated crystalline particles, oriented parallel to one another, and possessing a "positive anisotropy." Experiments with lobster shell show that the chitin fibrils possess a negative specific double refraction, on which a considerably stronger positive rod-like double refraction is superimposed. L. L. BIRCUMSHAW.

"Form"-birefringence through absorption. O. WIENER (Koll.-Chem. Beih., 1926, **23**, 189—198).—The question is considered whether, in a system exhibiting dichroism, the birefringence is due to crystalline structure of a component or to the anisotropic arrangement of isotropic parts. For completely transparent heterogeneous systems the effect disappears as the refractivities of the components become equal; but if one of the components absorbs light, "form"-birefringence appears. Various aspects of the case are treated mathematically. E. S. HEDGES.

Does the failure of *X*-ray examination to reveal crystalline nature exclude true birefringence? O. WIENER (Koll.-Chem. Beih., 1926, **23**, 198—200).—Certain substances when stretched exhibit birefringence, but *X*-ray examination does not confirm a crystalline structure. Consideration of the effect of stretching glass leads to the conclusion that no help is to be expected from *X*-ray examination. E. S. HEDGES.

Anomalous dispersion and absorption of electric waves. IV. Anomalous dispersion and Debye's dipole theory. S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 143—145; cf. this vol., 886).—According to Debye (Verh. Physikal. Ges., 1913, **15**, 770), the abnormally large dielectric polarisation observed in static fields and in long electric waves is due to the orientation of permanently dipolar molecules in the dielectric. Discussion of the author's previous results indicates that this theory holds as a first approximation for primary aliphatic alcohols. The viscosities of ethyl, propyl, *iso*butyl, and amyl alcohols at low temperatures (0 to −60°) are recorded. S. K. TWEEDY.

Anomalous dispersion and absorption of electric waves. V. Anomalous dispersion and Debye's dipole theory. S. MIZUSHIMA (Bull. Chem. Soc. Japan, 1926, **1**, 163—168; cf. preceding abstract).—The experiments have been repeated on some aliphatic alcohols with waves of 3·08 and 50 metres between 60° and −60°. The results obtained are analogous to those recorded for the wave of 9·5 metres. For different wave-lengths, the values of the dielectric constants of glycerol, propyl, *iso*butyl, and amyl (and probably ethyl) alcohols approach one another at low temperatures. For a definite wave-length, the anomalous absorption first increases to a maximum and then decreases with decreasing temperature. The results are discussed from the point of view of Debye's dipole theory. A. S. CORBET.

Refraction and dispersion of gaseous carbon disulphide. H. LOWERY (Proc. Physical Soc., 1926, **38**, 470—472).—The refractive index, $(\mu-1)\times10^6$, of carbon disulphide, reduced so as to show the refractivity by the same number of molecules as 1 c.c. of hydrogen contains at *N.T.P.*, is 1477 for 5461 Å. Values for other wave-lengths are given by the equation $\mu-1=5{\cdot}3530\times10^{27}/(3926{\cdot}6\times10^{27}-n^2)$. A. GEAKE.

Crystalline nitrogen. D. VORLÄNDER and W. H. KEESOM (Ber., 1926, **59**, [*B*], 2088—2092).—Contrary to the observations of Wahl (A., 1912, ii, 1044), crystalline nitrogen is not regular and optically isotropic, but doubly refractive and optically anisotropic from its solidifying point, −210° to −253°. Crystals of argon are regular to −253°. In general, the transition isotropic → anisotropic does not occur at very low temperatures. H. WREN.

Determination of the constitution of inorganic substances by spectroscopic methods. W. STRECKER and R. SPITALER (Ber., 1926, **59**, [*B*], 1754—1775).—Difference in optical properties is observed between a dialkyl sulphide and the corresponding sulphoxide and between symmetrical and unsymmetrical sulphites, whereas the transformation from sulphoxide to sulphone or from symmetrical sulphite to sulphate has no effect. The constancy of molecular refraction is due to the balance between the increment caused by the addition of the oxygen atom and the decrement due to the passage of the sulphur atom to a higher state of valency. The molecular dispersion of the sulphur atom depends to an even greater extent on its valency being at a maximum for the bivalent atom. The results of optical investigation harmonise most satisfactorily with the constitutions $R_2S\leqslant^{O}_{O}$, $O{:}S(OR)_2$, $\overset{R}{RO}>S\leqslant^{O}_{O}$, and $(RO)_2S\leqslant^{O}_{O}$, for sulphones, symmetrical and unsymmetrical sulphites, and sulphates, respectively. Analogously, increase in the valency of phosphorus has a still more pronouncedly diminishing effect on the atomic refraction than in the case of sulphur, which more than compensates the increment due to the addition of an atom of oxygen or sulphur. On the basis of optical examination, the constitution $HP(:O):(OEt)_2$ is assigned to diethyl phosphite. The decrement due to the passage of nitrogen from the

tervalent to the quinquevalent stage is not quite sufficient to counteract the effect of the addition of an oxygen atom. Comparison of the optical properties of hydrogen peroxide, ethyl peroxide, and ethyl ether indicates that a similar constitution is to be assigned to the two former substances and that a multiple (probably triple) linking exists between the oxygen atoms.

The following data, among others, are recorded: methyl sulphide, b. p. 37·2°/758 mm., d_4^{20} 0·8449, $n_{He}^{17\cdot3}$ 1·43605; ethyl sulphide, b. p. 91·9°/760 mm., d_4^{20} 0·8378, $n_{He}^{16\cdot3}$ 1·44368; *n*-propyl sulphide, b. p. 140°/745 mm., d_4^{20} 0·8386, $n_{He}^{17\cdot6}$ 1·44920; dimethyl sulphoxide, m. p. 8°, d_4^{20} 1·1014, $n_{He}^{19\cdot7}$ 1·47699; diethyl sulphoxide, m. p. 15°, d_4^{20} 1·0107, $n_{He}^{16\cdot9}$ 1·47011; di-*n*-propyl sulphoxide, m. p. 18°, d_4^{20} 0·9654, $n_{He}^{25\cdot8}$ 1·46341; dimethyl sulphone, m. p. 109°, b. p. 233·5°/750 mm., d_4^{10} 1·1702, $n_{He}^{110\cdot1}$ 1·41337; diethyl sulphone, m. p. 72°, b. p. 246°/755 mm., d_4^{100} 1·0573, $n_{He}^{100\cdot2}$ 1·42225; di-*n*-propyl sulphone, m. p. 29·5°, d_4^{100} 0·9858, d_4^{20} 1·0278, $n_{He}^{100\cdot2}$ 1·42205; unsymmetrical dimethyl sulphite, b. p. 203°/750 mm., 110°/13 mm., d_4^{20} 1·2943, $n_{He}^{17\cdot2}$ 1·41327; unsymmetrical diethyl sulphite, b. p. 207°/745 mm., d_4^{20} 1·1508, n_{He}^{16} 1·42298; *unsymmetrical di*-n-*propyl sulphite*, b. p. 229°/745 mm., 117°/11 mm., d_4^{20} 1·0715, $n_{He}^{15\cdot5}$ 1·42870; dimethyl sulphite, b. p. 121·5°/755 mm., 26°/12 mm., d_4^{20} 1·2129, n_{He}^{13} 1·41157; diethyl sulphite, b. p. 155·2°/748 mm., 57°/13 mm., d_4^{20} 1·0831, $n_{He}^{17\cdot4}$ 1·41517; di-*n*-propyl sulphite, b. p. 194°/750 mm., 84°/18 mm., 77°/14 mm., d_4^{20} 1·0296, $n_{He}^{15\cdot5}$ 1·42528; dimethyl sulphate, b. p. 88·8°/27 mm., 82·8°/19 mm., d_4^{20} 1·3256, $n_{He}^{15\cdot8}$ 1·38771; diethyl sulphate, b. p. 101·2°/19 mm., 95·5°/13 mm., d_4^{20} 1·1785, $n_{He}^{16\cdot1}$ 1·40315; di-*n*-propyl sulphate, b. p. 121°/20 mm., 115°/16 mm., d_4^{20} 1·1064, $n_{He}^{16\cdot0}$ 1·41547; triethyl phosphate, b. p. 214°/745 mm., d_4^{20} 1·0702, $n_{He}^{17\cdot8}$ 1·40543; triethyl thiophosphate, b. p. 95·5°/12 mm., d_4^{20} 1·1132, $n_{He}^{17\cdot3}$ 1·45611; triethyl phosphite, b. p. 48·2°/12 mm., d_4^{20} 0·9612, $n_{He}^{19\cdot1}$ 1·41189; diethyl phosphite, b. p. 72—73°/9 mm., d_4^{20} 1·0728, $n_{He}^{18\cdot4}$ 1·40751; ethyl nitrite, b. p. 17°/752 mm., $d_4^{15\cdot5}$ 0·9009, $n_{He}^{8\cdot8}$ 1·34508; ethyl ether, b. p. 34·4°/750 mm., d_4^{20} 0·7166, $n_{He}^{18\cdot2}$ 1·35374; ethyl peroxide, b. p. 64·2°/749 mm., d_4^{20} 0·8235, $n_{He}^{19\cdot3}$ 1·36853. H. WREN.

Molecular structure of methane. V. GUILLEMIN, jun. (Ann. Physik, 1926, [iv], **81**, 173—204).—Cooley's observations on the band-spectrum of methane (Astrophys. J., 1925, **62**, 13) show that the intense bands at 3·3 and 7·7 μ exhibit line separations of 9·77 cm.$^{-1}$ and 5·51 cm.$^{-1}$ in their fine structure. The existence of two values for the moment of inertia does not support the tetrahedral model for methane, but can be shown to be consistent with a pyramidal model. Although stereochemistry requires in general a tetrahedral symmetry for the carbon linkings, exceptions have been noted, notably as a result of the *X*-ray investigation of pentaerythritol (Mark and Weissenberg, A., 1923, i, 1055; cf. this vol., 227). No evidence is forthcoming that methane is not also an exception, even if the relative stability of the two models does not preclude ready transformation of the tetrahedral to the pyramidal arrangement when the hydrogen atoms are replaced by more complex groups. Analogy with hydrofluoric acid, water, and ammonia indicates that just as the molecule of the last is best regarded as consisting of a pyramid (with the nitrogen atom at the apex and hydrogen atoms occupying the corners of a triangular base), so also that of methane may be regarded as a pyramid on a quadrilateral base, with the carbon atom at the apex. A successful model for methane is advanced which is in agreement with the observed fine structure of the infra-red bands. On the view that a molecule consists of point-charges and dipoles, the shape, size, polarisability, and potential energy are calculated, and good agreement is obtained with data from other sources. A second method of testing the views advanced leads to a zero value for the permanent dipole of the molecule. When the theoretical treatment is extended to the tetrahedral model, the results afford unequivocal support to the pyramidal model.

R. A. MORTON.

Molecular structure of methane. D. DENNISON (Physical Rev., 1925, [ii], **25**, 108—109).—The normal methane molecule possesses an electronic angular momentum of $\frac{1}{2}(h/2\pi)$. A. A. ELDRIDGE.

Element 61 [illinium]. C. J. LAPP, R. A. ROGERS, and B. S. HOPKINS (Physical Rev., 1925, [ii], **25**, 106—107).—An examination of the *L*-series *X*-ray lines from carefully purified samples of rare earths revealed a single very faint line which might be *Lα* 61. The element 61 could not have been present in quantities greater than 1 in 2000.

A. A. ELDRIDGE.

[*X*-Ray spectrum of] element 61 [illinium]. L. ROLLA and L. FERNANDES (Gazzetta, 1926, **56**, 435—436).—A preliminary notice of work on the *K*-absorption spectrum of this element.

E. W. WIGNALL.

***X*-Ray analysis of certain alloys.** W. C. PHEBUS and F. C. BLAKE (Physical Rev., 1925, [ii]. **25**, 107).—Aluminium and zinc (0—20%) form solid solutions, the aluminium lattice decreasing from 4·0435 to 4·0345 Å.; for 20—95% Zn, the diffraction patterns of both components are superimposed. No compounds were observed. Lead and tin (0—3·6%) form solid solutions, the lead lattice decreasing from 4·942 to 4·931 Å.; for 10—95% Sn, both lattices were present. No compounds were observed. Nickel and chromium (up to 60%) form solid solutions, the nickel lattice increasing from 3·521 to 3·576 Å.; unlike the zinc and tin lattices, the aluminium and nickel lattices were distorted proportionally to the atomic percentages of added solute. The following data are recorded: aluminium, face-centred cubic; zinc, hexagonal close-packed, a=2·664, c=1·850 Å.; lead, face-centred cubic; tin, diamond tetragonal, a=8·235, c=3·165 Å.; chromium, body-centred cubic, a=2·875 Å.; nickel, face-centred cubic, a=3·521 Å. A. A. ELDRIDGE.

***X*-Ray study of some structural modifications of long-chain compounds.** S. H. PIPER, T. MALKIN, and H. E. AUSTIN (J.C.S., 1926, 2310—2318).—*X*-Ray measurements show that the higher members of the fatty acid series exist in two forms, each having its characteristic chain, and that palmitic and stearic acids have yet a third form. The longer form of chain appears in the true single crystal. Both

chains give planar spacings which are proportional to the number of carbon atoms in the molecule. The longer chain is always converted into the shorter when the acid is fused, but there is no change in m. p. Measurements of the long spacings must be used with caution for purposes of identification, since not only may the crystals exist in two or more forms, but also in many cases they are easily distorted by treatment in mounting and by the presence of impurity. This is especially the case if the impurity is of a similar nature and has nearly the same number of carbon atoms in the molecule. R. A. MORTON.

X-Ray analysis of the systems tungsten–carbon and molybdenum–carbon. A. WESTGREN and G. PHRAGMÉN (Z. anorg. Chem., 1926, **156**, 27—36).—Powdered tungsten and molybdenum were intimately mixed with fine Acheson graphite in different proportions, heated for 10 min. at 2000° in a carbon tube vacuum oven, the resulting sintered mass was finely powdered and again heated. This process was repeated twice and the alloys so obtained were subjected to *X*-ray analysis by the powder method.

Tungsten forms two intermediate phases with carbon, of which one contains somewhat more than 30 at.-% of carbon; a similar phase arises with molybdenum. This phase is probably a solid solution of carbon in molybdenum or tungsten and may be analogous to the carbon-containing γ-iron. The carbon content of a molybdenum–carbon phase of this type is variable within narrow limits.

In the tungsten–carbon system, there is also a 50 at.-% carbon-containing phase. The tungsten atoms are arranged in a simple hexagonal lattice with the carbon atoms probably interspersed in the free space between them. The side of the base surface of the elementary prism is 2·901 Å., height 2·830 Å. (mean error about 0·003 Å.), and axial ratio 0·975. This is probably the WC phase; if it has this chemical constitution, it must have trigonal symmetry, and the co-ordinates of the carbon atoms in the elementary prism are probably $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$. M. CARLTON.

Chemistry of metal systems [copper or silver with zinc, aluminium, or tin]. A. WESTGREN and G. PHRAGMÉN (Z. Metallk., 1926, **18**, 279—284).—Examination of copper–tin alloys by *X*-ray methods shows that at least three different lattices are present according to the composition. Alloys containing about 20 at.-% Sn have a face-centred cubic lattice (a=17·91 Å.), those containing about 25 at.-% Sn a hexagonal prism lattice (a=2·755, c=4·319 Å.; $a:c$=1 : 1·568), and finally alloys containing about 15 at.-% Sn have at temperatures above 500° a complex structure which appears to consist of two concentric cubes. Corresponding structures have been found already in copper–zinc and copper–aluminium alloys, but the results are not strictly analogous, for the unit cubic lattice in these two cases has only half the parameter of the copper–tin lattice, the copper–zinc lattice is body-centred, and the copper–aluminium a simple cube. The copper–zinc series between 80 and 86 at.-% Zn has a hexagonal lattice of similar structure to that occurring in the copper–tin series, and both the zinc and aluminium series at certain compositions exhibit the concentric cube structure at high temperatures. Similar analogies are found in the silver alloys with zinc, aluminium, and tin; *e.g.*, those containing, respectively, 39·5, 89·9, and 80·7% Ag have hexagonal close-packed lattices, the respective $a:c$ ratios of which are 1 : 1·578, 1 : 1·612, and 1 : 1·630. Thus, in both copper and silver alloys the areas of similar structure are closer to the copper or silver side of the binary diagram the higher the valency of the alloying element. A. R. POWELL.

Crystal structure of meteoric iron as determined by *X*-ray analysis. J. YOUNG (Proc. Roy. Soc., 1926, **A**, **112**, 630—641).—Crystals of kamacite are body-centred cubic, with parameter 2·870 Å., whilst taenite crystals are face-centred and have the parameter 3·590 Å. In the Widmanstätten structure, the (110) planes of the former are parallel to the (111) planes of the latter, and the structure of plessite is the same. The origin of the Widmanstätten structure is discussed from the point of view of these observations. R. CUTHILL.

Structure of γ-brass. A. J. BRADLEY and J. THEWLIS (Proc. Roy. Soc., 1926, **A**, **112**, 678—692).—It is shown from the data of Westgren and Phragmén (A., 1925, ii, 746) that the crystal structure of γ-brass is very nearly body-centred cubic, 1 atom in 27 being removed and the remaining atoms slightly displaced, but in such a manner as to preserve the cubic symmetry. Each unit cell contains 20 copper atoms and 32 zinc atoms, the interatomic distances being about 2·6 Å. The formula is Cu_5Zn_8, not Cu_4Zn_9, as Westgren and Phragmén suggested. The formulæ given by these authors for γ-Ag–Zn and γ-Au–Zn, which are constituted similarly to γ-brass, are incorrect, and should be Ag_5Zn_8 and Au_5Zn_8, respectively. R. CUTHILL.

***X*-Ray investigation of albumin crystals.** E. OTT (Koll.-Chem. Beih., 1926, **23**, 108—110).—The reasons why various crystalline substances appear from their *X*-ray spectrograms to be amorphous are discussed. A suspension of albumin crystals in about half-saturated ammonium sulphate solution contained in a thin-walled collodion tube gives a line spectrogram characteristic of small crystals if the camera is kept saturated with water vapour. The diagram obtained is quite different from that for pure ammonium sulphate, although the salt appears to be necessary for the crystallisation of the albumin.
L. L. BIRCUMSHAW.

Crystal structure of sodium periodate. L. M. KIRKPATRICK and R. G. DICKINSON (J. Amer. Chem. Soc., 1926, **48**, 2327—2334).—Tetragonal sodium periodate (d 4·12) is not holohedral, but tetragonal bipyramidal. The space-group symmetry is C_{4h}^6; the unit cell contains 4 mols., d_{100}=5·322, d_{001}=11·93 Å. The sodium and iodine atoms form two interpenetrating diamond lattices; each iodine atom is surrounded by four equidistant oxygen atoms at the corners of a tetragonal bisphenoid. All the bisphenoids are alike, but half of them are rotated 90° about a vertical axis from the position of the other half. The formula $Na_2I_2O_8$ for solid sodium periodate is not justified by this structure. The results support

the presumption that periodates, tungstates, and molybdates are structurally very similar.
S. K. TWEEDY.

Oxides and hydroxides of cobalt. II. Crystalline structure of the saline oxide of cobalt. G. NATTA and F. SCHMID (Atti R. Accad. Lincei, 1926, [vi], **4**, 145—149).—The oxide Co_3O_4 crystallises in the monometric system, isomorphous with magnetite. The elementary cell of the crystal lattice, of the spinel type, has the side 8·02 Å. and contains 8 mols. The calculated density is 6·21, almost identical with the highest of the somewhat discordant published values.
T. H. POPE.

Stannic acids. E. POSNJAK (J. Physical Chem., 1926, **30**, 1073—1077; cf. Weiser, A., 1922, ii, 853).—The X-ray spectra of α- and β-stannic acids are identical with the spectrum of crystalline stannic oxide. The spectra are rather weak and consist of broad, diffuse lines, the lines from α-stannic acid being the wider, indicating a greater fineness of particles. The results confirm the conclusions of Mecklenburg (A., 1912, ii, 355) on the colloidal nature of these acids. The work of Willstätter, Kraut, and Fremery (A., 1924, ii, 266) is adversely criticised.
L. S. THEOBALD.

Crystalline nature of a sputtered tellurium film. L. P. SIEG (Physical Rev., 1925, [ii], **25**, 116).—The film probably consists of crystals, few or many in number, with some definite orientations predominating.
A. A. ELDRIDGE.

Anomalous optical properties of some new series of isomorphous double tartrates. H. E. BUCKLEY (Min. Mag., 1926, **21**, 55—72).—In addition to the mixed crystals $\{m\text{NaK},n\text{Na(NH}_4)\}\text{C}_4\text{H}_4\text{O}_6,4\text{H}_2\text{O}$, previously examined (*ibid.*, 1924, **20**, 159), optical anomalies of the same kind have now been determined for the series $\{m\text{KNa},n\text{K(NH}_4)\}\text{C}_4\text{H}_4\text{O}_6,4\text{H}_2\text{O}$ and $\{m\text{(NH}_4)\text{Na},n\text{(NH}_4)\text{K}\}\text{C}_4\text{H}_4\text{O}_6,4\text{H}_2\text{O}$. All these crystals are orthorhombic and isomorphous, but when freshly prepared they show crossed dispersion characteristic of monoclinic crystals (borax type). On keeping, the crystals show a slow change in the size of optic axial angles and in position of the optic axial planes for different colours; and finally, after a lapse of some time, they settle down with all the optic axial planes lying in the plane (100) or (010) or in both, giving in the last case crossed axial-plane dispersion of the orthorhombic (brookite) type. This change is hastened by rise in temperature and retarded by pressure. Sections from the outer and inner portions of the crystals showed a difference, evidently due to the time taken for growth; but in the final state they are identical, suggesting that the crystals are homogeneous. Other isomorphous series of mixed crystals each containing only two of the three bases, viz., $\{m\text{Na}_2,n\text{Na(NH}_4)\}$, $\{m\text{(NH}_4)_2,n\text{(NH}_4)\text{Na}\}$, $\{m\text{Na}_2,n\text{NaK}\}$, and $\{m\text{K}_2,n\text{NaK}\}$, showed, in the range of the visible spectrum, the optic axial planes all in one plane, but with wide differences in the optic axial angle.
L. J. SPENCER.

Symmetry of sylvine and the nature of the etching figures. J. J. P. VALETON (Z. Physik, 1926, **39**, 69—74; cf. this vol., 889).—The conclusion of Herzfeld and Hettich (*loc. cit.*) that sylvine is holohedral, and the asymmetry of its etching figures due to adsorption of organic matter, is criticised. The symmetry of the etching figures is not necessarily inconsistent with plagihedral–hemihedral character. It is also difficult to understand why the presence of the impurity should cause one half of crystal faces, presumed to be of equal value to the other half, to be influenced in a totally different manner. If they are influenced differently they are not physically equivalent and the substance is not holohedral. The evidence in favour of holohedry from X-ray data still remains unexplained.
E. B. LUDLAM.

Magnetisation curves of single crystals of iron. W. GERLACH (Z. Physik, 1926, **38**, 828—840).—Magnetic measurements were made on single crystals of iron of which the largest was 12 cm. long and 4 mm. thick. The general conclusion was reached that the abnormal magnetic behaviour was not a consequence of crystal form as such, but of the development of ideal elementary magnets accompanying ideal crystal development. Compared with the original material, electrolytic iron, the single crystal had a very narrow hysteresis surface, very low remanence and coercive force. Suddenly switching off the current gave less remanence than when the magnetising current was slowly reduced. Repeated bending of the crystal made it hard and greatly increased the remanence. A wire consisting of polycrystals behaved similarly; heating in a Bunsen burner restored it to its former condition. In non-crystalline iron, the elementary magnets are absent until they are produced by the applied magnetic field. The magnetisation curves obtained with ordinary iron are the result of the iron being present in both states, the one with, the other without the elementary magnets.
E. B. LUDLAM.

Relation between fine-structure and optical anomalies. F. RINNE (Koll.-Chem. Beih., 1926, **23**, 348—354).—A discussion of the author's views, especially in regard to the mineral milarite. The causes of strain in crystals are considered under two groups.
E. S. HEDGES.

Plastic deformation of single metallic crystals. W. E. W. MILLINGTON and F. C. THOMPSON (Nature, 1926, **118**, 409—410).—Polemical (cf. Wright, this vol., 783; Goucher, *ibid.*, 891).
A. A. ELDRIDGE.

Deformation lines in large and small crystals of ferrite. H. O'NEILL (J. Iron and Steel Inst., 1926, **113**, 417—445).—See this vol., 564.

Relation between lattice-constant and density of iron–nickel alloys. A. ÔSAWA (J. Iron and Steel Inst., 1926, **113**, 447—456; Sci. Rep. Tôhoku Imp. Univ., 1926, [i], **15**, 387—398).—See this vol., 564.

Tensile tests of large gold, silver, and copper crystals. C. F. ELAM (Proc. Roy. Soc., 1926, **A**, **112**, 289—296).—The crystals were prepared by melting rods of the metal in graphite tubes 0·25 inch in diameter and 10 inches in length, tapered at one end. The tubes were slowly lowered through an electric furnace, the middle portion being maintained

at 100° above the m. p. of the metal in a neutral atmosphere. Tensile tests were carried out with these crystals, the crystal axes being determined at each stage, and by the method described in a previous paper (A., 1925, ii, 488) the positions of the axis of the test-piece in reference to the crystal axes were plotted for each extension on the stereographic diagram. The main direction of the movement of the axes closely resembles that found for aluminium, and it is assumed that the distortion of these metal crystals is of the same type. The slip plane and direction of slip were deduced, and the tangential component of shear stress, S, was calculated for each extension. The curves showing the relationship of S to the ratio of the extended to the initial length of specimens of gold, silver, copper, and aluminium indicate that, although the aluminium hardens more rapidly at first than the gold or silver, it finally becomes the weakest; similarly, the gold is stronger at first than the silver, but finally is weaker. The hardening is not merely due to bending and breaking up of the crystals during the slipping process, but some specific property of the metal is concerned. L. L. BIRCUMSHAW.

Surface energy of the alkali halides. J. BIEMÜLLER (Z. Physik, 1926, **38**, 759—771).—The specific surface energy is defined as the energy necessary to separate slowly the two halves of a crystal that is regarded as cut along a plane of symmetry. In consequence of the lack of symmetry of the forces in the surface, this becomes polarised and the ions become distorted by the forces which previously held the two halves of the crystal together. These forces are calculated and the surface energy is deduced. Satisfactory agreement is obtained between the theoretical and experimental values for the capillarity constant of the fused salt, the temperature coefficient of the surface energy of the crystal right up to the m. p. being very small. E. B. LUDLAM.

Mol. wts. of proteins in phenol. E. J. COHN and J. B. CONANT (Z. physiol. Chem., 1926, **159**, 93—101).—See this vol., 891.

Interpretation of deviations from Ohm's law. K. T. COMPTON (Proc. Nat. Acad. Sci., 1926, **12**, 548—551).—Two theories of metallic conduction are examined in the light of the deviations from Ohm's law observed by Bridgman for thin films of gold and silver (*ibid.*, 1921, **7**, 299). The experimental data definitely disprove Thomson's doublet theory, but are consistent with the free electron theory. A. B. MANNING.

Measurements by the help of liquid helium. Resistance of gold, silver, zinc, cadmium, platinum, nickel, and iron down to 1·3° Abs. W. MEISSNER (Z. Physik, 1926, **38**, 647—658; cf. A., 1925, ii, 1135).—The resistance of wires and of single crystals of these metals was determined at various temperatures down to 1·3° Abs. (2 mm. pressure of helium). Although the metals were very pure, none of them showed super-conductivity; for cadmium, special purity from lead appeared to have the opposite effect, preventing super-conductivity. Apparently super-conductivity is a property of a particular group of metals. For all the metals, a change in conductivity was measurable between 1·34° and 4·2° Abs., the order of magnitude indicating that they were not in the region of super-conductivity. For single crystals, no maximum was observed for the ratio of the resistances parallel and perpendicular to the crystal axis. E. B. LUDLAM.

Super-conducting state of copper. W. P. DAVEY (Physical Rev., 1925, [ii], **25**, 248).—The specific conductivity at 20° along the cubic axis of single-crystal copper is $0{\cdot}662\times10^6$ ohms per c.c.; after polycrystallisation and annealing, the value is $0{\cdot}584\times10^6$. That of ordinary annealed polycrystal copper is $0{\cdot}578\times10^6$. A. A. ELDRIDGE.

Specific resistance and thermo-electric potentials of some steels differing only in carbon content. E. D. CAMPBELL and H. W. MOHR (J. Iron and Steel Inst., 1926, **113**, 375—392).—See this vol., 566.

Magnetic changes in iron and steel below 400°. W. H. DEARDEN and C. BENEDICKS (J. Iron and Steel Inst., 1926, **113**, 393—416).—See this vol., 566.

Influence of a constant magnetic field on the magnetic spectrum. W. K. MITIAEV (Z. Physik, 1926, **38**, 716—726).—The magnetic permeability of iron wire in a constant magnetic field of 600 gauss is reduced for electromagnetic waves of length 55—114 metres. E. B. LUDLAM.

Magnetic susceptibility of gases. Dependence on temperature and pressure. E. LEHRER (Ann. Physik, 1926, [iv], **81**, 229—261).—The magnetic susceptibility has been determined for the following gases (absolute values $\times10^{-6}$): oxygen, 104·4; air, $24{\cdot}1_6$; carbon dioxide, $-0{\cdot}47_4$; argon, $-0{\cdot}50_4$; hydrogen, $-2{\cdot}5_2$ (cf. Soné, A., 1920, ii, 222; Wills and Hector, A., 1924, ii, 293, 854). The Curie law has been tested by means of the constant $\Delta p(1/T_2^2-1/T_1^2)$ and found to be valid within the limits of accuracy. The deviations from the mean value of the constant for a particular gas exceed $\pm2\%$ only with hydrogen ($\pm5{\cdot}4\%$). The differences in the volume-susceptibility brought about by temperature changes are proportional to the pressure over the range 60—720 mm. An anomalous result recorded by Glaser (A., 1925, ii, 82, 642) for diamagnetic gases is not confirmed. The Wiedemann mixture law is valid for gases. R. A. MORTON.

Are gaseous molecules oriented? K. S. KRISHNAN (Proc. Indian Assoc. Cult. Sci., 1926, **10**, 35—44).—No change in the refractive index of a diamagnetic gas in a magnetic field, when examined by an interference method, has been observed; when the gas is placed between two crossed Nicols, there is no restoration of light in the field; the depolarisation of the transversely scattered light does not change in the magnetic field. These results suggest that the change with pressure of the susceptibilities of diamagnetic gases cannot be explained by Glaser's theory of the orientation of the molecules in a magnetic field (A., 1925, ii, 82; Physikal. Z., 1925, **26**, 212; this vol., 230). M. S. BURR.

Effect of light on the thermo-electric power of selenium. R. M. HOLMES (Physical Rev., 1925, [ii], **25**, 250).—Light decreases the thermo-electric

power of grey, crystalline selenium by about 5% and increases the conductivity by about 700% of the dark value. The results could be interpreted if light increases the interatomic space occupied by conducting electrons. A. A. ELDRIDGE.

Thermal conductivity of lithium and sodium by a modification of the Forbes bar method. C. C. BIDWELL (Physical Rev., 1926, [ii], **28**, 584—597).—Values of k are given for lithium at 16 temperatures between 23° and 423° Abs., and for sodium at 12 temperatures between 33° and 348° Abs. Values at 0° are 0·155 and 0·335, and at 20°, 0·149 and 0·300, respectively. The specific heats, determined from the cooling curves, agree with existing measurements. It is suggested that the excess specific heat over the Dulong–Petit maximum is heat required for the disintegration of the crystal lattice. A. A. ELDRIDGE.

Heat capacity of calcium silicate [pseudowollastonite]. G. S. PARKS and K. K. KELLEY (J. Physical Chem., 1926, **30**, 1175—1178).—The heat capacities of the pseudo-wollastonite used by White (A., 1919, ii, 133) have been measured between 88° and 298° Abs. Above 200° Abs., Kopp's molecular heat law holds for this silicate as well as for that of magnesium. L. S. THEOBALD.

M.-p. curve of arsenious oxide. G. TAMMANN and G. BÄTZ (Z. anorg. Chem., 1926, **156**, 94—98).—The m. p. of arsenious oxide, octahedral crystals, and vitreous modifications has been studied. Results are tabulated and the graph temperature–log pressure has been drawn. Results of previous investigators are discussed with reference to those now obtained. M. CARLTON.

Additivity of the m. p. of compounds. H. CARLSOHN (Ber., 1926, **59**, [*B*], 1916—1922; cf. Hantzsch and Carlsohn, A., 1925, ii, 1043).—Of two hundred and seventy intermetallic compounds examined, forty obey the m.-p. rule (*loc. cit.*). Additivity is not observed with about forty compounds of the alkali metals, and boron, selenium, tellurium, arsenic, bismuth, and mercury do not appear to yield compounds conforming to the law. The tendency of a metal to give an intermetallic compound of which the m. p. can be calculated additively appears to be related to its ability to form complex compounds. H. WREN.

Volatility of organic compounds. H. HERBST (Koll.-Chem. Beih., 1926, **23**, 313—344).—A formula is developed for the volatility of a liquid: $F_t = Mp_t \times 10^6/760v_t$, where, at a temperature t, F_t is the volatility of the liquid, M the mol. wt. in g., p_t the vapour pressure of the saturated vapour in mm., and v_t the mol. vol. Methods for determining p_t both by experiment and from theoretical considerations are reviewed fully. E. S. HEDGES.

Spontaneous ignition temperatures of inflammable liquids and the effect of water on them. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1926, **2**, 219—220).—Moore's method of determining spontaneous ignition temperatures (J.S.C.I., 1917, **36**, 109; 1920, **39**, 36R) has been slightly improved and applied to acetone, ether, and a variety of alcohols and hydrocarbons. Of these, ether and the paraffin hydrocarbons possess much the lowest spontaneous ignition temperatures. With ethyl alcohol and n-propyl alcohol, these temperatures are raised considerably by water, whereas with ether water has little effect. R. CUTHILL.

Latent heat of fusion of some metals. J. H. AWBERY and E. GRIFFITHS (Proc. Physical Soc., 1926, **38**, 378—398).—Latent heats of fusion were determined by measuring, by the method of mixtures, the total heat of liquid and solid from a series of initial high temperatures. The following values were obtained: aluminium, 92·4; antimony, 24·3; bismuth, 13·0; lead, 6·26; magnesium, 46·5; tin, 14·6; zinc, 26·6 cal. per g. The results also provide data for the specific heats. A. GEAKE.

Latent heats of vaporisation of ethyl and methyl chlorides. G. W. C. YATES (Phil. Mag., 1926, [vii], **2**, 817—826).—The latent heats of vaporisation of ethyl and methyl chlorides have been determined, by an electrical method, over the range 10—30°. For the former, $l_t = (93·1 - 0·06t)$ cal./g.; for the latter, $l_t = (97·7 - 0·13t)$ cal./g. The results are in fair agreement with those of Regnault and others. A. E. MITCHELL.

Alternation in the heats of crystallisation of the normal monobasic fatty acids. II. W. E. GARNER, F. C. MADDEN, and J. E. RUSHBROOKE (J.C.S., 1926, 2491—2502).—The heats of crystallisation of hexoic, heptoic, tridecoic, myristic, pentadecoic, palmitic, and eicosoic acids have been determined. A marked alternation is shown as the series is ascended. Above decoic acid, the heat of crystallisation of the even acids is given by the equation $Q = -3·61 + 1·030n$, where n is the number of carbon atoms in the chain. An equation is derived statistically for the m. p. of these acids. Similar equations have been derived for the odd acids. The arrangement of the methylene groups is concluded to be the same for both the odd and the even acids in the solid state. The convergence temperature for the monobasic acids is 115°, in agreement with that for the dibasic acids. The heat of crystallisation of the terminal methyl and carboxyl groups changes from a positive to a negative value as the number of carbon atoms changes from 2 to 10. The heat of transition of the α- to the β-form of the odd acids is erratic, owing very possibly to the presence of water. R. A. MORTON.

Distribution of thermal energy in organic molecules. D. H. ANDREWS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 744—753).—The heat capacity of organic compounds in the solid state is accounted for fairly satisfactorily by assuming it to be due to vibrations of the molecule and of the constituent atoms and to an expansion effect; each mode of vibration is assumed to act as a simple Planck oscillator. The individual items are evaluated for benzene and quinol for temperatures from 10° Abs. to the m. p., and their sums agree approximately with the experimental values. A. GEAKE.

Chemical constants of the halogen hydrides. F. I. G. RAWLINS (Trans. Faraday Soc., 1926, **22**, 233—240).—The chemical constants (i) of the halogen

hydrides are deduced from the vapour-pressure equations for the equilibrium (Halogen hydride)$_{\text{diatomic}}$ $\rightleftharpoons$ (Halogen hydride)$_{\text{solid}}$+λ. The equation obtained is $\log p = -\lambda_0/4{\cdot}571T + 3{\cdot}5 \log T - \log [1-e^{-h\nu_0/kT}] - \frac{1}{4{\cdot}571}\int_0^T dT/T^2 \int_0^T C_k dT + i$, where C_k is the molecular heat of the solid at constant pressure. The method involves the following assumptions: (*a*) that since ν_0 is large, the Planck term can be omitted, (*b*) that the rotations of the diatomic molecules are fully excited, (*c*) that ν from the Lindemann m.-p. equation corresponds with Debye's $\nu_{max.}$, (*d*) that one frequency gives the specific-heat curve for binary compounds, (*e*) that the Debye function is applicable to these simple diatomic substances, (*f*) that the difference $(C_k - C_v)$ for the solid can be neglected. The following values are obtained for i: −0·585, +0·590, and +0·780 for hydrogen chloride, bromide, and iodide, respectively. The last two values are in good agreement with the experimental values of Eucken (A., 1924, ii, 820), but all differ considerably from those deduced on the Ehrenfest statistical theory (A., 1920, ii, 738).

W. HUME-ROTHERY.

Germanium. XIV. Germanium tetrachloride. A. W. LAUBENGAYER and D. L. TABERN (J. Physical Chem., 1926, **30**, 1047—1048).—Germanium tetrachloride prepared by the method of Tabern, Orndorff, and Dennis (A., 1925, i, 1108) and by a modification of that of Dennis and Hance (A., 1922, ii, 302) has a vapour pressure at 0° of 24·3 mm., b. p. 83·2°/760 mm., m. p. −50°, d_{20}^{20} 1·879, and R_L 31·465. No decomposition of the tetrachloride was observed during slow heating to 950°. L. S. THEOBALD.

Vapour pressure of sulphur monochloride. E. H. HARVEY and H. A. SCHUETTE (J. Amer. Chem. Soc., 1926, **48**, 2065—2068).—The vapour pressure of sulphur monochloride between 0° and the b. p. (138°) is given by $\log_{10} p$ (mm.) = 7·4550 − (1880·1/T), from which the latent heat of evaporation is calculated to be 63 cal./g., and the molecular b.-p. elevation 52·9°/100 g. (cf. Orndorff and Terrasse, A., 1896, ii, 357). Other physical constants are recorded. Sulphur monochloride is a stable, well-defined compound up to its b. p. S. K. TWEEDY.

Dependence of the vacuum obtainable by means of a diffusion pump on the purity of the mercury vapour. W. MOLTHAN (Z. Physik, 1926, **39**, 1—5).—A small quantity of air or hydrogen, respectively, was allowed to enter the vacuum produced by a three-stage mercury pump and the degree of exhaustion measured by means of a large McLeod gauge. The limiting vacuum is that of the partial pressure of the admixed gas, a result in agreement with the theory that diffusion is the true explanation of the action of the pump, not an "injection" effect, parallel-stream condensation effect, etc.

E. B. LUDLAM.

Relation between the temperature and energy of a gas. E. WERTHEIMER (Z. Physik, 1926, **38**, 675—705; cf. A., 1925, ii, 784).—The collision between a molecule and the walls of a vessel is not merely an elastic process, but is also electrodynamical. For low-pressure gas in a state of equilibrium, the radiation energy $U = aT^4 + T \cdot \varphi(v)$.

E. B. LUDLAM.

Measurement of coefficients of expansion at low temperatures. Some thermodynamic applications of expansion data. R. M. BUFFINGTON and W. M. LATIMER (J. Amer. Chem. Soc., 1926, **48**, 2305—2319).—The coefficients of expansion, α, at low temperatures (about 80—300° Abs.) of aluminium, copper, silver, rock salt, "Pyrex" glass, and quartz (parallel to the optic axis) were measured by Fizeau's method. The results with "Pyrex" glass were not reproducible, probably because of lag in expansion. The following equation represents the results for quartz between 170° and 310° Abs.: $\alpha = (0{\cdot}1304 + 0{\cdot}002111T) \times 10^{-5}$. The values of α approach zero at low temperatures; they change slightly more rapidly with temperature than the specific heats. With the aid of Grüneisen's expression for the vibration frequency of a solid, terms representing the constraints between the atoms are introduced into the entropy equation for solids (Latimer, A., 1921, ii, 380), whence the equation: $S_p^{298} = 3/2 \cdot R \log M + R \log V - 3/2 \cdot R \log (C_p/3\alpha)_{T=160} + 26{\cdot}5$ is obtained, which, when applied in its generic form to a perfect monatomic gas, reduces to Sackur's entropy equation. The equation is applied satisfactorily to six metals and is extended so as to apply to binary compounds.

S. K. TWEEDY.

Coefficient of expansion and free space. W. HERZ (Z. Elektrochem., 1926, **32**, 460—462).—Defining the coefficient of expansion as: $\alpha = (d - d_1)/d_1(T_1 - T)$, where d and d_1 are densities at two neighbouring absolute temperatures T and T_1, it is found that for many liquids of various types the increase of α with temperature is such that the ratio V_f/α, where V_f = the free space (cf. this vol., 670), remains nearly constant over a wide range of temperature, but decreases somewhat as the critical temperature is approached. With water, however, approximate constancy of V_f/α is attained only at relatively high temperatures.

H. J. T. ELLINGHAM.

Equation of state of solid substances etc. in connexion with the general expression for the energy and the entropy. Simple derivation of the so-called entropy constant. J. J. VAN LAAR (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 683—698).—Mathematical. A. GEAKE.

Natural series of substances according to their cohesive power. V. KIREJEV (Z. anorg. Chem., 1926, **155**, 121—129).—Experimental data for the function $p(dT/dp)$ lead to an arrangement of substances according to their cohesive power. From this it follows that (*a*) in the co-existing vapour liquid condition the arrangement of the substances scarcely changes with change of temperature and (*b*) with this arrangement the different magnitudes (*e.g.*, Trouton's constant, critical coefficient $RT_k d_k/Mp_k$, refractive index at the critical point, law of corresponding states, etc.), to which are generally ascribed a constant value for different substances, are closely allied. For all these functions, the parallelism of the change of magnitude is established in this

series, so that van der Waals' theory relates to a limiting case in which the group of associated liquids shows systematic and parallel deviations.

M. CARLTON.

Solubility and rate of solution of oxygen in silver. E. W. R. STEACIE and F. M. G. JOHNSON (Proc. Roy. Soc., 1926, **A**, **112**, 542—558).—The solubility, Q, of oxygen in silver has been determined at intervals of 100° at temperatures between 200° and 800°, and is found to be a minimum at about 400°, above which temperature $1/Q=K(930-t)$, where t is the temperature and K is a constant depending on the pressure. The existence of this minimum solubility may be due either to a polymorphic change of the silver or to a change in the state of the dissolved oxygen. From the fact that, except at very low pressures, Q is proportional to the square root of the pressure, it would seem that the oxygen must dissociate in some way on solution. The rate of solution is related to the pressure in the same way, and can be expressed by the equation $K'=1/\tau.\{\log[S/(S-X)]-C\}$, where S is the saturation concentration, X the amount dissolved in time τ, and K' and C are constants. With increasing temperature up to 400°, C remains constant at 0·10, whilst K' increases. Between 400° and 440°, C increases and K' decreases. Above 440°, both increase. R. CUTHILL.

Reduction of weights of powders in air to weights in a vacuum. R. RUER and J. KUSCHMANN (Z. anorg. Chem., 1926, **154**, 69—78).—When cupric oxide has been previously heated at 850° and 1000°, the weight of air adsorbed is 0·00086% and 0·00056%, respectively, and when ferric oxide is heated at 1000°, the weight adsorbed is 0·00055%; these amounts are negligible, being within the errors of weighing. When ferric oxide is heated at 700°, the weight of air adsorbed is 0·0025%; to obtain the true vacuum weight, the material must be weighed in a vacuum after evacuating at a high temperature, as evacuation at the ordinary temperature does not remove the adsorbed air. A. GEAKE.

Derivation of the logarithmic rule of mixtures by the Maxwell-Rayleigh method of limits. K. LICHTENECKER (Koll.-Chem. Beih., 1926, **23**, 285—291).—Mathematical. E. S. HEDGES.

Structure of native platinum. S. F. SHEMTSCHUSHNI (Z. anorg. Chem., 1926, **156**, 99—142).—Examination of samples of native platinum from different sources shows that they do not differ structurally from metal alloys the components of which are able to form a series of solid solutions. Polyhedral structure, hatching, zoning, appearance of recrystallisation, and disintegration of solid solutions, all of which are characteristic of metal alloys which, after transition from the glowing liquid to the solid state, have crystallised and cooled more or less slowly, are observed.

The hardness of these samples is notably higher than for pure platinum, and this leads to the conclusion that native platinum consists of a solution of metals of the platinum group and of iron, sometimes with copper and nickel. The presence of well-formed crystals of osmium and iridium shows that these separated from the molten state before crystallisation of platinum, whilst air holes etc. show that the platinum was once molten. Obviously the platinum settled as solid during the cooling period of the magma in which it was dissolved. In this way, the platinum would sink through the cooling mass and act as centres of crystallisation; the small deposits grew and sank, and so started the large separation which occasionally appears in the form of very large ingots. These primary deposits fall into two groups, according as platinum separation occurred in dunite with chrome-ironstone or, in absence of this, crystallised immediately under olivine, of which dunite consists. The form of the platinum separation is different for these two types. In the latter case, the iron containing platinum would separate prior to the olivine from the molten magma. Apparently the largest ingots originate for the most part from such deposits. In deposits of the first type, where the platinum is closely linked with the chrome-ironstone, the platinum shows the greatest irregularity in form, owing to its having filled up intermediate spaces between the previously crystallised chrome-ironstone.

Geological investigations and observations of the macrostructure of platinum deposits agree in their results with those obtained by study of the microstructure and other properties of native platinum, and show that platinum contained in massive rocks is of magmatic origin. M. CARLTON.

Solubility in binary liquid mixtures. T. DISSELKAMP (Z. physikal. Chem., 1926, **123**, 99—110).—It is suggested that the dissolution of a solid in a liquid is effected by certain active molecules of the solvent withdrawing molecules of the solute from their lattice. If a second solvent is present which combines with the first, the number of these active molecules, and therefore also the solubility, will probably fall, whilst according to Dolezalek's theory the vapour pressure should decrease at the same time. If, on the other hand, admixture of the two solvents causes the dissociation of either to increase, the solubility and vapour pressure should rise. In general, therefore, the changes in solubility and in vapour pressure may be expected to run parallel. By measurements of the solubility of anthracene in binary mixtures of organic liquids, this is shown to be the case, exceptions occurring only with liquids known to be associated, where the relations are necessarily very complex. The relation between surface tension and solubility which Skirrow (A., 1902, ii, 600) and Christoff (A., 1905, ii, 806) found to exist for the solubility of gases is not valid in the present case. R. CUTHILL.

Solubility of silver oxide in mixtures of water and alcohol. S. KLOSKY and L. WOO (J. Physical Chem., 1926, **30**, 1179—1180).—The solubility of silver oxide in water–alcohol has been determined at 25° by a nephelometric method. L. S. THEOBALD.

Influence on the solubilities of salts in water of the addition of a non-electrolyte. J. MCAULAY (J. Physical Chem., 1926, **30**, 1202—1208).—Calculations of the value of the average radius of the ions of various salts in water–alcohol and water–acetone show the existence of a relation between solubility and the dielectric constant of the mixed solvent. This

relation may be used for the calculation of either dielectric constants or solubilities. Curves showing the distribution of alcohol and water in the vicinity of an ion are given. L. S. THEOBALD.

Solubility of monocalcium phosphate in water. W. STOLLENWERK (Z. anorg. Chem., 1926, **156**, 37—55; cf. Cameron and Bell, U.S. Dept. Agric. Bull., **41**, 1997).—Previous measurements have given very contradictory results (cf. Basset, Stoklasa-Versuchsstat., **38**, 197, 401; Rindell, Akad. Abh. Helsingfors, 1899). Variations in solubility are due to the previous heat treatment of the salt. Samples dried at 100° (d 2·04) dissolved in an hour, decomposition taking place only slowly. Samples dried at 130° (d 2·7) and treated similarly were undissolved after several days and were correspondingly slowly decomposed. The chemical composition of this salt is identical with that dried at 100°. An isomeric change is indicated. Experiments on the combination with ammonia using Hüttig's eudio-tensiometer (A., 1921, ii, 195) showed that monocalcium phosphate which had been heated at 100° absorbed only 0·5 mol. of ammonia at 18°. The vapour pressure could not be measured because of the non-homogeneity of the product. The salt which had been heated at 130° took up 4 mols. of ammonia at 18°; the corresponding vapour pressure was 49 mm. Isotherms indicated the formation of a diammine and a monoammine.

The values of Q deduced from Nernst's equation $\log p = -Q/4{\cdot}57T + 1{\cdot}75 \log T + \alpha T + 3{\cdot}3$, where $\alpha = -0{\cdot}0094$, were in good agreement. It is assumed that the above phenomena are due to hydrate isomerism. When the temperature is raised, the water of hydration passes into the interior of the molecule; the whole structure thus expands and the ammonia molecule is taken up more readily. Application of the law of mass action shows that the decomposition of monocalcium phosphate is a unimolecular reaction. M. CARLTON.

Traube's rule applied to phenomena of partition between two phases. A. FRUMKIN (Trans. Karpov Inst. Chem. [Russia], 1925, No. 4, 90—92).—From the work of Wroth and Reid (A., 1917, ii, 17) it follows that on transferring the group CH_2 from the body of the liquid into the space filled with vapour the forces of cohesion exerted between the molecules of the liquid produce work (W) equivalent to 350 g.-cal. From Rehbinder's results (A., 1924, ii, 662), the work (W') of absorption produced by the force of cohesion during the transfer of the group CH_2 from the solution to its surface is equivalent to 650 g.-cal. Hence $W - W' = W''$, the work necessary to transfer the CH_2 group from the surface of water into the space filled with vapour, is 300 g.-cal. Since W'' is positive, the CH_2 group is attracted by the surface of the water (cf. Adam, A., 1922, i, 424, ii, 687).

CHEMICAL ABSTRACTS.

Adsorption of mercury vapour by activated wood charcoal. N. D. ZELINSKY and M. A. RAKUSIN (Ber., 1926, **59**, [*B*], 2072—2074).—A sample of birch charcoal absorbed 5·65% of mercury when exposed to mercury vapour at the ordinary temperature. After protracted exposure to air, the charcoal retained 4·69% of mercury. H. WREN.

Adhesive forces in solutions. VII. Adsorption from dilute aqueous solutions. M. DUBININ (Z. physikal. Chem., 1926, **123**, 86—98; cf. this vol., 238).—The adsorption of various substances from aqueous solutions by activated wood charcoal at the ordinary temperature has been studied. If the amount adsorbed is plotted against the concentration of the solution in equilibrium with it, the resulting curves are, for strong electrolytes such as the halogen acids and the halides of potassium, convex to the concentration axis, and their equations differ only by a constant. With weak electrolytes and non-electrolytes, the curves are related to each other in a similar manner, but are much more nearly rectilinear. Sulphuric acid and other polybasic acids behave like the other strong electrolytes. Mixtures of hydrochloric and acetic acids give isotherms which, with increasing proportions of the former acid, change continuously from the form characteristic of weak electrolytes to that characteristic of strong electrolytes.

R. CUTHILL.

Adsorption from solution by ash-free adsorbent charcoals. II. Properties of purified adsorbent charcoals. E. J. MILLER (J. Physical Chem., 1926, **30**, 1162—1169; cf. A., 1924, ii, 664; 1925, ii, 656).—The properties of adsorbent charcoals of animal, vegetable, and carbohydrate origin, purified by the method previously described (this vol., 898), have been studied. All these charcoals after purification have the same properties of selective adsorption from solutions of electrolytes, which are also identical with those of pure, ash-free sugar charcoal. Acids, but not bases, are adsorbed, whilst salts (potassium chloride) are adsorbed hydrolytically, as also are methylene-blue and ammonium eosin (cf. Bartell and Miller, A., 1923, ii, 464). Purification of the charcoals does not affect the adsorption capacity or the fundamental nature of the adsorbent carbon. The activity of a charcoal is most easily determined in a simple manner by measuring the adsorption capacity for benzoic acid, and the purity, by separate treatments with hydrochloric acid and a strong base. The prevailing idea that charcoals adsorb acids and bases equally is erroneous.

L. S. THEOBALD.

Influence of electrolytes on the absorption of hydrogen ions. B. AARNIO (Proc. Int. Soc. Soil Sci., 1926, [ii], **2**, 1—7).—The addition of 0·1N-solutions of electrolytes reduced the absorption of ammonium ions from 0·1N-ammonium sulphate and 0·1N-diammonium hydrogen phosphate by a clay soil in the decreasing order: strong acids (50—60% reduction), neutral and acid salts, alkaline salts. Treatment of an acid clay, an acid sphagnum moss, and a neutral soil with 0·01N-solutions of potassium or calcium chloride did not appreciably affect the p_H values of the suspensions when increasing amounts of hydrochloric acid and sodium hydroxide were added. Hydrogen ions absorbed by a clay are not replaced by contact with 0·01N-potassium and calcium chloride solutions. The increase in acidity of the soil solution caused by potassium chloride is due to replacement of aluminium by potassium.

CHEMICAL ABSTRACTS.

Adsorption by animal charcoal. G. Rossi and A. Basini (Annali Chim. Appl., 1926, **16**, 306—313).—The adsorption of methyl-violet, indigo-carmine, night-blue, alkali-blue, Congo-red, methylene-blue, and diamine-blue by animal charcoal between 19·5° and 70° has been examined. No generalisation can be drawn from the results (cf. Pelet-Jolivet and Siegrist, A., 1911, ii, 374). Charcoal which has adsorbed Congo-red is more active towards alkali-blue and methylene-blue than before, but less active towards the other dyes mentioned above.

E. W. Wignall.

Adsorption on solids with special reference to molecular orientation. W. E. Garner (Trans. Faraday Soc., advance proof, Oct., 1926).—A general survey of work relating to the adsorption of gases and dissolved substances by solids. The bearing of the molecular orientation in the surface on the formation of unimolecular or multimolecular adsorption films is stressed. The transitions involved in the building up of successive molecular layers make it impossible to express the complete course of adsorption by a single equation. A. E. Mitchell.

Ionic adsorption at the water surface. A. Frumkin, S. Reichstein, and R. Kulvarskaja (Kolloid-Z., 1926, **40**, 9—11; cf. A., 1924, ii, 462).—The series of adsorbabilities of inorganic anions at the surface of separation between air and a solution of an inorganic salt, determined by *P.D.* measurements (*loc. cit.*), has been confirmed by surface-tension measurements with solutions of the corresponding tetrapropylammonium salts. Measurements were carried out at 25° by the capillary rise method. The rise of adsorbability in the series $F'<Cl'<Br'<I'$ depends on the increase in ionic volume and the consequent decrease in hydration energy. An attempt was made to compare the adsorbabilities of different cations by determining the surface tensions of solutions of alkali ααβ-trichlorobutyrates, but the differences between the values obtained were within the limits of experimental error. It was shown experimentally that a marked hydrolytic adsorption does not occur. L. L. Bircumshaw.

Selective adsorption of colloids. L. Hugounenq and J. Loiseleur (Bull. Soc. Chim. biol., 1926, **8**, 523—549).—Selective adsorption differs from general adsorption in the existence of a limit, which depends on the charge of the particle and on the nature of the ion. The latter also determines the limiting value of the electrolyte concentration in presence of colloid. The reality of selective adsorption is shown by the formation of metalloid colloids on positively-charged particles, and of metal colloids on negatively-charged particles. Such reactions as the biuret (for protein) and Axenfeld's are, partly or wholly, manifestations of selective adsorption. Metallic oxides, deposited by selective adsorption on colloidal particles, are able to catalyse certain reactions in the same way as enzymes, manganese hydroxide on glycogen providing a powerful oxydase, whilst oxides of bismuth, manganese, and iron adsorbed on lecithin behave as catalases. It is claimed that the partial synthesis of enzymes can be considered as accomplished, at least in their action *in vitro*, since it has been possible to reproduce artificially adsorption compounds, the structure of which coincides with that of natural enzymes. It would seem that the electrolyte which is actually adsorbed on a colloid may be much more active than the portion which is not adsorbed. C. P. Stewart.

Absorption of water by colloidal fibres. J. J. Hedges (Trans. Faraday Soc., 1926, **22**, 178—193).—The moisture contents of wool in atmospheres of various humidities at 17—29° and the heats of wetting of wool of different moisture contents at 22° have been determined. The heats of absorption at moisture contents within the experimental range (0—18% moisture content) were independently calculated from these two sets of data and are compared with Shorter's values (B., 1924, 628); the three series are in rough agreement. The heats of wetting of silk at four different moisture contents were also determined, and are in fair accordance with the heats of absorption calculated with the aid of Schloesing's values for the moisture contents at different humidities and temperatures (Bull. Soc. d'Encour., 1893; A., 1893, ii, 368). The mechanism of absorption is discussed.

L. F. Gilbert.

Adsorption. XV. Adsorption of ions by aluminium hydroxide and by a mixture of barium sulphate and aluminium hydroxide. M. R. Mehrotra and N. R. Dhar (J. Physical Chem., 1926, **30**, 1185—1193; cf. Ghosh and Dhar, A., 1924, ii, 733).—Adsorption of anions by aluminium hydroxide gives the series $C_2O_4'' > Cr_2O_7'' > Fe(CN)_6'''' > IO_3' > BrO_3' > S_2O_3'' > NO_2' > Fe(CN)_6''' > CNS' > MnO_4' > Cl'$, and by a mixture of aluminium hydroxide and barium sulphate the series $Cr_2O_7'' > C_2O_4'' > IO_3' > BrO_3' > Cl' > S_2O_3'' > NO_2' > Fe(CN)_6''' > MnO_4' > Fe(CN)_6'''' > CNS'$. In the adsorption of anions by barium sulphate or aluminium hydroxide there is no marked promoter action, due to the presence of the second adsorbent. The potassium ion is also adsorbed from solutions of potassium oxalate and bromate by the above mixture. L. S. Theobald.

Spectrophotometric and cataphoretic studies of the adsorptive power of proteins for methylene-blue chloride. A. Fodor and K. Mayer (Kolloid-Z., 1926, **40**, 41—51; cf. this vol., 238).—The adsorption of methylene-blue hydrochloride by by albumin, casein, yeast phosphoprotein, and globulin has been investigated by means of cataphoresis measurements and a spectrophotometric method. The transport experiments were carried out first with the sol alone, then with addition of varying amounts of the dye. The optical measurements were carried out on the same sols under the conditions outlined previously (*loc. cit.*). With yeast protein, globulin, and casein, the two methods lead to the same conclusions; for the first two, the cataphoresis measurements show a migration of the dye with the sol, and the spectrophotometric experiments indicate an adsorption of the dye, whilst both methods give negative results with casein. For albumin, cataphoresis indicates adsorption, but the optical measurements do not. With yeast protein and globulin, the direction of migration is anodic. It is proved potentiometrically that the chlorine ions of

the methylene-blue salt disappear from the solution, and it is inferred that both the anion and the cation of the salt are adsorbed. Albumin, on the contrary, migrates in presence of methylene-blue hydrochloride to the cathode. From the cataphoretic measurements with yeast protein, combined with ultramicroscopic examination, it is found that 1 g. of the protein adsorbs 0·007—0·0014 g. of the dye, a result in good agreement with the optical measurements. It is calculated that the protein particle has a radius of $1{\cdot}02\times10^{-4}$ cm. and that the thickness of the adsorbed layer is 4×10^{-8} cm. L. L. Bircumshaw.

Adsorption by an optical method. Fixation of methylene-blue by yeast-phosphoprotein sol within the disperse phase. R. Riwlin (J.C.S., 1926, 2300—2303).—By a spectrophotometric method previously described (this vol., 238), it has been observed that, when methylene-blue is added to a yeast-phosphoprotein sol, the light absorption is not as great as might be expected from the turbidity of the two separate solutions. When the actual and the calculated transmissions are plotted against the wave-lengths, the two curves are of the same form and have a minimum at the same wave-length. This indicates that true lyosorption of the methylene-blue has taken place. This result is in accord with the fact that the final value is attained almost immediately. The fraction of methylene-blue adsorbed has been measured by a graphic method. M. S. Burr

Phase boundary forces at gas-liquid interfaces. IV. Adsorption and orientation of molecules of benzene derivatives. A. Frumkin, A. Donde, and R. Kulvarskaya (Z. physikal. Chem., 1926, **123**, 321—338; cf. A., 1925, ii, 873).—The surface tension at 25° and the *P.D.* at the air–liquid interface have been determined for aqueous solutions of various benzene derivatives. The relation between the lowering of the surface tension and the concentration can be in general represented by the equation previously proposed in the case of the higher fatty acids (*ibid.*, 109). Introduction into the molecule of a methyl group increases the amount of solute adsorbed at the interface to an extent depending on the position of the group, but in all cases the adsorption is less than it is for an aliphatic compound containing the same number of carbon atoms. Compounds containing a polar group in the nucleus impart a positive charge to the surface of the solution, but accumulation of such groups may efface or even reverse this effect. The *P.D.*–concentration curves of these compounds and also of those which are substituted in the side-chain show a slow rise in the surface charge, followed by a rapid fall, a phenomenon which is apparently due to the charge of the adsorbed ion opposing the charge resulting from orientation. Comparing the behaviour of isomerides, it is apparent that the one which takes up least space in the surface film produces the most positive charge on the surface. The differences here are so great that it is necessary to assume that the molecules of the isomerides possess different electrical moments. R. Cuthill.

Adsorption and diffusion in an electric field. J. Gicklhorn, R. Fürth, and O. Blüh (Z. physikal. Chem., 1926, **123**, 344—362).—Fürth's method of determining the sign of the charge on colloid particles (A., 1925, ii, 1057) has been used to investigate the influence of an electric field on the adsorption of electrolytes and non-electrolytes from solution and of gases by solids. Electrolysis of solutions of electrolytes using filter-paper strips as electrodes causes both anions and cations to pass into each electrode, *i.e.*, a process analogous to the adsorption of colloids takes place. Sulphates are adsorbed by both electrodes in approximately equal amounts, whilst chlorides are preferentially adsorbed at the cathode. Starch is preferentially adsorbed at the anode, sucrose and carbamide at the cathode. It therefore seems that solutions of non-electrolytes must contain charged molecules. If solutions of hydrogen peroxide are electrolysed in the dark or in presence of alkali so as to prevent spontaneous decomposition, using starch–iodide paper electrodes, iodine appears at the cathode only, apparently owing to the action of oxygen ions. When two electrodes are suspended in gaseous ammonia, ammonia is adsorbed at the anode only, although all the molecules of the gas are without charge. Various explanations of the above effects can be given, but it is not yet possible to decide between them. R. Cuthill.

Adsorption and reaction. II. Setting of litharge-glycerol cement. H. A. Neville (J. Physical Chem., 1926, **30**, 1181—1184).—The setting of litharge–glycerol cement has been studied by the thermometric method used for plaster of Paris (this vol., 899) and an analogous two-stage process observed. The rate of setting depends on the form of lead monoxide used and on the dryness of the glycerol. Water, hydroxyl ions, and stirring accelerate setting, whilst hydrogen ions retard it. Water is a definite product of the reaction, which is best represented by the equation $3PbO+2C_3H_5(OH)_3=Pb_3(C_3H_5O_3)_2+3H_2O$. The set product when powdered and boiled with water is completely hydrolysed to lead oxide and glycerol, and when heated in the absence of air yields pyrophoric lead.

L. S. Theobald.

Regularities in the precipitation and adsorption of small quantities of substances and its relationship to the radioactive precipitation rule. O. Hahn [with O. Erbacher and N. Feichtinger] (Ber., 1926, **59**, [*B*], 2014—2025).—Observations on the precipitation of mercuric iodide or mercurous chloride in the presence of thorium-*B*, the crystallisation of gypsum in the presence of thorium-*X* or thorium-*B*, the precipitation of copper fumarate in presence of thorium-*X* or thorium-*B*, and the precipitation of uranyl sulphate in presence of uranium-*X* are not in harmony with Fajans' rule (A., 1913, ii, 1010), but accord with the generalisation that "an element is precipitated from its solution, however dilute, with a crystallising precipitate when it is built into the crystal lattice of the precipitate and thus forms mixed crystals with the ions of the crystallising precipitate. If this is not the case, the element remains in the filtrate, no matter how sparingly soluble its compound with the oppositely charged component of the lattice in the particular solvent may be." A further general rule is that "an element

is adsorbed from its solution, however dilute, by a precipitate when a surface charge is imparted to the precipitate opposite to the charge of the adsorbed element and the adsorbed compound is sparingly soluble in the solvent employed." This rule is based on observations on the rapid precipitation of gypsum by alcohol in the presence of thorium-*B* or thorium-*X*, and the precipitation of silver iodide in the presence of thorium-*B* in presence of an excess of iodine or silver ions. Adsorption by hydroxides rich in surfaces requires further investigation. H. WREN.

Physico-chemical processes in the sintering of powders without fusion. J. A. HEDVALL (Z. physikal. Chem., 1926, **123**, 33—85).—Compressed pastilles of powdered ferric oxide and ferrosoferric oxide were heated under various conditions, and the extent to which they caked together was estimated from the reduction in their cross-section and the increase in their resistance to a crushing strain. With increase in the temperature at which the pastilles are heated, the rigidity increases slowly until a certain temperature, T, is reached, above which the rate of increase is much greater. The cross-section decreases fairly rapidly throughout, except near T, where it changes very little. T is considered to represent the temperature of recrystallisation, the only force acting below this temperature being that of shrinkage, whilst above this temperature the forces of recrystallisation come into play as well. This view is borne out by determinations of the recrystallisation temperature. The hardness of the pastilles increases with increase in the time of heating and in the amount of initial compression, and is the greater the smaller and more irregularly shaped are the granules constituting the pastilles. The sintering is much increased if chemical reactions occur in the powder, and very considerable hardness may be attained at temperatures below that at which recrystallisation commences. Thus the oxidation of ferrosoferric oxide to ferric oxide and the reverse process are accompanied by considerable increase in hardness and shrinkage. This effect is still more pronounced if the oxides are heated with lime or silica. These results are of importance in connexion with briquetting processes for the treatment of ores. R. CUTHILL.

Effects of gases on the surface tensions of some liquids. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1926, **1**, 173—177).—Measurements have been made of the depressing effect of air, carbon dioxide, nitrous oxide, and hydrogen sulphide on the surface tensions of water, ethyl alcohol, ethyl ether, carbon disulphide, and carbon tetrachloride. A modified form of the apparatus of Ramsay and Shields (J.C.S., 1893, **63**, 1089) was used and the depression of surface tension expressed in the form $100\Delta\sigma/\sigma$, where σ is the surface tension of the pure solvent and $\Delta\sigma$ the difference between that of solvent and solution. For a given gas with different liquids, the values of $\Delta\sigma/\sigma$ are almost constant, whilst for systems of the same liquid and different gases the empirical relation holds: $\Delta\sigma/\sigma=kC^{\frac{1}{3}}+\alpha$, where C is the concentration of gas in the liquid phase and k and α are constants.
A. S. CORBET.

Surface tension of gelatin solutions. II. J. H. S. JOHNSTON and G. T. PEARD (Biochem. J., 1926, **20**, 816—824).—There is no evidence that the sudden fall of the surface tension of gelatin below p_H 2·0 is due to immediate hydrolysis. A certain amount of hydrolysis takes place on long keeping at this p_H value (cf. A., 1925, ii, 659). The "protein error" of certain indicators with gelatin solutions has been investigated. Bromophenol-blue gives a minimum error at the isoelectric point and a maximum error at about p_H 2·4. The surface tension–p_H curves of gelatin have been corrected as regards p_H for the "protein error" in the colorimetric determination of p_H. S. S. ZILVA.

Structure of the surface layer. III. Capillary curves of the higher fatty acids and the equation expressing the state of the surface layer. IV. Electric properties of unimolecular layers. V. Method of verifying Gibbs' equation. A. FRUMKIN (Trans. Karpov Inst. Chem. [Russia], 1925, No. 4, 56—89).—III. Capillary curves of higher fatty acids up to lauric (dodecoic) acid deviate from those of lower acids on account of an attraction between long hydrocarbon chains; layers formed by adsorption on the surface of solutions behave similarly to those obtained from insoluble fatty acids with still longer chains. Shishkovskii's equation, when modified to express the action of these forces of attraction, accords with the experimental curves. Polymerisation in the surface layer must also be taken into consideration.

IV. The use of a platinum wire covered with ionium permits the measurement of the magnitude of the potential jump on the border between air and the surface of the liquid. Examination of unimolecular layers of insoluble substances shows that the phenomena observed can also in this case be explained on the basis of Langmuir's views on the orientation of molecules, but the ratio of the magnitude of the change of the potential jump to the quantity of adsorbed molecules is smaller for substances with short chains.

V. Gibbs' equation can be tested experimentally by using a substance, such as lauric acid, which combines an intense capillary activity with a very slight solubility in water. By measurement of the time required for the evaporation of drops of a solution of lauric acid in light petroleum on the surface of water the moment of saturation of the surface can be determined. From this, and from data expressing the relation between the concentration and surface tension of solutions of lauric acid, the adsorbed quantity is calculated by means of Gibbs' equation to be $5{\cdot}7\times10^{-10}$ g.-mols. per c.c. Harkins and Roberts (A., 1922, ii, 422) obtained the limiting value $5{\cdot}5\times10^{-10}$ for decoic acid. CHEMICAL ABSTRACTS.

Physical phenomena and molecular orientation. E. K. RIDEAL (Trans. Faraday Soc., 1926, advance proof, Oct., 1926).—An introductory survey of the literature and problems involved.
R. CUTHILL.

Insoluble films on water surfaces. N. K. ADAM and G. JESSOP (Trans. Faraday Soc., 1926, advance proof, Oct., 1926).—A summary of recent papers (cf. this vol., 348). R. CUTHILL.

Fine structure of surface films. Influence of temperature on the surface tension of pure dielectric liquids. G. JUNG (Z. physikal. Chem., 1926, **123**, 281—302).—The Langevin-Weiss theory of the spontaneous magnetisation of α-iron below the Curie point is applied to the orientation of molecules on the surfaces of dielectric liquids. A method is given for calculating the moments of dipoles and the polarisation of molecules from critical data. Eötvös' formula is valid for substances with very small dipole moments, and in the case of anomalous substances the constant in the formula approaches a universal value with increase of temperature. The total surface energy is an additive property of the constituent atoms and groups of the molecules. The contribution of the heat of demagnetisation of iron to its specific heat is compared with factors affecting the specific heat of the surfaces of dipolar liquids. The mathematical expressions derived in this paper are regarded as approximate only, as various effects, such as the mutual influence of the molecules, and electrostriction, have not been taken into consideration.

L. F. GILBERT.

Electrification at interfaces. H. FREUNDLICH (Trans. Faraday Soc., advance proof, Oct., 1926).—The importance of a distinction between the thermodynamic potential and the electrokinetic potential as a factor governing electrification at interfaces is pointed out. It is assumed that the electric double layer at an interface is not truly of the Helmholtz type, but of the "diffuse" type of Billiter, in which the ions of at least one layer are not strictly bound to the one surface, so that when the two phases undergo displacement the surface of separation is not identical with the true interface between the phases. It is assumed also that a thin film of the liquid or other second phase adheres firmly to the solid wall of the other phase. Then the thermodynamic potential is the true potential between the phases, whilst the electrokinetic potential is that between the movable liquid phase and the thin film of liquid adhering to the solid wall. The thermodynamic potential of a glass electrode was compared with the electrokinetic potential of a glass capillary, of the same glass, measured with the help of the stream potential. The Nernst potential showed no marked variation with the nature of the electrolyte, whilst the electrokinetic potential varied greatly with the nature of the cation. The quadrivalent thorium ion caused a change of sign at very low concentrations. By reference to various experimental results on the lowering of surface tension and coagulation of sols, a parallelism between the two potentials is shown to exist, in that both follow the rule of Traube. This parallelism is attributed to the effects of the orientation of the molecules.

A. E. MITCHELL.

Electrification at interfaces. R. K. SCHOFIELD (Trans. Faraday Soc., advance proof, Oct., 1926).—Largely a discussion of results already published (cf. this vol., 239, 572).

R. CUTHILL.

Arrangement of molecules on the surface of pure liquids. S. SUGDEN (Trans. Faraday Soc., advance proof, Oct., 1926; cf. A., 1924, ii, 662).—The existence of oriented molecules to any great extent on the surface of pure liquids is in conflict with the requirements of the kinetic theory. Application of Einstein's theory of the Brownian movement leads to a similar conclusion. It is therefore probable that the molecules on the surface of such liquids are arranged at random.

R. CUTHILL.

Physical properties of composite surfaces. W. RAMSDEN (Trans. Faraday Soc., advance proof, Oct., 1926).—A *résumé* of some physical properties of composite surfaces; discrepancies between observations and theory are indicated.

A. E. MITCHELL.

Rate of spreading of oil on water. E. LANDT and M. VOLMER (Z. physikal. Chem., 1926, **122**, 398—399; cf. A., 1925, ii, 508; this vol., 349).—The rate of spreading of olive oil on water has been determined with the aid of talcum powder as an indicator. A rapid followed by a slow decrease of rate occurs as the radius of the film increases. Theoretical considerations are advanced with which these phenomena are in accordance. A method of calculating the relative rates of spreading, under comparable conditions, of adsorbed substances on liquid and solid surfaces, respectively, is given.

L. F. GILBERT.

Spreading of proteins. E. GORTER and F. GRENDAL (Trans. Faraday Soc., advance proof, Oct., 1926).—Proteins may spread on water to form a unimolecular layer. Under proper temperature conditions and suitable hydrogen-ion concentrations (about p_H=1), hæmoglobin, casein, serum proteins, and muscle proteins spread in a film of thickness 6—7·5 Å. The behaviour of other proteins such as gelatin and gliadin is comparable with that of short-chain fats. The proteins do not spread on distilled water to give a film of minimum thickness; the spreading is a function of the time, although with strongly acid water it is independent of time. With hydrogen-ion concentrations on either side of the isoelectric point the layer is thicker than unimolecular and in some cases is 3 mols. thick. Increasing temperature has an accelerating effect on the spreading of proteins of the hæmoglobin and casein type, whilst those of the gelatin type spread better at low temperatures. It is suggested that the spreading in thin films is due to the attraction of the terminal CO·NH groups of the molecules for water.

A. E. MITCHELL.

Capillarity and evaporation. II. K. SCHULTZE (Kolloid-Z., 1926, **39**, 362—371; cf. A., 1925, ii, 287).—A description and discussion of experiments on the rate of evaporation of water, alcohol, ether, and light petroleum from regularly and irregularly shaped capillary tubes.

N. H. HARTSHORNE.

Capillarity and wetting. II. K. SCHULTZE (Kolloid-Z., 1926, **40**, 12—16; cf. A., 1925, ii, 856).—A true "wetting process" occurs only when a liquid spreads on a plane surface. In other cases—*e.g.*, the so-called wetting of a powder by a liquid—the process is always closely connected with capillary filling processes. These filling processes have been investigated in glass, agar, and gelatin capillary tubes of varying cross-section, with one closed end, and the influence of cross-section, position of tube

with reference to liquid, and surface tension of liquid have been studied. Considering the capillary rise of liquids in granular media, it is suggested that the lowering of velocity and height of capillary rise are due, not to frictional resistance (cf. Mitscherlich, Bodenkunde, 1923, 139), but to difficulties of spreading of the liquid caused by the non-vertical capillary passages. The swimming of powders on liquids is also to be traced to such difficulties of capillary filling. L. L. BIRCUMSHAW.

Origin of the movements of camphor on water, and other allied phenomena. L. A. RAMDAS (Proc. Indian Assoc. Cult. Sci., 1926, **10**, 1—34).—The movements of solid particles or droplets of various organic compounds on a clear water surface have been observed. Streams of material leave the edges and stream-lines are found to be convergent when the boundary is concave and divergent when it is convex. It has been shown by direct measurement that the denser surface film thus formed at the concave edge has a lower tension than the film at the convex side. The forces thus set up cause the dissolving particle or droplet to move away from the concave boundary. When crystals of a dye such as methyl-violet are thrown on water, there is often a short initial stationary period during which spreading takes place uniformly. Then streams of microcrystals are rapidly shot off from particular points, resulting in a recoil movement of the original crystal, which movement often becomes spiral. In some cases, a liquid unimolecular film and in others a solid film is formed. When a solid film is touched with an oiled platinum wire it cracks, whilst a liquid film is swept away. Spreading is most marked among compounds containing such groups as –OH, $-CO_2H$, $-NH_2$, and –CHO, whilst non-polar compounds, such as benzene, *cyclo*hexane, carbon tetrachloride, etc., spread very little or not at all. The scattering of light by a unimolecular film has been observed, and in some cases, *e.g.*, tetraiodofluorescein, this is accompanied by an intense fluorescence. M. S. BURR.

Properties of Blau's complex salts. H. FREUNDLICH and V. BIRSTEIN (Koll.-Chem. Beih., 1926, **23**, 27—40).—Blau's complex salts embrace the ferrous salts which contain the tridipyridylferro ion and the triphenanthrolineferro ion. Adsorption measurements showed that the sulphate of the ferro-tridipyridyl, and the bromide of the ferro-triphenanthroline salt are strongly adsorbed by blood charcoal, wool, and arsenic trisulphide in aqueous solution, in accordance with the usual adsorption isotherm. The salts exert a strong coagulating action on negative sols, such as arsenic trisulphide. Equivalent quantities of the complex cations are adsorbed by arsenic trisulphide at the coagulation value. It was found that an aqueous solution of the dipyridyl salt at first wets glass or quartz completely, but after a few minutes no longer does so. It appears as if a non-wetting organic substance is formed. The addition of an excess of ferrous sulphate prevents the reduction of wetting power. This behaviour may be explained by assuming the splitting of dipyridyl from the complex salt, as first suggested by Werner (J. Amer. Chem. Soc., 1923, **45**, 35). Blau's salts are plastic, and may be rubbed into a thin layer on a glass surface. Such a layer, in the case of the dipyridyl salt, shows double refraction and strong positive dichroism in the direction of rubbing. If left for some time in dry air, the optical properties of the layer change, and the dichroism becomes negative for long waves. It is suggested that this is due to the dehydration of a hydrate, the suggestion being supported by microscopical observations of small crystals. The double refraction changes with the dichroism, and follows the rule given by Zocher (Naturwiss., 1925, **13**, 1015). L. L. BIRCUMSHAW.

Fundamental principles of colloid chemistry. J. W. MCBAIN (Kolloid-Z., 1926, **40**, 1—9).—An address delivered at the fourth colloid symposium, in which a general survey is given of modern views on colloidal structure and stability, and suggestions are made for the further investigation of a number of problems. L. L. BIRCUMSHAW.

Colloidal systems in nitromethane. J. W. WILLIAMS and J. A. SKOGSTROM (J. Physical Chem., 1926, **30**, 1170—1174; cf. this vol., 15).—The formation of colloidal systems of phosphorus pentoxide in nitromethane in the presence of traces of water is described. Above and below a definite concentration of water no gel is formed, and the most rapid formation of the gel occurs at a definite concentration of water. Similar systems are formed with the aliphatic acids, aldehydes, ketones, and alcohols as peptising agents, and there is considerable evidence that the formation of these colloidal systems results from a chemical reaction between the pentoxide and the peptising agent. Aldehydes and ketones give highly coloured gels. L. S. THEOBALD.

Formation of disperse systems by the electrolysis of aqueous solutions by direct and alternating currents. E. JIRSA (Kolloid-Z., 1926, **40**, 28—33).—A study has been made of the formation of sols from the electrode materials in the electrolysis of aqueous solutions. The anodic polarisation of silver and copper in alkaline liquids and of gold in dilute sulphuric acid indicates that a passivating medium is essential. Theoretically a sol can be formed at any oxidation stage if the medium acts in a passivating way, not only for one, but for every stage, and if the medium contains an anion which is specific for the stability of a particular sol. In the formation of sols at the cathode, the sol is never formed by direct discharge at the cathode. If the sol is formed from the cathode material, the cause is to be sought in some secondary reaction between the cathode and the decomposition product of the electrolyte, leading to the disintegration of the cathode. The sols formed at the cathode are always metals. With silver, copper, platinum, and gold, sols of the lowest oxides are formed by electrolysis by alternating current between these metals in passivating media. The behaviour of lead electrodes in alkaline liquids is also considered. L. L. BIRCUMSHAW.

Growth of small gold particles in the preparation of gold hydrosols from dilute alkaline gold chloride solutions. J. ZAKOWSKI (Koll.-Chem. Beih., 1926, **23**, 117—142; cf. Zsigmondy and Hückel, A., 1925, ii, 775).—Measurements of the

velocity of growth of colloidal gold particles in the preparation of gold hydrosols by the formaldehyde method confirm the conclusions of Reitstötter with respect to the general course of the growth of the nuclei, its dependence on the amount of added gold hydrosol and on the temperature, and its relation to the velocity of growth calculated from the Zsigmondy–Hückel formula $y/b=1/a.[(1+2k.t/l_0)^3-1]$, where y is the fraction of gold reduced in time t, a and b are the volumes of the gold chloride solution and the added gold hydrosol, l_0^3 is the volume of a nucleus (regarded as cubical) at time $t=0$, and k is the velocity of linear growth. The growth of the gold particles takes place in two stages: a stage of slow growth (the induction period), for which region the formula does not hold, and a stage of rapid growth, for which period the formula, corrected by means of extrapolation, holds well. The magnitude of the induction period is dependent on the total surface area of the added nuclei, being smaller the greater the area. It decreases with rise of temperature, is diminished by previous illumination of the gold solution by ultra-violet light, and is almost independent of the age of the gold chloride solution. The velocity of growth, on the other hand, decreases in an irregular manner with the age of the solution. In unboiled gold salt solution, the rate of growth and spontaneous nucleus formation are greater than in boiled solution. Measurements with fresh, boiled gold solution show that the factor $2k/l_0$ is independent of the quantity of added gold hydrosol. The relation between the rate of growth and the magnitude of the added nuclei agreed well in some cases with the formula; in other cases, k decreased with increasing l_0.

L. L. Bircumshaw.

Colloidal solutions of alkaline-earth carbonates. II. Constitution of barium carbonate sol. A. von Burzágh (Kolloid-Z., 1926, **39**, 218—230).—Barium carbonate sols prepared as described previously (this vol., 469) are highly individual; even those with approximately the same concentration show quite different behaviour, *e.g.*, as regards conductivity and coagulation. The constitution of the colloid particles is deduced to be $\{(BaCO_3)_x[Ba(OH)_2]_n \,.\, Ba_n\}^{2n}$, with which are paired $2n$ hydrogen carbonate ions. From conductivity measurements of a 0·12656 molar sol with a particle diameter of 87 μμ and of its ultrafiltrate and from measurements of its migration velocity it is calculated that when $n=2$, x is 120 and on dilution to 1/16 decreases to 43. x also depends greatly on the particle size: *e.g.*, with a 0·1472 molar sol with a particle diameter of 198 μμ it is 486, whilst with a 0·0632 molar sol with particles 39 μμ it is 45.

Coagulation experiments show that two classes of electrolytes are to be distinguished, viz., those which cause fractional coagulation, such as alkali hydroxides, carbonates, sulphates, chromates, and iodates, and those which cause complete coagulation at all concentrations at which they coagulate at all; to this class belong the alkali chlorides, bromides, iodides, nitrates, and acetates, and other salts of which the anions form easily soluble salts with barium. In fractional coagulation, the larger particles are coagulated first, as was found by Odén in the coagulation of sulphur sols by sodium chloride. The concentrations of electrolytes of this class necessary to effect complete coagulation increase with increasing solubility of the barium salts of the anions.

The conductometric titration of barium carbonate sols with sodium hydroxide, lithium and sodium sulphates, and potassium chromate and iodate gives results in agreement with the above sol constitution. Partly coagulated calcium carbonate sols left in contact with their coagulate manifest the phenomenon of "after-coagulation," which may occur periodically like Liesegang rings. This is due to the fact that calcium sulphate is slowly dissolved from the coagulate and causes a further coagulation of the sol.

N. H. Hartshorne.

Origin of the electric charge on small particles in water. T. Alty (Proc. Roy. Soc., 1926, **A**, **112**, 235—251).—With the apparatus previously described (*ibid.*, 1924, **A**, **106**, 315) measurements have been made of the mobility of air bubbles 2—0·05 mm. in diameter in conductivity water. If the bubble is assumed to acquire a charge E by ionic adsorption, then E can be calculated from measurements of the velocity by the application of Stokes' law. The dependence of the charge on the age of the surface of the bubble and on its diameter was studied, and it was found that in very pure, air-saturated water, the charge is extremely small at first, increases to a maximum, and then falls to a value of about one third of this maximum, after which it appears to be independent of time. Similar experiments were made in water from which some of the air had been removed, so that the bubble decreased continuously during the experiments. A curve of similar type was obtained, and when equilibrium had been reached, the total charge on the bubble remained independent, not only of time, but also of bubble diameter. From this it would appear that, after equilibrium, the surface density of the charge must increase inversely as the square of the bubble radius, since the total charge remains practically constant while the bubble area decreases. In a theoretical treatment, these results are explained on the basis of adsorption, not of hydrogen and hydroxyl ions, but of ionic impurities in the water. This theory is supported by the fact that the greater the purity of the water the lower is the mobility of the bubble. Negative ions are assumed to be adsorbed on the inner surface of the bubble, and these tend to become covered by the positive ions in the liquid. Equilibrium is attained when the number of positive ions bound per sec. is equal to the number removed by thermal collisions in the liquid. From further assumptions, it is possible to calculate the total charge on the bubble at any time after its formation, and the values so obtained agree excellently with the experimental ones. The *P.D.* between the surface of the bubble and the interior of the liquid, due to excess of adsorbed negative ions, can be calculated by the use of the Boltzmann equation, and the value $V=0·064$ volt is obtained, which agrees well with the values determined directly by other observers.

L. L. Bircumshaw.

Beer's law and Congo-red solutions. G. Rossi and A. Basini (Annali Chim. Appl., 1926, **16**, 299—306).—Congo-red solutions follow Beer's law only when the concentration is below a certain limit; concentrated solutions have a colour which is not appreciably weakened on dilution. This fact is ascribed to the change in degree of dispersion of the Congo-red on changing the concentration. Methylene-blue and phenosafranine, with smaller particles, do not deviate from the law. E. W. Wignall.

Electrical resistance of protein–water systems. M. H. Fischer and M. O. Hooker (Koll.-Chem. Beih., 1926, **23**, 200—217).—The resistance increases with the dilution both in acid and alkaline solutions. For a given dilution the resistance of the latter increases in the order $KOH<NH_4OH<NaOH<LiOH<Ba(OH)_2<Ca(OH)_2$, which is not the order of strength of base. The resistance increases rapidly as the temperature is lowered, the magnitude of the change increasing with the dilution of the solution. For different alkalis, the temperature effect changes in the order given above. For different acids, the resistance increases in the order HCl<HBr<formic<oxalic<lactic. The enormous increase of resistance observed with lowering of temperature is analogous to the change from sol to gel, and is regarded as favourable to Fischer's view that the change consists of the interchange of rôles between the disperse phase and the dispersion medium. The bearing of this work on the problem of the permeability of plant cells is discussed. E. S. Hedges.

Colloidal properties of complex mercury derivatives of sulphosalicylic acid. Wo. Ostwald and M. Mertens (Koll.-Chem. Beih., 1926, **23**, 242—285).—A crystalline compound (decomp. 240°), probably *sodium 3-chloromercuri-5-sulphosalicylate*, is obtained by mercuration of sulphosalicylic acid and treatment of the product with sodium chloride. The course of the mercuration of sulphosalicylic acid gives rise to stiff hydrogels, but if the mixture is stirred, a sudden fall in viscosity takes place after 24 hrs. when the experiment is conducted at the ordinary temperature. The reaction was followed viscosimetrically under various conditions, and an α-gel and a β-gel were distinguished. The effects of concentration, temperature, and pressure on the viscosity of solutions of these gels were compared, the β-gels being characterised by a sudden rise or fall in viscosity. In their influence on the β-gel the anions fall into two groups: (1) those which cause complete dissolution, *e.g.*, Cl′, Br′, CN′, SCN′. This is a case of true chemical combination, since equivalent weights are required; (2) those which produce a marked increase in viscosity, or at higher concentrations even cause a precipitate. The order of influence is: sulphate>citrate>oxalate>nitrate>chlorate, which, with the last two terms reversed, is identical with the Hofmeister series. Cations produce an increase in viscosity in the order $K^{\cdot}>NH_4^{\cdot}>Na^{\cdot}>H^{\cdot}$. E. S. Hedges.

Optical anisotropy of coloured sols of sodium mercurisulphosalicylate. S. Berkmann and H. Zocher (Koll.-Chem. Beih., 1926, **23**, 292—309).—In presence of various colouring matters, sols of sodium mercurisulphosalicylate exhibit dichroism through parallel arrangement of the thread-like colloidal particles. The effect is positive in some cases and negative in others. It is probable that a parallel arrangement of the molecules of colouring matter is involved. *X*-Ray examination of the dried gel gave no interference figures. E. S. Hedges.

Slow hydrolysis of potassium pentachlororutheniate. H. Freundlich and A. Paris (Kolloid-Z., 1926, **40**, 16—19).—The course of hydrolysis of potassium pentachlororutheniate has been followed by measurements of the increase in conductivity and of the p_H value. These afford no support for the view that the process is accompanied by the formation of large amounts of a highly dispersed colloid, and that the process is similar to the slow hydrolysis of ferric chloride. The substance in the hydrolysed solution is only partly in the colloidal form, and diffusion experiments in agar gel showed that a large part of the ruthenium salt is in true solution. Experimental evidence points to the probability that from the complex ruthenium anion, basic ruthenium chloride ions are formed which have either a lower valency or a higher mol. wt. than the ruthenium pentachloride ion. This assumption is supported by the fact that the coagulation value of the original ruthenium salt towards a ferric oxide sol corresponds with that of a bivalent anion, but increases strongly in course of time. L. L. Bircumshaw.

Viscosity of suspensions of rigid particles and their dependence on the shear gradient. E. Hatschek and R. S. Jane (Kolloid-Z., 1926, **40**, 53—58).—An extension of previous work (Proc. Physical Soc., 1916, **38**, 274). The viscosities of suspensions of rigid microscopic particles (well-dried rice starch) in an indifferent liquid (100 parts of carbon tetrachloride and 12·8 parts of B.P. paraffin) increase with decreasing shear gradient, as with emulsoid sols. The measurements were made in the Couette apparatus, at volume concentrations of 2, 4, 6, and 8%. The increase of viscosity is more pronounced with increasing concentration. It is assumed that suspensions of this nature could not possess shear elasticity, and the variability of viscosity is explained by assuming that the virtual volume of the disperse phase is increased either by liquid envelopes or by Hess' conception of "dead space" (cf. Kolloid-Z., 1920, **27**, 1), this enlargement decreasing with rise of shear gradient. L. L. Bircumshaw.

Zocher's vortex method. W. König (Koll.-Chem. Beih., 1926, **23**, 110—117; cf. Zocher, Z. physikal. Chem., 1921, **98**, 293; Freundlich, Stapelfeldt, and Zocher, A., 1925, **ii**, 200).—A description is given of a simple apparatus for studying the vortex phenomenon. The liquid under observation is contained either in a rotating cylinder or in the annular space between the walls of an outer rotating cylinder and an inner stationary one. Observations were made with benzopurpurin sol (0·025% benzopurpurin and 0·025% sodium chloride, diluted ten times with water and with glycerol) and with aniline-blue 2 BL alcohol-soluble (1% solution in alcohol, greatly diluted with water). Similar effects were observed with the two sols. A 1% gelatin solution, 10% sugar solution, collodion, and an ethereal solution of copal varnish

did not show the phenomena. On testing in the vortex apparatus a diluted soap solution, a mixture of boric acid in benzol, and of asbestos in water, no dark cross was observed, but a figure composed of two dark and two bright sectors.

L. L. Bircumshaw.

Gels with anomalous accidental double refraction. A. Möhring (Koll.-Chem. Beih., 1926, 23, 152—161).—A description is given of the preparation and optical behaviour of "cresol-gelatin," a substance prepared from *p*-cresol and gelatin, which shows anomalous accidental double refraction and represents an optical analogy with cherry gum on the one hand and cellulose on the other. It is concluded that in all known cases of anomalous accidental double refraction of gels, the anomaly of the double refraction is due to the orientation of anisotropic particles. No case of anomalous "tension double refraction" has been found. L. L. Bircumshaw.

Reversibility of acid gelatin on dialysis. A. Fodor and C. Epstein (Kolloid-Z., 1926, 40, 51—53).—By dialysis in Wegelin's apparatus, acid gelatin (hydrochloric acid concentration 0·002—0·015*N*) can be separated in a completely reversible manner from the acid within 24 hrs. The original viscosity values are again reached, within the limits of experimental error, after the lapse of this time. The reaction is also reversible with very high acid concentration (0·5*N*). The reversibility of the swelling process is evidence against the amphoteric nature of gelatin. The decrease of the swelling process on the addition of acids or alkalis is apparently not due to the reduced dissociation of the salt-like compounds formed by the gelatin, but to the effect of the added acid or alkali on the adsorbed water. L. L. Bircumshaw.

Mol. wt. and gel state of gelatin. J. Eggert and J. Reitstötter (Z. physikal. Chem., 1926, 123, 363—382).—From osmotic pressure measurements with gelatin sols, the mol. wt. of gelatin purified by electrodialysis is found to be about 40,000, commercial gelatins giving values round about 30,000. Assuming that all the water in gelatin gels is combined, it is found that the m. p. of such gels are very near those of hydrated salts containing the same amount of water per molecule of anhydrous salt. The heat of the initial stages of the swelling of gelatin per g.-mol. of water is also approximately equal to the heat of hydration of many salts. With further swelling, however, the former value decreases and tends towards a value near that of the heat of hydration of an average ion. The following mechanism of swelling is therefore suggested. The first water taken up interpenetrates the mass, entering into more or less intimate combination with the micelles, this being accompanied by contraction of the water molecules (this latter effect has been experimentally observed). Further amounts of water form envelopes round the micelles, and finally fill up the spaces between them. If still more water is added, the gel passes into a sol, an effect which is also produced by splitting off some of the combined water with the aid of heat. This theory is shown to be quite compatible with the results of other authors.

R. Cuthill.

Swelling pressure of gelatin and the mechanism of swelling in water and neutral salt solutions. J. H. Northrop and M. Kunitz (J. Gen. Physiol., 1926, 10, 161—177).—Measurements of the swelling pressure of isoelectric gelatin at various temperatures and concentrations support the view that gelatin consists of a network of fibres of a relatively insoluble substance enclosing a more soluble material and that the swelling pressure is due to the osmotic pressure of the solution of the soluble material. In accordance with this view, two fractions have been isolated from gelatin having the expected properties, and the behaviour of these two fractions has been investigated. W. O. Kermack.

Thixotropic behaviour of aluminium hydroxide gels. H. Freundlich and L. L. Bircumshaw (Kolloid-Z., 1926, 40, 19—22; cf. Szegvari and Schalek, A., 1923, ii, 423; Freundlich and Rosenthal, A., 1925, ii, 967).—A quantitative study has been made of the thixotropic behaviour of aluminium hydroxide gels, prepared by Crum's method (hydrolysis of aluminium acetate). The velocity of the sol-gel transformation increases strongly with rising electrolyte concentration. Amino-acids such as glycine act in a liquefying manner, as with iron oxide sol, thus reducing the velocity of change. The aluminium hydroxide sol shows a thixotropic behaviour at lower concentration than the iron oxide sol. No difference was observed in the effect of addition of α- and δ-aminovaleric acids to the sol, and the effect of addition of morin was negligible. The sol shows a positive streaming anisotropy, which is weak with the pure sol and in presence of high concentrations of electrolytes, but much stronger at low electrolyte concentrations. This corresponds closely with the behaviour of benzopurpurin sol (cf. Freundlich and Dannenberg, this vol., 471) and may be explained in the same manner. L. L. Bircumshaw.

Ultramicroscopic investigation of the structure of the vitreous humour in animal eyes. K. Heesch (Koll.-Chem. Beih., 1926, 23, 78—84).—The ultramicroscopic structure of the vitreous humour, described by Thiessen and Baurmann (cf. Zsigmondy, "Kolloidchemie," 5th ed., p. 59) has been confirmed. It is a fine fibrillar structure, the length of the fibrils and the closeness of packing varying considerably with distance from the centre of the vitreous humour.

L. L. Bircumshaw.

Structure of stretched caoutchouc. E. A. Hauser and H. Mark (Koll.-Chem. Beih., 1926, 23, 64—78; cf. B., 1926, 334).—The results obtained in a previous *X*-ray investigation of stretched caoutchouc (*loc. cit.*) are discussed in connexion with other physical properties of the material, with the view of explaining its characteristic extensibility. The view is emphasised that, whereas the occurrence of interference bands of a certain intensity and width indicates the presence of a crystalline structure, the absence of such bands does not necessarily imply the absence of a crystalline phase. Thus the *X*-ray results previously obtained for caoutchouc may be explained by assuming that a phase is present composed of molecular aggregates ("primary particles") which are, however, not sufficiently oriented to cause interference.

Three working hypotheses are advanced to account for the experimental facts: (1) on the assumption that rubber consists of two phases (one liquid), the effect on stretching is considered to be due to the squeezing out of liquid from the " primary particles "; (2) the primary particles are considered to have the structure of a three-dimensional net, which in the unstretched state resembles a random arrangement of molecules; (3) the increased orientation of the primary particles on stretching is due to the alteration of the interfaces between the two phases (cf. Le Blanc and Kröger, B., 1925, 932).

L. L. BIRCUMSHAW.

Theory of needle-shaped rubber molecule. E. LINDMAYER.—See B., 1926, 924.

X-Ray study of the thermal contraction of tendons and the effect of treatment with formaldehyde. O. GERNGROSS and J. R. KATZ (Koll.-Chem. Beih., 1926, **23**, 368—376).—Tendons of birds and mammals give an *X*-ray spectrum due to the fibrillar arrangement of collagen. The tendons shrink and thicken when placed in hot water, and on drying fail to give an *X*-ray pattern, but the *X*-ray pattern can be produced again if the shrunken tendon is stretched mechanically to its original length. With tendons steeped in 4% formaldehyde for 24 hrs., boiling water is necessary for shrinkage to occur, and then the *X*-ray pattern can no longer be obtained. If the shrunken tendon is subsequently placed in cold water, a lengthening to about 75% of the original spontaneously takes place. By this process, the tendon recovers its ability to give an *X*-ray pattern, which is intensified by stretching to the original length. The change is reversible, for the shrinking and stretching may be repeated several times on the same tendon. The bearing of the results on the theory of tanning is discussed. E. S. HEDGES.

Pleochroic fat fibres on the needles used for spearing insects. W. J. SCHMIDT (Koll.-Chem. Beih., 1926, **23**, 51—63).—The free fatty acids obtained from fat which spreads over tinned brass needles on which certain insects have been speared reacts with the needle, which becomes deeply corroded, and green fat threads (often joined together to form lamellæ) are formed on the needle. The threads may be several cm. long, and are composed of leaf- or rod-like elements, parallel to the axis of the needle. These are doubly refracting, extinguishing almost uniformly throughout their length. The colour of the threads is due to a pleochroic copper–fat compound, soluble in organic media, which is present in the fat threads in sub-microscopic division. If the particles are oriented parallel to the direction of vibration of the polarisor, the threads appear bright green, if perpendicular, they appear bluish-green. The extraction of this compound leaves colourless, non-dichroic fat threads. These phenomena are analogous to the artificial pleochroism, discovered by Ambronn, due to the deposition of oriented organic dyes and metals in animal and plant fibres. Under certain conditions, the green copper–fat compound decomposes, leaving a brown substance (which may be free copper), which is insoluble in organic solvents and causes no pleochroism. L. L. BIRCUMSHAW.

Coagulating power of ions of the same valency and their radii. Heat of adsorption of electrolytes. H. LACHS and F. LACHMANN (Z. physikal. Chem., 1926, **123**, 303—314).—The coagulating effect of dilute solutions of the sulphates and nitrates of lithium, potassium, and cæsium, and of the nitrates of magnesium, calcium, strontium, and barium on Prussian-blue and antimonic acid hydrosols, and of various potassium salts on the latter has been determined. The coagulation values rise from lithium to cæsium and from magnesium to barium; the successive differences are much smaller for bivalent than for univalent ions. The heats of adsorption of the alkali nitrates on charcoal increase from lithium to cæsium. The heat effect represents the sum of the heat of dehydration of the alkali ion (which increases with increase of atomic weight) and of the heat of adsorption of the free ion. It is deduced theoretically that in series of ions of increasing radii, as in the lithium–cæsium and magnesium–barium groups, the net heats of adsorption from solution must also increase. L. F. GILBERT.

Protective colloids. I. Influence of concentration. S. SUGDEN and M. WILLIAMS (J.C.S., 1926, 2424—2432).—An investigation of the precipitation of arsenious sulphide and aluminium hydroxide sols by electrolytes in the presence of the protective colloids gelatin or blood-serum, both normal and syphilitic. The concentrations of protective colloid and electrolyte were simultaneously varied. When the results are plotted, the coagulation areas have a characteristic shape and indicate that small quantities of protective colloid produce a greater sensitivity towards electrolytes, which increases until the two colloids precipitate one another, even in the absence of electrolyte. At high concentrations of gelatin, the peculiar form of the curve shows that protection may take place at both low and high concentrations of electrolyte, whilst there is an intermediate region in which precipitation occurs. Increase in concentration of the sol causes a shift of the coagulation curve toward the region of greater concentration of protective colloid. The precipitation of both positive and negative sols by gelatin may perhaps be ascribed to the amphoteric character of the latter. The p_H values are probably constant throughout each series, and can therefore have no appreciable influence on the results. For arsenious sulphide sols with concentrations of less than 1 g. per litre, the amount of gelatin causing maximum precipitation is proportional to the arsenious sulphide content. M. S. BURR.

Periodic precipitate formation of calcium phosphate salts. B. DOGADKIN (Kolloid-Z., 1926, **40**, 33—31).—Calcium phosphate rings are formed by the reaction $Na_2HPO_4+CaCl_2 \rightleftharpoons CaHPO_4+2NaCl$, where sodium phosphate is the outer electrolyte. The system is neither qualitatively nor quantitatively changed by replacing the calcium chloride by an equivalent quantity of calcium nitrate, but on replacing sodium phosphate by ammonium phosphate no rings are formed. The phenomenon of ring formation depends quantitatively on the relation between the concentrations of the two electrolytes. If

the concentration of the outer or inner electrolyte decreases while that of the other component remains constant, the distances between the rings increase. Addition of sodium chloride to the gelatin also causes an increase in the distances between the rings. On increasing the concentration of the gelatin, the number of rings and the distance between them become smaller. For every concentration of the electrolytes, a maximum concentration of gelatin exists at which ring formation stops and the precipitate separates in the form of crystalline aggregates. In a concentrated agar solution (1% and above), ring formation of double periodicity was observed. The phenomena observed may be explained on the basis of Ostwald's theory of Liesegang ring formation, supplemented by the assumption that at the moment of ring formation the calcium phosphate is in the form of a sol. The influence of the medium must also be given special consideration. A series of experiments was made to show the peptising action of gelatin on the calcium phosphate precipitate. L. L. BIRCUMSHAW.

Effect of p_H on the permeability of collodion membranes coated with protein. D. I. HITCHCOCK (J. Gen. Physiol., 1926, **10**, 179—183).—The permeability of collodion membranes coated with gelatin is greatest at the isoelectric point of the gelatin, and on varying the hydrogen-ion concentration from the isoelectric point the permeability reaches a minimum and then increases. These results, which are analogous to the effect of variation of the hydrogen-ion concentration on the swelling of gelatin, indicate that the change of permeability is due to the swelling of gelatin in the pores of the membrane. Similar results have been obtained in the case of membranes coated with egg-albumin, edestin, serum-euglobulin, and serum-albumin.

W. O. KERMACK.

Liesegang rings. K. JABŁCZYŃSKI (Kolloid-Z., 1926, **40**, 22—28).—On the assumption that the determining factor in the formation of Liesegang rings is the diffusion of one of the reactants (*e.g.*, silver nitrate), an equation is derived, $h^2/t=2kDC_0$, where h is the distance to which the silver nitrate has diffused in the time t, D the diffusion coefficient of silver nitrate in gelatin, and C_0 the concentration of silver nitrate for $h_0=0$. Equations are also derived for diffusion in two and three directions. These equations are found to be completely confirmed, the velocity of ring formation being studied in one direction, in a section from the centre towards the periphery, from the periphery towards the centre, and in a sphere. It is shown that the concentration of silver nitrate remains constant at the places where the rings appear, and that the ratio of the distances between successive rings is constant. There is no analogy between the formation of rings in the wood of trees and Liesegang ring formation.

L. L. BIRCUMSHAW.

Influence of electrolytes in electro-endosmosis. H. C. HEPBURN (Proc. Physical Soc., 1926, **38**, 363—377).—The rate of flow of liquid and the current through a diaphragm of powdered glass have been measured for water and for aqueous solutions of hydrogen, potassium, and barium chlorides of concentrations up to 0·005 mol. per litre. With each solute, the potential of the glass–liquid interface and the thickness of the electrical double layer increase with increasing concentration to a maximum, and then decrease regularly. The conductivity is greater than that measured in the usual way. The negative charge per unit surface increases with the concentration of barium and hydrogen chlorides through the whole range investigated, and with the concentration of potassium chloride from $0{\cdot}0005M$ upwards.

A. GEAKE.

Restriction of the formation of hydrogen bromide by iodine. W. MÜLLER (Z. physikal. Chem., 1926, **123**, 1—27).—Investigation of the above effect at 275° and 305° has shown that the explanation previously proposed (A., 1924, ii, 745) is untenable. The results are, however, explicable on the assumption that iodine bromide is formed in the reaction mixture, the equilibrium $Br_2+I_2 \rightleftharpoons 2IBr$ lying well over to the right. The rate of formation of hydrogen bromide is determined by the speed of the reaction $Br+H_2=HBr+H$, and this is diminished in consequence of the combination of bromine with iodine. It is computed that at 300° iodine bromide is 20% dissociated into its elements, whilst according to Nernst's theorem its heat of formation is about +5000 cal.

R. CUTHILL.

Equilibrium $I_2+Br_2 \rightleftharpoons 2IBr$. M. BODENSTEIN and A. SCHMIDT (Z. physikal. Chem., 1926, **123**, 28—32).—From simultaneous measurements of the vapour density of bromine, iodine, and mixtures of the two the constant of the above equilibrium is found to have the value 0·093 at 1222°, which agrees satisfactorily with Müller's estimated value of 0·0130 at 304·8° (cf. preceding abstract).

R. CUTHILL.

Reaction provinces. W. P. JORISSEN (Chem. Weekblad, 1926, **23**, 441—444; cf. this vol., 246, 690, 906, 909).—The criticisms of Coward and Jones (Ind. Eng. Chem., 1926, **18**, 970) on the author's previous work in connexion with the effect of inert gases on the explosion limits of inflammable gases in oxygen and air are dealt with.

S. I. LEVY.

Water equilibrium. W. D. BANCROFT (J. Physical Chem., 1926, **30**, 1194—1201).—Theoretical. The displacement of the water equilibrium is apparently the important factor in the peptisation of gelatin by potassium iodide and in the effect of neutral salts on p_H values. These values, as at present determined, are not necessarily related to actual hydrogen-ion concentration. Further, there is no satisfactory evidence, as yet, that the addition of sodium chloride to hydrochloric acid causes any increase in the actual hydrogen-ion concentration. The agreement between p_H values determined potentiometrically and by indicators is not an independent confirmation.

The displacement of the water equilibrium may be important in causing variations from the dilution law. The use of the activity concept is adversely criticised.

L. S. THEOBALD.

Influence of the ionic charge on the osmotic behaviour of alcoholic solutions. O. E. FRIVOLD (J. Physical Chem., 1926, **30**, 1153—1161).—From

ebullioscopic measurements of lithium and cobalt chlorides in methyl alcohol, and of lithium and cobalt chlorides as well as lanthanum nitrate in ethyl alcohol, the influence of ionic charge on osmotic behaviour has been studied. The results, as far as they go, support the Debye–Hückel theory of interionic attraction. Except in the case of lithium chloride in methyl alcohol, where values are large, the mean diameters of the ions calculated by the method of Debye and Hückel (A., 1923, ii, 724) are of the same order of magnitude as those for aqueous solutions. L. S. THEOBALD.

Electrical forces operating between ions. N. BJERRUM (Svensk Kem. Tidskr., 1926, **38**, 2—18; from Chem. Zentr., 1926, I, 2174).—A general discussion. It is suggested as characteristic of strong electrolytes that their ions do not combine to form molecules, but approach one another very closely without further deformation. The author distinguishes between association products of slightly deformed ions on the one hand and chemical complexes of much deformed or entirely denatured ions on the other. W. A. CASPARI.

Colour change of Congo-red in acidified acetone–water solutions. F. M. CRAY (J. Physical Chem., 1926, **30**, 1276—1282).—The colour change of Congo-red in acetone–water mixtures acidified with hydrochloric acid shows a time effect which depends on the concentration of the acid and the dye, the composition of the solvent, and the temperature. For a given solvent and a constant concentration of dye, this time increases with decreasing hydrogen-ion concentration, and for fixed concentration of hydrogen-ion and composition of solvent, the time increases with decreasing concentration of Congo-red. For fixed times of colour change with fixed concentration of the dye the curves relating hydrogen-ion concentration to composition of solvent show maxima of hydrogen-ion concentration in the solvent containing 35% of water.

Comparisons between the colour change and the coagulation of gold sols by electrolytes support Ostwald's view (A., 1919, ii, 400) that the change is due principally to variations in the degree of dispersion. L. S. THEOBALD.

Proteins. IX. Influence of salt concentration on the acid-binding capacity of egg-albumin. K. LINDERSTRØM-LANG and (MISS) E. LUND (Compt. rend. Trav. Lab. Carlsberg, 1926, **16**, 1—56).—An equation is derived giving β_H, the equivalent of hydrogen ion taken up or given off by albumin in the presence of salts, in terms of the hydrogen-ion activities in solutions of salt alone, and of salt plus albumin. Experimental results are given for $NH_4Cl+HCl$, $(NH_4)_2SO_4+H_2SO_4$, and $KCl+HCl$, the hydrogen-ion activity being determined electrometrically. Specific hydrogen ionisation is defined as β_H/concentration of ampholyte; the hydrogen-ion activity when this quantity becomes zero is termed the isoionic reaction, and is identical with the older isoelectric reaction. Mean valency is defined as the algebraic sum of the equivalents of all the ions taken up or given off by the ampholyte divided by the concentration of ampholyte, and is used similarly to define isoelectric reaction. The two reactions coincide when hydrogen ions alone are capable of being taken up by the ampholyte. It is shown on the basis of the Debye–Hückel theory that the hydrogen-ion activity at the isoelectric point will not vary with the ampholyte or salt concentration unless the activity coefficients of the positive and negative ions vary in different ways with the concentration. The effect of the salt concentration on the shape of the ionisation curves is discussed; for a univalent acid or base, increase in the salt concentration moves the curve parallel to itself along the pa_H axis, and for a multivalent electrolyte, the curve is turned about the isoelectric point in such a manner that the mean valency increases with the salt concentration on the acid side of isoelectric reaction. A summary of the experimental results indicates that the isoionic reaction is independent of the ammonium chloride concentration. For isoionic reaction, $pa_H=4{\cdot}898$, and the difference between this value and that previously determined for ammonium sulphate (4·844) is discussed. It is shown that the alteration in the direction of the ionisation curves is due solely to interionic forces; the possibility of calculating the shape of the ionisation curves is demonstrated, together with the deviations due to the salt effect at different concentrations. L. F. GILBERT.

Thermo-balance analysis of chemical changes in metals, oxides, and sulphides at high temperatures. H. SAITO (Proc. Imp. Acad. Tokyo, 1926, **2**, 58—60).—Honda's thermo-balance (Sci. Rep. Tôhoku Imp. Univ., 1915, **4**, 97) has been modified so that it can be used to follow continuously the changes accompanying the heating of solids in various gases. No experimental results are given. R. CUTHILL.

Thermal dissociation of the ammonia compounds of silver nitrate. F. JIRSA and J. DIAMANT (Z. physikal. Chem., 1926, **123**, 261—274).—The pressures corresponding with the dissociation $AgNO_3,3NH_3 \rightleftharpoons AgNO_3,2NH_3+NH_3$ were measured by a tensimetric method between 13° and 18°. No concordant data for the dissociation of the diammonia compound could be obtained; this is due, probably, to the formation of solid solutions with silver nitrate. New experimental evidence is adduced in support of Kurilov's view (Bull. Acad. St. Pétersbourg, 1903, **17**, 149) that the monoammonia compound does not exist. The heats of dissociation of the ammonia compounds, as calculated from the dissociation pressures, agree with those determined from measurements of the heats of solution of the compounds, silver nitrate, and ammonia in *N*-nitric acid, and of the diammonia compound and silver nitrate in *N*-ammonium hydroxide.

The triammonia compound employed was prepared by the action of dry ammonia on the diammonia compound, which is readily formed by methods described by other authors. L. F. GILBERT.

System water–acetic acid–toluene. R. M. WOODMAN (J. Physical Chem., 1926, **30**, 1283—1286; cf. Herz and Fischer, A., 1905, ii, 304).—A triangular

diagram for this system at 25° is given, together with the densities and viscosities of the layers. L. S. THEOBALD.

System sodium sulphate–sulphuric acid–ethyl alcohol. H. B. DUNNICLIFF, I. S. SIKKA, and R. C. HOON (J. Physical Chem., 1926, **30**, 1211—1218).—A triangular diagram for this system at 18·3° is given and the existence of solid phases having the formulæ $3Na_2SO_4,H_2SO_4$ and $2Na_2SO_4,H_2SO_4$ is indicated. The effect of ester formation on the equilibrium has been examined. L. S. THEOBALD.

Phases in the ternary system Fe_2Cl_6–Fe_2O_3–H_2O. E. BAUR (Z. Elektrochem., 1926, **32**, 428—430).—A brief review of the results of work done in the author's laboratory by E. Stirnemann (Jahrb. Min. Beil.-Bd., 1925, **52A**, 334—377; **53A**, 59—94). H. J. T. ELLINGHAM.

Reciprocal salt pair $[K_2,(NH_4)_2]$-$[SO_4,CrO_4]$ at 25°. T. ISHIKAWA (Bull. Chem. Soc. Japan, 1926, **1**, 139—142).—The system shows two complete series of solid solutions which exist in equilibrium with liquid solutions. The solubility of ammonium chromate at 25° is 39·60 g./100 g. of water (cf. Araki, A., 1925, ii, 786). S. K. TWEEDY.

Equilibria in systems containing phases separated by a semi-permeable membrane. XV. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 699—707).—Theoretical. A. GEAKE.

Pseudo-ternary systems containing sulphur. I. Sulphur and quinoline, pyridine, and *p*-xylene. D. L. HAMMICK and W. E. HOLT (J.C.S., 1926, 1995—2003).—Stable, pseudo-ternary equilibria and metastable equilibria in the systems sulphur and quinoline, pyridine, and *p*-xylene have been investigated by the synthetic method. In the systems sulphur–quinoline and sulphur–*p*-xylene, attainment of internal equilibria in the phases containing liquid sulphur results in a lowering of the mutual miscibility of those phases. Contrary to deductions from the work of Aten (A., 1914, ii, 121), in the system sulphur–*p*-xylene the solubility of the liquid equilibrium sulphur is less than that of the labile S_λ. The conclusions of Hildebrand (A., 1921, ii, 307) are borne out, the critical solution temperature in xylene being 190° for S_λ, and the descending series xylene, toluene, benzene is thus established (cf. Kruyt, A., 1909, ii, 802). Hildebrand's view, that if one of the liquids in a binary mixture has a high dielectric constant, then the mutual solubility will be diminished is supported by the results of experiments on the systems sulphur–pyridine (160°) and sulphur–quinoline (97°), the figures in parentheses being the critical solution temperatures. R. W. WEST.

Generalised expression of the phase rule and its particular application to osmotic, thermoelectric, and electro-osmotic phenomena. E. DENINA (Gazzetta, 1926, **56**, 357—365).—If any two phases are separated by an unlimited number of semi-permeable membranes, each of which is permeable to one and one only of the several components of the system such as thermal energy or electrons, then the number of degrees of freedom possessed by the system is equal to the difference between the total number of variables defining the system less the sum of the number of phases and of the number of independent equations determining the contact conditions between the phases. The expression so deduced for the number of degrees of freedom of the system has the advantage that neither pressure nor temperature is necessarily uniform throughout the system. A discussion is given of the application to the thermoelectric effect, the galvanic cell, and to osmotic, thermo-osmotic, and electro-osmotic systems. R. W. LUNT.

Nomogram for the van 't Hoff–Arrhenius temperature equation. O. W. RICHARDS (J. Physical Chem., 1926, **30**, 1219—1221).—A nomogram from which the value of the thermal increment, μ, can be readily obtained has been constructed from the equation $\log K_2-\log K_1=y=\mu(1/T_1-1/T_2)/4·6$. L. S. THEOBALD.

Entropy of aqueous ions. W. M. LATIMER and R. M. BUFFINGTON (J. Amer. Chem. Soc., 1926, **48**, 2297—2305).—The values obtained for the relative entropies of some aqueous ions at 25° suggest that the entropy of solution of the gaseous ions is mainly a function of the size and charge of the ion. Some of the values referred to $H^{\cdot}=0$ at hypothetical molal concentration and 298° Abs. are: OH', −2; CO_3'', −14; Cl', 15·5; Br', 20·5; I', 27; $Na^{\cdot}$, 15; $Cu^{\cdot\cdot}$, −23; $Fe^{\cdot\cdot\cdot}$ −67. The application of the results is illustrated by the calculation of the potential of the normal magnesium electrode (−2·40 volts), the heat of solution of cuprous chloride (8·9 kg.-cal.), the entropy of solid magnesium hydroxide (26·0), and the free energy of solution of zinc chloride (−22·8 kg.-cal. for molal concentration). S. K. TWEEDY.

Thermodynamic properties of electrolytes in acetic acid and in liquid ammonia. T. J. WEBB (J. Amer. Chem. Soc., 1926, **48**, 2263—2271).—The f.-p. depressions of solutions of lithium and sodium bromide and of sodium acetate in acetic acid were determined and the results compared with the appropriate Debye–Hückel equation. At moderate concentrations, the physical properties of the solvent and the effective radius of the ions are found to account satisfactorily for the results. The measurements of Turner and Bissett (J.C.S., 1914, **105**, 1782) on acetic acid solutions of lithium iodide and nitrate indicate that the dielectric constant of the solvent is increased when the concentration is sufficiently high, which suggests that incomplete ionisation occurs. The results of f.-p. experiments on solutions of potassium iodide and of sodium nitrate in liquid ammonia lead to similar conclusions. S. K. TWEEDY.

Free energy and heat of transfer of barium in its liquid amalgams. P. A. ANDERSON (J. Amer. Chem. Soc., 1926, **48**, 2285—2295).—The *E.M.F.* at 15°, 25°, and 30° of some barium amalgam concentration cells were measured. The electrolyte consisted of a carefully dehydrated solution of barium chloride in anhydrous hydrazine, and the amalgams, which varied over the concentration range 0·2629—0·0108 weight-% of barium, were prepared *in situ* in an atmosphere of hydrogen. Two reference electrodes were used at each concentration. The

observed *E.M.F.* are higher than those calculated from the Nernst equation (cf. Ramsay, J.C.S., 1889, **55**, 521); better agreement is obtained when Cady's equation is used (A., 1899, ii, 394), the deviations being almost entirely due to the failure of the osmotic energy term in this equation to represent the actual osmotic effect. By extrapolation of the results to infinite dilution, the activities of barium and the free energies of transfer in the cell are calculated. The heat of transfer of barium is of the same sign as that of sodium (Richards and Conant, A., 1922, ii, 340).

S. K. TWEEDY.

Thermodynamic studies on zinc iodide and mercurous iodide. F. ISHIKAWA and E. SHIBATA (Bull. Chem. Soc. Japan, 1926, **1**, 169—172).—The fictitious heat of solution (cf. Cohen and Bruins, A., 1918, ii, 297) of zinc iodide has been evaluated from the relation connecting the temperature coefficients, $(dE/dT)_A$ and $(dE/dT)_B$, of the *E.M.F.* of reversible cells with and without solid salt, viz., $(Q)_T = T[(dE/dT)_A - (dE/dT)_B]23074n$ . . . (1). Data for the cells: 10% zinc amalgam|ZnI_2, saturated solution with solid salt, Hg_2I_2|Hg(A) and 10% zinc amalgam|ZnI_2, saturated solution, Hg_2I_2|Hg (B) gave $E_A = 0{\cdot}52429 + 0{\cdot}0001336(t - 25) - 0{\cdot}000001496(t - 25)^2$, whence $(dE/dT)_{A298} = 0{\cdot}0001336$ volt/degree, and $E_B = 0{\cdot}52415 + 0{\cdot}0002427(t - 25) + 0{\cdot}0000027(t - 25)^2$ whence $(dE/dT)_{B298} = 0{\cdot}0002427$ volt/degree. By substitution in (1) the fictitious heat of solution of zinc iodide at 298° Abs. is −1500 g.-cal./mol.

The heat of formation of zinc iodide, determined by application of the Gibbs–Helmholtz equation to cell A and taking the heat of formation of (HgI) to be 14200 g.-cal., is −50760 g.-cal.

The entropy change for the reaction $Hg_2I_2 + Cd = CdI_2 + 2Hg$ is calculated from the relation $\Delta S_{298} = 2F[(dE_1/dT)_{298} + (dE_2/dT)_{298}] = 5{\cdot}68$ entropy units, where $(dE_1/dT)_{298}$ and $(dE_2/dT)_{298}$ are the (known) temperature coefficients of the cells Cd amalgam|CdI_2, Hg_2I_2|Hg and Cd|solution|Cd amalgam, respectively. The entropies of mercury, cadmium, and cadmium iodide being known, $S_{Hg_2I_2} = 56{\cdot}8$ entropy units. The entropy change and free energy change in the formation of mercurous iodide from its elements are $\Delta S_{298} = -5{\cdot}4$ entropy units and $\Delta F_{298} = -26790$ g.-cal., respectively.

From the reaction $Zn + Hg_2I_2 = ZnI_2 + 2Hg$ the free energy of formation of zinc iodide is $\Delta F_{298} = -50985$ g.-cal., which agrees closely with −50628 g.-cal., obtained from the reaction $Zn + 2AgI = ZnI_2 + 2Ag$.

A. S. CORBET.

Salicylic acid as a standard in calorimetry. E. COHEN, P. E. VERKADE, S. MIYAKE, J. COOPS, jun., and J. A. VAN DER HOEVE (Proc. Physical Soc., 1926, **38**, 667—672).—When salicylic acid is to be used as a standard in calorimetry, the final crystallisation must be from dry ether. The heat of combustion is then 5242 cal. per g. When the final crystallisation is from water, low values are obtained, owing to occluded water, which cannot be removed completely by ordinary drying methods.

A. GEAKE.

Heat of combustion of benzoic acid. P. E. VERKADE (Z. physikal. Chem., 1926, **123**, 275—280).—A reply to Jaeger and Steinwehr (this vol., 477), maintaining the author's previously expressed views (*ibid.*, 28).

L. F. GILBERT.

Specific heats at low temperatures. F. SIMON. (*a*) **Specific heats of sodium, potassium, molybdenum, and platinum.** W. ZEIDLER. (*b*) **Deviation of chemical constants of monatomic gases from theoretical values.** F. SIMON (Z. physikal. Chem., 1926, **123**, 383—405).—By means of an improved form of Lange's adiabatic vacuum calorimeter (A., 1925, ii, 96), the specific heats of the above metals and of andalusite, sillimanite, and disthene have been measured at temperatures from the temperature of liquid hydrogen up to the ordinary temperature. For the three minerals, Debye's T^3 law is valid at the lowest temperatures. For the metals, the results can be represented by Debye functions, the characteristic temperatures being 159°, 99·5°, 379°, 225° for sodium, potassium, molybdenum, and platinum, respectively. For sodium and potassium the chemical constants are calculated to be $+0{\cdot}97 \pm 0{\cdot}23$ and $+1{\cdot}13 \pm 0{\cdot}32$, respectively, whilst the Stern–Tetrode formula requires the values $+0{\cdot}52 \pm 0{\cdot}23$ and $+0{\cdot}33 \pm 0{\cdot}32$, respectively. An explanation of this deviation is suggested on the basis of the rule (A., 1925, ii, 98) that the deviation of chemical constants from the theoretical values is the greater the greater the energy difference between the two states from the thermal equilibrium of which the constants are calculated. The total and free energies of the metals examined have been calculated.

R. CUTHILL.

Specific heats of aqueous homogeneous phases. G. F. HÜTTIG and H. WEHLING (Koll.-Chem. Beih., 1926, **23**, 354—367).—An introductory paper. The following mean specific heats are recorded: lithium bromide, 0·1438 (3·6—91·0°) and 0·1433 (3·2—810°); sucrose, 0·3227 (1·7—39·9°), 0·3475 (3·6—80·6°); ignited zirconuim oxide, 0·1312 (3·5—80·5°), precipitated zirconium oxide after heating at 300° in a vacuum, 0·1425 (2·9—80·0°). Measurements are tabulated for the specific heats of the solutions of varying concentration. The conclusions are reserved for a subsequent paper.

E. S. HEDGES.

Latent heat of dilution of cane sugar [sucrose] solutions. (MISS) F. M. HUNTER (Trans. Faraday Soc., 1926, **22**, 194—206).—The heats of dilution and the specific heats of solutions of sucrose up to $4M_w$ concentration have been determined between 12° and 30°. These data were combined with Morse's values for the osmotic pressure at 20° to calculate the osmotic pressures at other temperatures, and gave results in fair agreement with those directly measured by Morse (A., 1912, ii, 835). The apparent hydration per molecule of sucrose, as calculated from the osmotic pressure, decreases with increase of concentration and is nearly constant at different temperatures. The logarithm of the ratio vapour pressure of solvent : vapour pressure of solution decreases with increase of temperature in accordance with Wood's experimental results (Trans. Faraday Soc., 1917, **13**, 131; cf. Perman and Lovett, this vol., 127).

L. F. GILBERT.

Dependence of heat of adsorption of a gas on a solid on pressure. Extension of the laws of surface tension of solutions to the phenomena of gas adsorption. B. Ilin (Physikal. Z., 1926, **27**, 591—598).—The equation $Q/S=b\log(ac+1)$ obtained earlier (A., 1925, ii, 856, 958, 1149) is justified theoretically. The variation of the heat of adsorption with the pressure of the surrounding gas follows the same laws as the variation of surface tension of surface-active solutions with concentration. Correlation of the equations of Gibbs and Szyszkowski with the isotherm equations of Langmuir permits the evaluation of significant constants in the author's treatment. Among the possibilities discussed is a method for calculating the surface tension of a solid in a vacuum. R. A. Morton.

Motion of ions in liquids. B. Cassen (Physical Rev., 1925, [ii], **25**, 249).—Maxwell's distribution law does not hold for the motion of ions in liquids. There is a maximum velocity due to thermal agitation which, for lithium ions in liquid ammonia, is equivalent to a fall in potential of about $1\cdot8\times10^{-5}$ volt.
A. A. Eldridge.

Direct measurement of the velocity of migration of ions in a solution. J. J. Grebe (Physical Rev., 1925, [ii], **25**, 113).—An apparatus is described whereby the migration velocity of ions is measured by determining the time required for them to travel a known distance in pure water under a measured potential gradient, as indicated by the rate of increase of the conductivity of the water. The results are in close agreement with the calculated velocities.
A. A. Eldridge.

Conductivities in acetone. P. Walden, H. Ulich, and G. Busch (Z. physikal. Chem., 1926, **123**, 429—471).—The conductivities of acetone solutions of sodium and potassium iodides, lithium picrate, barium perchlorate, and various salts of the substituted ammonias, pyridines, and guanidines have been measured at 0°, 25°, and 50° at dilutions up to about 100,000 litres. The two iodides, barium perchlorate, and most of the salts of the tetra-substituted bases behave as strong electrolytes, but for dilutions of 2000 litres and upwards the Kohlrausch square-root formula and the modified Ostwald–Bredig rule (A., 1921, ii, 423) are both applicable. With the other salts the dilution law is approximately fulfilled, and the general behaviour is that of weak electrolytes. For all the salts, the product of the conductivity at infinite dilution, Λ_∞, and the viscosity of the solution, η, is a constant independent of the temperature, which means that the ions obey Stokes' law. For a few salts with bulky ions the value of $\Lambda_\infty\eta$ is also independent of the solvent, so that from mobility data for aqueous solutions, mobilities in acetone solutions can be calculated, since for these solutions Kohlrausch's law proves to be valid. In this way it is found that the mobilities of the sodium, potassium, and lithium ions are about the same, and are about two thirds that of the iodide ion, which itself migrates somewhat more rapidly than the chloride ion. R. Cuthill.

Determination of the mobility of proteins. T. Svedberg and A. Tiselius (J. Amer. Chem. Soc., 1926, **48**, 2272—2278).—A moving-boundary method for determining the mobility of proteins is described. The boundaries are detected by photographing in light of wave-length below 300 $\mu\mu$; this method is more accurate than the fluorescence method previously described (Scott and Svedberg, A., 1925, ii, 204), since there is evidence that at least some of the fluorescence is not due to the albumin itself. Preliminary experiments with electrodialysed egg albumin gave mobilities somewhat different from those found by Scott and Svedberg. S. K. Tweedy.

Solubility and electrolytic conductance of mesitylenephosphinous acid. H. J. M. Creighton (J. Physical Chem., 1926, **30**, 1209—1210).—The solubility of mesitylenephosphinous acid in water (g. per 100 g. of solution) increases from 0·289 at 1° to 0·700 at 85°. The conductance of the acid and of its sodium salt has been measured at 25° and Λ_∞ is given as 376. The value of the mass action constant decreases steadily with decreasing concentration of the acid. L. S. Theobald.

Mercury dropping electrodes. A. Frumkin and A. Donde (Z. physikal. Chem., 1926, **123**, 339—343).—The *P.D.* at the interface air/solution has been determined for aqueous solutions of various substances by an apparatus in which a fine stream of mercury from a capillary jet falls in drops down the axis of a vertical tube, along the walls of which flows the solution under investigation (cf. A., 1923, ii, 54). When the solute is not too volatile, the results agree satisfactorily with those obtained by using Kenrick's arrangement, and a stream of water in place of a stream of mercury. R. Cuthill.

Electrode potential and replacing power of manganese. H. D. Royce and L. Kahlenberg (Trans. Amer. Electrochem. Soc., 1926, **50**, 137—154).—Reproducible values of the potential of manganese against aqueous solutions of manganous salts can be obtained in the absence of oxygen by using a liquid or pasty manganese amalgam electrode which is stirred continuously. The potential is independent of the amalgam concentration above about 1·2% of manganese. Taking the potential of the normal calomel electrode as +0·560 volt and neglecting (apparently) the liquid junction potential, the following are some values obtained for the electrode potential of manganese against the solutions stated: 0·5*N*-manganous sulphate, −1·452 volt; *N*-manganous sulphate, −1·449 volt; *N*-manganous chloride, −1·436 volt; *N*-manganous nitrate, −1·232 volt. Manganese will replace from their salt solutions zinc and other metals which have more positive electrode potentials. H. J. T. Ellingham.

Dependence of the potential of the oxygen electrode on pressure. G. Tammann and F. Runge (Z. anorg. Chem., 1926, **156**, 85—93).—Exhaustive experiments on the dependence of potential on pressure in the so-called oxygen electrodes, platinised platinum, copper, or silver in oxygen, show that they are not true oxygen electrodes, but only oxide electrodes. It is probable that a true oxygen

electrode is realisable only at high temperatures. Such an electrode is that constructed by Haber, $O_2|Pt|glass|Pt|H_2$, the calculated potential of which, 1·152 volts at 575°, agrees with the experimental value. M. CARLTON.

_E.M.F._ measurements with cells of the type $M|MO|NaOH|H_2(Pt)$, and their application to the verification of Nernst's heat theorem. F. FRIED (Z. physikal. Chem., 1926, **123**, 406—428).—Measurements of the _E.M.F._ of the cell $Hg|HgO|NaOH|H_2(Pt)$ at 0°, 23·5°, 39°, and 58° have confirmed Brönsted's results (A., 1909, ii, 10), giving a value of −0·0003053 volt per degree for the temperature coefficient, and 46,880 g.-cal. for the heat of the reaction $HgO+H_2=Hg+H_2O$. Using the cell $Hg|HgO|NaOH|PbO|Pb$, the temperature coefficient of the _E.M.F._ of the cell $Pb|PbO|NaOH|H_2(Pt)$ at 0° is found to be −0·0003653 volt per degree, and the heat of the reaction $PbO+H_2=Pb+H_2O$ is 16,603 g.-cal. From these data, following the arguments of Eucken and Fried (A., 1925, ii, 97), it is shown that finite entropies must exist at 0° Abs. Attempts to measure the temperature coefficient of the _E.M.F._ of the cell $Ag|Ag_2O|NaOH|H_2(Pt)$ have not been very successful. R. CUTHILL.

Influence of temperature on the electrode potential of the decinormal calomel electrode. Y. KATSU (J. Biophys., 1924, **1**, 44).—The p_H is determined electrometrically by means of the relation $p_H=(\pi-\pi_0)/0·0001983T$, where π is the _E.M.F._ found against the 0·1_N_-calomel electrode and π_0 the constant for the calomel electrode at a given temperature T. The temperature coefficient of π_0 is found by using 0·1_N_-butyric acid as electrode liquid for the hydrogen electrode; $(\pi_0)_t=(\pi_0)_{18}-0·000002(t^2+9t-489)$. CHEMICAL ABSTRACTS.

Oxidation potentials of quaternary ammonium radicals and alkali metals in liquid ammonia. G. S. FORBES and C. E. NORTON (J. Amer. Chem. Soc., 1926, **48**, 2278—2285).—The oxidation potentials of 10 quaternary ammonium radicals in liquid ammonia were determined against silver in a saturated solution of silver nitrate in ammonia. The observed potentials, and those of lithium, sodium, and potassium in the same solvent, are all within 25 millivolts of one another, which accentuates the similarity between the fifth valency linking of nitrogen and the single linking of the alkali metals. The differences between the potentials are not readily correlated with chemical composition. S. K. TWEEDY.

Reduction potential of _iso_valeraldehyde. M. SHIKATA and I. TACHI (Proc. Imp. Acad. Tokyo, 1926, **2**, 226—228).—The reduction potential has been measured with the mercury dropping cathode and the polarograph (A., 1925, ii, 674). In neutral solution, the reduction occurs more readily than would be expected from theory. In slightly acid or neutral solution, desorption of the _iso_valeraldehyde from the mercury surface occurs, so that in concentrated solutions of neutral salts the reduction potential is scarcely changed. From the saturation curve, the solubility of _iso_valeraldehyde in water is calculated to be 0·4475 g.-mol./litre. By the above measurements extremely small quantities of the aldehyde can be detected. R. CUTHILL.

Geo-electrical phenomena. L. BRAUNER (Koll.-Chem. Beih., 1926, **23**, 143—151).—An apparatus is described for testing whether, and under what conditions, an electrical _P.D._ is developed in plant cells when their position in space is altered. Experiments with shoots and roots gave practically similar results. When the organ is placed horizontally, the under surface becomes at first negative with respect to the upper surface, and then, after about 15 sec., positive. The _P.D._ increases until in 10 min. a maximum value is reached, which, in the case of the _Helianthus_ hypocotyl, is 2·38 millivolts, and in the case of the seed root of _Vicia faba_, 2·00 millivolts. To decide whether the charge transference is due to the movement of statolithic starch or to the microsomes of the protoplasm, plant-tissue was boiled for a short time in water, and the dead tissue found to behave similarly to the living. The geo-electrical effect is therefore not due to the larger cell constituents. It is suggested that it may be caused by the unequal diffusion of ions through the cell-wall, cations being more diffusible (cf. Michaelis and Fujita, this vol., 120). _P.D._ measurements, made with sheets of parchment paper saturated with different electrolyte solutions in place of plant organs, support this theory. L. L. BIRCUMSHAW.

Electrochemical behaviour of aluminium. I. R. MÜLLER (Z. anorg. Chem., 1926, **156**, 56—64).—The conductivity of aluminium bromide in specially purified anhydrous pyridine and benzonitrile was measured by a combination of the methods used by Ulich (A., 1925, ii, 671) and by Lorenz and Klauer (Z. anorg. Chem., 1923, **136**, 121). Pyridine solutions show two conductivity minima; the mean value of Λ_∞ is 62·5. Above 42° the change in conductivity with temperature is linear, the temperature coefficient being −3·165. Benzonitrile solutions give Λ_∞ 72·5 (mean). A minimum occurs at about 350 litres. M. CARLTON.

Electrochemical behaviour of aluminium. II. Potential of the aluminium electrode in a solution of aluminium bromide in anhydrous pyridine and the solution equilibrium pyridine-aluminium bromide. R. MÜLLER (Z. anorg. Chem., 1926, **156**, 65—72).—The potential of aluminium and aluminium amalgam in a saturated solution of aluminium bromide in pyridine was determined using the Dolezalek electrometer. A silver electrode dipping in a 0·1_N_-solution of silver nitrate in pyridine was used for comparison.

The potential of aluminium amalgam was 0·3—0·33 volt more negative than that of the pure metal at 25°. The variation of the aluminium potential with temperature shows breaks corresponding with transition points.

This was confirmed by measurements of the solubility of aluminium bromide in pyridine. Five transition points correspond with $AlBr_3,3C_5H_5N$; $AlBr_3,6C_5H_5N$; $2AlBr_3,11C_5H_5N$; $2AlBr_3,15C_5H_5N$ and at 60° a mixture $AlBr_3$ with 10·8 (?) and 12·7 (?) C_5H_5N.

The _E.M.F._-solubility curves are parallel, but not

superimposed, due to a lag between attainment of solution equilibrium and the measurement of the potential. The fact that the aluminium potential runs parallel, on the whole, with the solubility of aluminum bromide supports the view that the concentration of aluminium ion in the solution determines the potential in accordance with Nernst's theory.

M. CARLTON.

Oscillographic study of anodic polarisation. V. H. L. SEARLE (Phil. Mag., 1926, [vii], **2**, 733—740).—The phenomenon of anodic polarisation and its application to the rectification of alternating currents has been examined by an oscillographic study of a cell comprising a nickel cathode and an aluminium anode with a saturated solution of ammonium phosphate as electrolyte. The rate of formation of the anodic films indicates that the rectifying action is incomplete. The final steady current density per volt increases with the area of the anode surface. The cutting off of the polarisation current is accompanied by a rapid recovery, indicating that the rectification of slow alternations would not be complete. The resistance of the anode is attributed almost entirely to the gas film formed on it.

A. E. MITCHELL.

Anodic behaviour of ferromanganese. A. N. CAMPBELL (Trans. Faraday Soc., 1926, **22**, 226—232).—The anodic behaviour of a ferromanganese alloy (C 6·9%, Si 0·66%, P 0·21%, Mn 77·9%) has been investigated in *M*-solutions of manganese sulphate, nitrate, and chloride, ferrous sulphate, and also of ferrous chloride containing a slight excess of free acid. Passivity was absent in the last named, possibly owing to the effect of the free acid. In the other cases, passivity, whilst never complete, was always observed at the ordinary temperature and was specially marked with manganese sulphate solution. The potential of visible oxygen discharge from a neutral electrolyte at the ordinary temperature was about +2·15 volts (abs.). This is near the potential of permanganate formation in manganese sulphate electrolyte, and such formation was observed. The passivity was destroyed by heating at 25°, and also by activating the anode by charging with hydrogen or by etching with sulphuric acid. The passivity was reduced by a superposed alternating current. In *N*-potassium hydroxide electrolyte at 15° and 75° there was no formation of manganate, and nothing entered into solution, but heavy slimes were formed. In other cases, both components entered into solution; the efficiency was often less than 100%, possibly owing to solution being followed by immediate precipitation. Under a gas discharge the anode disintegrated and ferromanganese is thus useless as an insoluble anode.

W. HUME-ROTHERY.

Propagation of combustion in gaseous mixtures. T. TERADA and K. YUMOTO (Proc. Imp. Acad. Tokyo, 1926, **2**, 261—263).—The combustion of mixtures of hydrogen with air or oxygen has been photographed, the ignition being effected by an electric spark. With a hydrogen–air mixture containing 12·5% of hydrogen, combustion is at first propagated most rapidly perpendicularly to the electrodes. Later, however, there is some acceleration along the line of the electrodes. With mixtures containing 7—9% of hydrogen the wave-front is not symmetrical with respect to the spark. If the electrodes consist of parallel fine wires, the wave-front is spherical except along the electrodes. If there is an electrically heated wire near the spark-gap, the combustion proceeds along it at a high speed.

R. CUTHILL.

Inflammability of hydrogen. I. Influence of ethyl bromide on the limits of inflammability of hydrogen–air mixtures. II. Influence of organic bromine and iodine compounds on the upper limit of inflammability of hydrogen–air mixtures. Y. TANAKA and Y. NAGAI (Proc. Imp. Acad. Tokyo, 1926, **2**, 280—282, 283).—I. Addition of small quantities of ethyl bromide to mixtures of hydrogen and air narrows the range of inflammability considerably, both the limiting concentrations of hydrogen being lowered. If more than 0·7% of ethyl bromide is present, Le Chatelier's rule is valid for the composition of the mixtures constituting the upper limit. It is considered that the action of the ethyl bromide is caused by it taking up energy from the activated molecules of the flame and so preventing the activation of the hydrogen.

II. Methyl and ethyl iodides and ethyl bromide lower the upper limit to about the same extent.

R. CUTHILL.

Inflammability of alkyl halides and their influence on the limit of inflammability of ether–air and hydrocarbon–air mixtures. Y. NAGAI (Proc. Imp. Acad. Tokyo, 1926, **2**, 284—288).—The observed effects resemble those which are manifested by ethyl bromide and mixtures of hydrogen and air (cf. preceding abstract). With mixtures of ethyl ether or methyl*cyclo*hexane and ethyl chloride, Le Chatelier's rule holds for the lower limit. This is not so, however, in the case of ethyl bromide and methyl and ethyl iodides. This difference in behaviour is probably connected with the fact that the conductivity of a hydrocarbon flame is greatly increased by addition of ethyl bromide, whilst ethyl chloride has little effect.

R. CUTHILL.

Effect of moisture and paraffin surface on the rate of reaction of nitric oxide and oxygen. R. L. HASCHE (J. Amer. Chem. Soc., 1926, **48**, 2253—2259; cf. Hasche and Patrick, A., 1925, ii, 681).—The speed of combination of dry nitric oxide and oxygen is reduced by 20% when the reaction chamber is coated as completely as possible with paraffin, possibly because the amount of moisture, which acts as a catalyst in the reaction, is decreased. Neither sulphur dioxide nor the reaction product has any appreciable effect on the reaction velocity. The induction period is a function both of the initial pressures and of the moisture content. The effect of the latter may be explained as follows: $NO+H_2O=NO,H_2O$; $NO,H_2O+NO=(NO)_2,H_2O$; $(NO)_2,H_2O+O_2=N_2O_4(\rightleftharpoons 2NO_2)+H_2O$. An induction period of 10 sec. occurs when the initial partial pressures are below 14 mm. of mercury. When the reaction chamber is covered with shellac, which is attacked by oxides of nitrogen, the reaction becomes more nearly bimolecular than termolecular.

S. K. TWEEDY.

Unimolecularity of the inversion process. G. SCATCHARD (J. Amer. Chem. Soc., 1926, **48**, 2259—2263).—The rate of inversion of sucrose increases slightly during the course of the reaction (Pennycuick, this vol., 249), so that the classical velocity equation, $r=-d\log y/dt$, cannot be integrated unless r is known as a function of t. By the application of accurate graphical methods to Pennycuick's results, the equation $r=k(1-0{\cdot}03e^{-0{\cdot}01t})$ is deduced, whence $dr/dt=\text{const.}\times(k-r)$. The latter equation for the change in rate indicates that equilibrium is attained in a process, originally somewhat displaced from equilibrium, for which the rate of attaining equilibrium is proportional to the displacement. From this it is concluded that the observed change in rate is due probably to slightly inefficient mixing; in homogeneous solution, the rates of sucrose inversion are probably constant to within a few parts per thousand. S. K. TWEEDY.

Reaction between picryl chloride and pyridine in alcoholic solution. F. W. HODGES (J.C.S., 1926, 2417—2423).—The reaction between picryl chloride and pyridine in alcoholic solution is bimolecular and involves the formation of an ionised additive compound $C_5H_5N,C_6H_2Cl(NO_2)_3$ (cf. Wedekind, A., 1902, i, 739). The main equilibrium reaction is accompanied by slow side reactions in which pyridine picrate and ethyl picrate are produced; the presence of water accelerates considerably the formation of pyridine picrate. A much slower side-reaction gives *picryl pyridinium picrate*, m. p. 226° (decomp.). Thus:—

$C_5H_5N+C_6H_2Cl(NO_2)_3 \rightleftharpoons C_5H_5{:}N(Cl){\cdot}C_6H_2(NO_2)_3$

$C_5H_5N+C_6H_2Cl(NO_2)_3+H_2O \longrightarrow C_5H_5{:}N(OH){\cdot}C_6H_2(NO_2)_3+HCl$

$C_6H_2Cl(NO_2)_3+EtOH \longrightarrow C_6H_2(NO_2)_3{\cdot}OEt+HCl$

$C_5H_5{:}N(OH){\cdot}C_6H_2(NO_2)_3+C_6H_2Cl(NO_2)_3 \longrightarrow C_6H_2(NO_2)_3{\cdot}N(:C_5H_5){\cdot}OC_6H_2(NO_2)_3+HCl.$

M. CLARK.

Kinetics of aquotisation. J. N. BRÖNSTED [with A. DELBANCO and K. VOLQUARTZ] (Z. physikal. Chem., 1926, **122**, 383—397).—The replacement of the acid group by water in a reaction such as $[CoNO_3(NH_3)_5]^{\cdot\cdot}+H_2O \longrightarrow [CoH_2O(NH_3)_5]^{\cdot\cdot\cdot}+NO_3'$ is defined as aquotisation (Aquotisierung). The aquotisation of the nitratopentamminecobalt ion, as followed by conductivity measurements at 15° and 20°, is a unimolecular reaction, and is independent of the acidity of the solution. The rates of aquotisation of the nitratoaquotetramminecobalt ion (at 15° and 20°) and of the chloroaquopentamminecobalt ion (at 20°) are, however, very sensitive to the presence of acid; this is ascribed to partial decomposition with the production of hydrogen ions, *e.g.*,

$[CoNO_3H_2O(NH_3)_4]^{\cdot\cdot} \rightleftharpoons [CoNO_3(OH)(NH_3)_4]^{\cdot}+H^{\cdot}$.

Both the hydroxo-ions thus formed, and the original aquo-ions can be directly aquotised, but the hydroxo-ion is aquotised far more rapidly, *i.e.*, about 10^6 faster, than is the aquo-ion. The velocity coefficients for the above reactions are calculated. L. F. GILBERT.

Method of investigating chemical reactions in the solid phase. N. SEMENOV and A. SCHALNIKOV (Z. Physik, 1926, **38**, 738—744).—Streams of cadmium vapour and sulphur vapour in a high vacuum were directed simultaneously on a tube cooled by liquid air. The deposit consisted of a most intimate mixture of solid cadmium and sulphur. In a short time, sudden combination took place, producing a small circular patch of cadmium sulphide, and this was followed by the formation of rings at intervals of a few seconds. When pentane at −130° was used to cool the tube this phenomenon was not observed, combination taking place without delay. With sodium in place of cadmium the results were similar. If films were deposited alternately and not simultaneously, the effect was not observed. If the cold tube was coated with a layer of "piccin" sufficiently thick to reduce the rate of cooling, the result was not obtained; if the cold tube was enclosed in a thick copper tube, the deposition lasted for half an hour before the sudden combination took place. E. B. LUDLAM.

Velocity of decomposition of solids. III. Rate of dissociation of silver carbonate. M. CENTNERSZWER and B. BRUZS (Z. physikal. Chem., 1926, **123**, 111—126; cf. this vol., 581).—The dissociation pressure of silver carbonate is 76 cm. at 219°, in good agreement with Colson's data (A., 1901, ii, 238). At temperatures between 239·5° and 252°, the crystalline carbonate decomposes in accordance with the unimolecular law, the temperature coefficient of the velocity constant being 2·14 for 10°. The rate of decomposition of the amorphous carbonate, which is much less than that of the crystalline form, first slowly falls to a constant value, at which it remains for some time, and then ultimately decreases to zero in the manner of a unimolecular reaction. In explanation, it is suggested that the reaction really occurs in two stages, the first of which—the formation of an oxycarbonate—is more rapid than the second—the decomposition of the oxycarbonate. The last stage of the reaction as actually observed then represents the decomposition of the oxycarbonate, whilst during the period of constant velocity the reduction in the rate of decomposition of the original carbonate is just balanced by the rise in the rate of dissociation of the oxycarbonate, due to its increasing mass. At 245°, the rate of decomposition of the amorphous carbonate is at a maximum, and between 245° and 260° the temperature coefficient is negative. This is explained by supposing that the oxycarbonate is stable only between 219° and 245°. Between 245° and 260°, less and less of it formed, whilst above 260° the reaction proceeds directly. The rate of recombination of silver oxide and carbon dioxide below 219° is shown to pass through a maximum value somewhere between 160° and 200°. R. CUTHILL.

Velocity of decomposition of solids. IV. Rate of dissociation of lead carbonate. M. CENTNERSZWER and A. AWERBUCH (Z. physikal. Chem., 1926, **123**, 127—133; cf. preceding abstract).—At 272°, 276°, and 282°, the speed of the above reaction first rises rapidly for about 7 min. to a maximum, then at once decreases in accordance with the simple unimolecular law. The period of induction is satisfactorily accounted for by assuming that the first stage of the reaction consists of a polymorphic change

of the carbonate (cf. this vol., 581). Traces of moisture accelerate the decomposition.

R. CUTHILL.

Formation of protective oxide films on copper and brass by exposure to air at various temperatures. W. H. J. VERNON (J.C.S., 1926, 2273—2282).—The rate of thickening of the film of oxide produced on copper by heating in the air at 75—250° is expressed by the equation $d \log W/dT = -Q/RT^2$ (cf. Dunn, this vol., 692) better than by Pilling and Bedworth's equation (B., 1923, 359A). Films produced by heating for 1 hr. at temperatures above 75° protect the metal from oxidation on subsequent exposure to the ordinary temperature, whereas films produced at lower temperatures are not protective. This suggests that a minimum film thickness is required for protection, and this minimum appears to be such that the unit lattice of oxide is completed over the whole surface. Protective films may be formed below 75° by prolonged exposure to a relatively pure atmosphere, but the rate of increase of thickness of film in this case is considerably greater than that taking place at 75°. Protective films may be formed on brass (60 : 40) by heating it at 200—400°, but the protection afforded is not nearly so great as in the case of copper. The rate of thickening of the oxide film on brass during heating is more nearly in accord with the exponential law of Pilling and Bedworth than with Dunn's equation.

A. R. POWELL.

Reaction velocity and the influence of constitution in the benzoylation of monohydric phenols. A. L. BERNOULLI and A. S. GOAR (Helv. Chim. Acta, 1926, **9**, 730—765).—The reaction velocity of the benzoylation of phenols has been measured, and the influence of temperature, excess of the reagents, catalysts, the benzoyl halide employed, and of various substituents in the phenol has been determined. No solvent was used, and the course of the reaction was followed either by absorption of the hydrogen halide evolved in a known volume of 0·5*N*-sodium hydroxide solution and titration of the excess of alkali at regular intervals, or by a control method involving the direct titration of the benzoyl chloride in aqueous solution with sodium hydroxide, using methyl-orange as an indicator, both methods giving the same values for the reaction constants. The main conclusions are as follows: even in such highly concentrated solution (0·1 mol. phenol : 0·1 mol. benzoyl chloride) the reaction is represented satisfactorily by the equation $dx/dt = k(a-x)^n$, the value of k at 25° being 0·0117. The mean value of the temperature coefficient between 25° and 95° is 1·782. Whilst the addition of an equal amount of pyridine (0·1 mol.) causes the reaction to proceed almost instantaneously with much evolution of heat, the addition of 0·01 mol. decreases the reaction velocity. An excess of phenol increases the velocity of the reaction, but excess of benzoyl chloride diminishes it. The use of benzoyl bromide or iodide in place of the chloride increases the velocity approximately proportionately to the atomic weight of the halogen used, but substitution of the nitro-group in the *m*- or *p*-positions greatly decreases the velocity. In general, the introduction of substituents into the phenol increases its stability towards benzoyl chloride, the effect being greatest in the *o*-, least in the *p*-, and intermediate in the *m*-position, these conclusions being based on a study of the cresols, chloro- and nitro-phenols. *p*-Chlorophenol is more stable than the *p*-bromo-compound, the relative values of the two reaction constants again being approximately proportional to the atomic weights of the two halogens. The following new data are given incidentally in the course of the investigation: benzoyl iodide, d^{15} 1·772; *o*-tolyl benzoate, d^{15} 1·5726; phenyl *m*-nitrobenzoate, m. p. 97·5—98°; phenyl *p*-nitrobenzoate, m. p. 127·5°, *m*-chlorophenyl benzoate, m. p. 70°.

J. W. BAKER.

Kinetics of the fission of diketopiperazine. H. VON EULER and E. PETTERSSON (Z. physiol. Chem., 1926, **158**, 7—14).—The reaction diketopiperazine → glycylglycine at 60° in the presence of a phosphate as buffer-salt is followed by titrations of free carboxyl after addition of formaldehyde (Sörensen, A., 1908, i, 115), and a stability curve for values of p_H between 1 and 10 at 60° is drawn.

C. HOLLINS.

Theory of catalysis. III. Inversion of sucrose by dilute hydrochloric acid. H. VON EULER and A. ÖLANDER (Z. anorg. Chem., 1926, **156**, 143—152; cf. A., 1925, ii, 876; this vol., 580).—In continuation of earlier work, the inversion of sucrose is studied at 25° and 40°. Results are tabulated and the temperature coefficients of the inversion for catalysis by enzymes and non-enzymes are compared.

M. CARLTON.

Action of varying quantities of arsenate on phosphorylation. C. NEUBERG and M. KOBEL (Biochem. Z., 1926, **174**, 493—496).—Potassium arsenate inhibits the combination of sucrose with phosphoric acid, the effect being proportional to the concentration of the arsenate.

E. C. SMITH.

Interaction of sulphur dioxide and hydrogen sulphide. E. MATTHEWS (J.C.S., 1926, 2270—2273).—Pure dry hydrogen sulphide does not react with pure dry sulphur dioxide either in the liquid or in the gaseous state, a third substance in the liquid phase being necessary to bring about the interaction. That the capacity of this substance to influence the reaction is not dependent on its dielectric constant has been proved by tests with 34 liquids having dielectric constants between 2 and 75. Apparently, the factor governing the catalytic activity of the third substance is either its solubility in the liquid mixture of the two gases or, alternatively, the solubility of the two gases in the substance, if a liquid.

A. R. POWELL.

Acid and salt effects in catalysed reactions. I. H. M. DAWSON and J. S. CARTER (J.C.S., 1926, 2282—2296).—The p_H values of solutions containing acetic acid and sodium acetate as measured by electrometric methods are in close agreement with those calculated by the mass law, but a slight divergence is noticeable in the case of solutions containing monochloroacetic acid and its sodium salt, although the difference is very small when the salt concentra-

tion does not exceed 0·2*N*. Measurements of the velocity of the reaction between acetone and iodine in the presence of acetic or monochloroacetic acid and the corresponding sodium salt indicate that the reaction is catalysed by the hydrogen ion, the undissociated acid, the acid ion, and the hydroxyl ion, and that the reaction velocities may be expressed in the form: $v=k_h[H]^+ + k_m[HA] + k_a[A]^- + k_{OH}[OH]^-$. In solutions in which the salt concentration is very low, the last-named term of the equation is negligible; when the converse is the case and the acid concentration is small, the coefficient k_{OH} is much greater than the other three and the catalytic activity of the hydroxyl ion may be 20,000 times as great as that of the hydrogen ion. Suitable conditions may also be found in which the undissociated acid or the acid ion plays the dominant rôle, but no evidence that the sodium cation has any measurable activity could be found. By the addition of an inert salt to the acetic acid–sodium acetate mixture changes are produced in the velocity of the reaction to an extent that depends on the relative magnitudes of the effects attributable to the positive and negative ions and to the undissociated molecule, respectively.

A. R. Powell.

Decomposition of nitrosotriacetoneamine in presence of hydroxyl ion. I. Region of small concentrations of alkali. J. Colvin (Trans. Faraday Soc., 1926, **22**, 241—246).—The velocities of decomposition of nitrosotriacetoneamine in aqueous solutions containing glycerol have been measured. The hydroxyl ion acts as a catalyst and was introduced in the form of potassium hydroxide of concentration less than 0·05*N*. The activity of the nitrosotriacetoneamine was estimated from the molar fraction, and also from direct measurements of the solubility in water–glycerol mixtures; the two methods gave results in good agreement. The measurable reaction probably consists of a unimolecular decomposition of a complex formed between the nitrosotriacetoneamine and the hydroxyl ion. The critical increment is calculated as approximately 16,000 g.-cal., but this value includes the heat of dissociation of the complex, which must be known if the true critical increment is desired. The mechanism suggested is in agreement with the theory of induced alternate polarities if the oxygen of the carbonyl group is assumed to be negative.

W. Hume-Rothery.

Thermal decomposition of methane at a glowing filament. G. M. Schwab and E. Pietsch (Z. Elektrochem., 1926, **32**, 430—434).—In the investigation previously described (this vol., 918) the ratio, ε, of effective to total collisions on the filament varies with temperature according to the expression $\log \varepsilon = 4{\cdot}55 - 1200/T$, whence is calculated the heat of activation, 50,000—60,000 g.-cal. This value is too low to correspond with $CH_4 = C(solid) + 4H(gas)$ as the primary reaction, but $CH_4(adsorbed) = C(solid) + 4H$ (adsorbed) is possible, since, according to Pólányi's theory of catalysis (cf. A., 1921, ii, 179), the heat of dissociation of a substance is notably reduced when it is in the adsorbed condition in that its free valencies are largely satisfied.

The rate of thermal decomposition is accelerated in an electric field when the *P.D.* across the gas exceeds 15—16 volts. This gives about 360,000 g.-cal. as the energy required to decompose methane by electron impact and corresponds approximately with the value for $CH_4 = C(atomic) + 4H(gas)$.

H. J. T. Ellingham.

Catalytic combustion. III. Influence of steam on the catalytic combustion of carbon monoxide. W. A. Bone (Proc. Roy. Soc., 1926, **A, 112**, 474—499; cf. this vol., 250).—Progressive drying of a system in which a mixture of carbon monoxide and oxygen is undergoing catalytic combustion at temperatures up to 500° on the surface of gold gauze, silver foil, porous porcelain, firebrick, cupric oxide, or nickel oxide causes at first an increase in the reaction velocity, probably due to the removal from the surface of a film of water, with consequent increase in surface area. With the first three substances, further drying results in a gradual fall in the reaction velocity to zero or very near it. If water is now introduced into the system, the catalytic activity of the gold and silver gradually returns to its original value, but that of the porcelain proves to have been completely destroyed, possibly due to some structural change. These effects are difficult to explain on the theory that such cases of catalytic combustion depend on the formation of an oriented unimolecular layer of the reacting gases on the surface. If, however, the function of the surface is to bring about the ionisation of the reacting gases, which in the neutral state are incapable of combination, water will promote the reaction by preventing the reversion of the ionised molecules to the neutral state. R. Cuthill.

[Catalytic] reduction of carbon monoxide. H. Tropsch, A. Schellenberg, and A. von Philippovich.—See B., 1926, 776.

Reduction of carbon monoxide by hydrogen in contact with a heated iron spiral in a hot–cold tube. F. Fischer and A. Jaeger.—See B., 1926, 777.

Catalytic removal of oxygen from gas mixtures containing hydrogen. J. A. Almquist and E. D. Crittenden.—See B., 1926, 820.

Displacement of equilibria by substances which simultaneously act as [catalytic] accelerators. N. Schlesinger (Ber., 1926, **59**, [*B*], 1965—1975).—Examination of the effect of lithium sodium, calcium, and potassium chlorides on the equilibrium between ethyl acetate and its hydrolytic products in aqueous solution at 100° in the presence of 0·2*N*-hydrochloric acid as catalyst shows that, not only is the attainment of equilibrium facilitated, but also its position is displaced, sometimes considerably, by the catalysts. The effect cannot be attributed to the withdrawal of varying amounts of water from the system by the formation of hydrates, and is probably explicable along the lines laid down by Debye and McAulay (A., 1925, ii, 171). The values of the equilibrium constants agree satisfactorily when obtained from either direction, provided reaction is not too prolonged, whereby complications ensue due to the production of diethyl ether. The value of the

equilibrium constants in the presence of sodium, lithium, or calcium chloride is expressed with sufficient accuracy by the linear formula $K=3045-21{\cdot}217c$ (c=salt content in millimols. or for calcium chloride in milliequivalents per mol. of water). With very concentrated lithium chloride solution, the equation probably does not hold. Potassium chloride has a less pronounced effect. At the highest salt concentrations examined the equilibrium constant is depressed to less than half of its normal value.

H. WREN.

Catalytic oxidation of hydrocyanic acid. II. H. SINOZAKI and R. HARA (Tech. Rep. Tôhoku Imp. Univ., 1926, **6**, 95—129).—Continuing previous work (A., 1925, ii, 983), the oxidation of hydrogen cyanide by air to nitric oxide has been examined by a streaming method with reference to the following catalysts, the mode of preparation of which is described: porcelain, silica, platinised asbestos, ferric oxide, ferric and bismuth oxides (5—30%), cobalt oxide, cobalt (85%) and bismuth oxides, copper oxide, chromic oxide, nickel oxide, manganic oxide, manganese dioxide (85%) with copper oxide. Porcelain and silica were practically ineffective. Data are given describing in detail the behaviour of each catalyst with respect to the hydrogen cyanide concentration in the air mixture, the gas velocity, and the temperature. The results are held to sustain the authors' view that cyanic acid is an intermediate stage in the oxidation. R. W. LUNT.

Catalytic action of Japanese acid earth. II. Action of oximes. H. INOUE (Bull. Chem. Soc. Japan, 1926, **1**, 177—179).—Acetophenoneoxime reacts violently in presence of Japanese acid earth at 180°, giving benzonitrile, acetic and benzoic acids, ammonia, aniline, acetophenone, and acetanilide among the reaction products, whilst the oximes of benzophenone and menthone behave similarly at 145° and 200°, respectively, to give analogous products.

Evidence is adduced to show that the Beckmann transformation is one of the principal reactions of oximes in presence of Japanese acid earth at 150—200°, the aniline, acids, and nitrile formed resulting from the hydrolysis of the anilides so formed.

A. S. CORBET.

Catalytic transformation of fatty acids into hydrocarbons. G. A. STADNIKOV and E. E. IVANOVSKII (Trans. Karpov Inst. Chem. [Moscow], 1925, No. 4, 175—187).—A mixture of fatty acids, obtained by the hydrolysis of linseed oil, was used, it being considered that unsaturated fatty acids would be more likely than saturated acids to form naphthenic hydrocarbons. The acids were passed, in an atmosphere of hydrogen, over reduced iron spread on asbestos and heated at 400°. Carbon dioxide, and only small quantities of carbon monoxide, were formed. The product (76% of the acids employed) had acid value 3—5 and iodine value 98—105 (corresponding with original values of 188 and 179, respectively), indicating decomposition at the double linkings as well as loss of carboxyl groups. The product consisted essentially of paraffin hydrocarbons, the amount of cyclic hydrocarbons being insignificant. Whilst it is likely that petroleums of the aliphatic series were formed by decomposition of animal fats, naphthenic petroleums must have originated otherwise. CHEMICAL ABSTRACTS.

Copper at low temperatures. G. J. ALEXANDER (Nature, 1926, **118**, 590—591).—When copper (but not lead, iron, tin, platinum, or aluminium) is immersed in liquid air, a sudden, short re-evolution of gas occurs after equilibrium has apparently been reached. The effect is possibly due to surface action or to an allotropic change. A. A. ELDRIDGE.

Electrolytic preparation of perborate. D. V. STEPANOV.—See B., 1926, 786.

Action of metals on nitric acid. E. J. Joss (J. Physical Chem., 1926, **30**, 1222—1275; cf. Bancroft, A., 1924, ii, 745).—A long, theoretical discussion of the electrolytic theory of the reduction of nitric acid supported by the data of many investigators is given. The action of metals on nitric acid is considered to be a special case of the electrolytic theory of corrosion. Many metals are identical in their chemical and electrochemical reactions when disturbing factors are eliminated. The true depolariser in the action of metals on nitric acid is nitrosic acid, $H_2N_2O_5$. The reduction of intermediate products is critically examined and a schematic representation of these products in the case of nitric acid is given.

L. S. THEOBALD.

Preparation of glyoxylic acid from oxalic acid. W. MOHRSCHULZ (Z. Elektrochem., 1926, **32**, 434—454).—A detailed study of the electrolytic reduction of oxalic acid in aqueous solutions to glyoxylic acid. The best results are obtained when: (1) the electrolyte contains 2—2·5% of sulphuric acid; (2) the cathode material has a high hydrogen overvoltage; mercury is better than lead and no reduction occurs at copper or nickel; (3) the temperature is below 25° and preferably about 10°; (4) the current density is high within the range investigated (2—8 amp./dm.^{2}); (5) electrolysis is stopped before the oxalic acid concentration becomes low, since otherwise the current efficiency is greatly reduced. Under such conditions a 6·5% oxalic acid solution yields a solution containing 3% of glyoxylic acid and 2% of oxalic acid, together with glycollic acid and very probably dihydroxytartaric acid, 82% of the oxalic acid reduced being converted into glyoxylic acid at a current efficiency of 75·5%. By continuous addition of oxalic and sulphuric acids during electrolysis a solution containing 12·3% of glyoxylic acid has been obtained with a bath voltage of 9 volts and an energy expenditure of 11·25 kw.-hrs./kg. of glyoxylic acid. From the final solution sulphuric acid is removed with barium carbonate and oxalic acid with calcium carbonate; calcium glyoxylate crystallises, the glycollate remaining in the mother-liquors.

Reduction of oxalic acid solutions with sodium amalgam is superior to the above electrolytic method in that glyoxylic acid is practically the sole product, and by using a sodium–zinc amalgam 93% of the total oxalic acid in solution can be reduced. The concentration of glyoxylic acid in the final solution is lower than that obtainable by the electrolytic method, but recovery of the glyoxylic acid from it is easier.

A method of determining glyoxylic acid as the semicarbazone has been worked out. Dibromoacetic acid, from which pure glyoxylic acid was prepared for this purpose, was obtained by heating solid dibromomalonic acid at about 125°, thus obtaining a better yield (about 85%) than by decomposing the latter in aqueous solution.

H. J. T. ELLINGHAM.

Preparation of amino-acids by electro-reduction of oximino-esters. A. ANZIEGIN and W. GULEWITSCH [with K. NORDHEIM] (Z. physiol. Chem., 1926, **158**, 32—41).—Yields of 50—80% are obtained by the electro-reduction of oximino-esters in a closed Tafel apparatus with a prepared lead cathode, the electrolyte being 50% sulphuric acid maintained below 27° by cooling in ice and salt. β-Aminobutyric acid (copper salt, $+4H_2O$), *β-aminovaleric acid*, m. p. 178—179° (*copper* salt, $+2H_2O$; *benzoyl* derivative, m. p. 145—146°; p-*nitrotoluene*-o-*sulphonyl* derivative, m. p. 185—188°; *β-naphthalene-sulphonyl* derivative, m. p. 134·5°), and γ-aminovaleric acid, m. p. 199° (benzoyl derivative, m. p. 131·5°; p-*nitrotoluene*-o-*sulphonyl* derivative, m. p. 161°), are prepared in this way. The *phenylcarbamido*-derivative, m. p. 141·5°, of β-aminovaleric acid is converted by evaporation of its aqueous solution into 1-*phenyl*-4-*ethyldihydrouracil*, m. p. 201—202°. The corresponding 2-thiodihydrouracil, m. p. 210°, results when the β-amino-acid is heated with phenylthiocarbimide at 140°. *β-α-Naphthylcarbamidovaleric acid*, m. p. 145—146°; *γ-α-naphthylcarbamidovaleric acid*, m. p. 156°. C. HOLLINS.

Electrochemical chlorination and bromination of benzene. C. W. CROCO and A. LOWY (Trans. Amer. Electrochem. Soc., 1926, **50**, 257—268).—When suspensions of benzene in hydrochloric acid are electrolysed, chlorobenzene and a little *p*-dichlorobenzene are produced. The yield of the former is increased by heating (optimum 45°), and by increasing the current density, rate of stirring, and time of reaction. Using 125 c.c. of concentrated hydrochloric acid and 50 c.c. of benzene, with a current density of 14·5 amp. per dm.^{2} at 45° for 3 hrs., the current efficiency was 74·9%. Bromobenzene is obtained in a similar way; the yield is improved by increasing the temperature and time of reaction, by using iron as a carrier, and by decreasing the concentration of benzene. Using 125 c.c. of 48% hydrobromic acid and 50 c.c. of benzene with a current density of 11·66 amp. per dm.^{2} at 60° for 9·3 hrs., the current efficiency was 22·5%. The effect of electrolysis is principally to liberate chlorine or bromine, since comparison experiments in which the halogens were introduced directly gave almost identical results. Iodobenzene could not be prepared in this way. H. E. F. NOTTON.

Electrolytic oxidation of *p*-bromotoluene and *o*-nitrotoluene. J. F. CONN and A. LOWY (Trans. Amer. Electrochem. Soc., 1926, **50**, 207—218).—*p*-Bromotoluene and *o*-nitrotoluene have been electrolytically oxidised in 20% nitric acid solution at 100° with platinum electrodes. Using a current density of 0·5 amp. per dm.^{2}, the former gave *p*-bromobenzoic acid with a current efficiency of 115·75%, together with a small quantity of a *substance*, m. p. 216° (? pp′-*dibromo*-oo′-*ditolyl*). The high current efficiency is due to the action of the solvent on the intermediate products of oxidation. *o*-Nitrotoluene, unlike the *p*-derivative (A., 1924, i, 639), yielded at the most only 4·3% of the corresponding acid, the main product being resinous matter, with some oxalic acid and carbon dioxide. H. E. F. NOTTON.

Electrochemical reduction of indigo. J. NEVYAS and A. LOWY (Trans. Amer. Electrochem. Soc., 1926, **50**, 245—256; cf. A., 1884, 942, 1448; 1908, i, 107).—An apparatus is described in which the electrochemical reduction of finely-divided indigo suspended in sodium hydroxide solution may be studied quantitatively. The current efficiency is very small at the ordinary temperature, but it is increased by increasing the temperature, rate of stirring, and concentration of alkali, and by decreasing the current density. These results favour the theory that the reduction is due to the dissolved indigo reacting with atomic hydrogen. When a 1% suspension of indigo in 20% sodium hydroxide solution is electrolysed for 4 hrs. at 105° with a current density of 0·08 amp. per dm.^{2}, a current efficiency of 94% is attained during the last 2 hrs.

H. E. F. NOTTON.

Photo- and radio-chemical interaction of hydrogen and chlorine. F. PORTER, D. C. BARDWELL, and S. C. LIND (J. Amer. Chem. Soc., 1926, **48**, 2603—2618).—The rates of reaction of hydrogen and chlorine in mixtures exposed to light and to α-rays indicate that in each case a chain reaction occurs, the chains being of the same length in mixtures of the same sensitivity. The results offer independent support of Einstein's law of photochemical equivalence. Two inhibitors appear to be present, oxygen and possibly chlorine monoxide. The apparently high temperature coefficients are due to the sensitivity increase accompanying rise in temperature; they are made up of a true temperature coefficient and of the retarding effect of the inhibitors as enhanced by higher temperatures.

S. K. TWEEDY.

Influence of water on the combination of the halogens with hydrogen. B. LEWIS and E. K. RIDEAL (J. Amer. Chem. Soc., 1926, **48**, 2553—2564).—The primary combination in the above system probably occurs between atoms of halogen and hydrogen, the former being produced by the collision of excited molecules with water molecules. Whilst water is essential for starting a "chain," it is probably not necessary for chain propagation. The thermal and photochemical union of hydrogen and bromine and the thermal combination of hydrogen and iodine can be stopped by desiccation. The decomposition of hydrogen iodide, however, may proceed in the absence of water (Coehn and Tramm, A., 1923, ii, 205); in this case, desiccation appears to shift the equilibrium, the reversible process being rendered irreversible. The reaction between hydrogen and iodine is considered to proceed as follows: $I_2 \rightleftharpoons 2I$; $I+I_2 \rightleftharpoons I_3$; $I_3+I \rightleftharpoons 2I_2$; $I_3+H_2 \rightarrow 2HI+I$ (low temperatures); $I+H_2 \rightarrow HI+H$. This system is photochemically sensitive at high

temperatures (450°), in agreement with theory. The chain mechanism of the combination of hydrogen and bromine can be detected at high temperatures and hydrogen pressures. If the life of an excited bromine molecule is 10^{-7} sec., the maximum rate of combination with hydrogen is calculated to occur when the water-vapour pressure is 0·1 mm.

S. K. TWEEDY.

Mechanism of photochemical processes. V. Surface catalysis in the photochemical production of hydrogen chloride. A. COEHN and G. HEYMER (Ber., 1926, **59**, [*B*], 1794—1798; cf. Coehn and Jung, A., 1923, ii, 206; Norrish, *ibid.*, 1925, ii, 1080, 1179).—Two types of apparatus are described in which a mixture of hydrogen and chlorine is exposed to visible light without opportunity of coming into contact with a solid surface. The formation of hydrogen chloride in these circumstances proves that the reaction does not depend on an initial catalysis at a glass wall. H. WREN.

Photochemical technique. III. Quartz mercury lamp. P. W. CUNLIFFE, R. G. FRANKLIN, R. E. W. MADDISON, and L. REEVE (J. Physical Chem., 1926, **30**, 1427—1431; cf. A., 1925, ii, 809).—Data concerning various lamps used are given together with the percentage total radiation emitted by each line in the wave-length range 2480—5790 Å. The intensity of the radiation 2890—2480 Å. is considerably reduced during the first 500 hrs. of the life of the lamp. Below 2480 Å., loss is less rapid, but still sufficient to entail a redetermination of the energy distribution every 200 hrs. in quantitative work. The useful life of a lamp is given as 1000 hrs.

L. S. THEOBALD.

Iodised salt. III. T. VON FELLENBERG (Biochem. Z., 1926, **174**, 364—372).—The addition of potassium iodide to moist commercial sodium chloride results in unequal distribution on keeping, the upper layers of the salt becoming slightly, the lower layers considerably, richer in iodine. A slight total loss of iodine occurs. E. C. SMITH.

Cupric-ammine compounds. W. LANGE (Ber., 1926, **59**, [*B*], 2107—2113; cf. Ephraim and Jahnsen, A., 1915, ii, 167).—The following salts are described; *copperpentammine fluoborate hemihydrate*, $Cu(BF_4)_2,5NH_3,0{\cdot}5H_2O$; *coppertetrammine fluoborate*, m. p. 188°, and its *dihydrate*; *coppermonoammine-diethylenediammine fluoborate*, $Cu(BF_4)_2,2\ en,NH_3$; *copperdiethylenediammine fluoborate*, m. p. 243°; the pyridine *compounds*, $Cu(BF_4)_2,4C_5H_5N$; $Cu(BF_4)_2,4C_5H_5N,2H_2O$, and $Cu(BF_4)_2,6C_5H_5N,2H_2O$; coppertetrammine chlorate, m. p. 142—145° after softening at 120°; *copperdiethylenediammine chlorate*, decomp. 168—173°; *coppertetrammine iodate dihydrate*; *copperdiethylenediammine iodate dihydrate*; *copperdiethylenediammine perchlorate hemihydrate*, decomp. 245°; *coppermonoamminediethylenediammine perchlorate hemihydrate*; *coppermonoammine-diethylenediammine fluorosulphonate hemihydrate*; *coppertetrammine amidosulphonate*; *copperdiethylene-diammine amidosulphonate monohydrate*, m. p. (hydrated) 110°; anhydrous 200°; *coppertetrammine selenate dihydrate*; *copperdiethylenediammine selenate*.

H. WREN.

Stability of bleaching powder. D. V. STEPANOV.—See B., 1926, 786.

Rare earth borates and phosphates. G. CANNERI (Gazzetta, 1926, **56**, 450—454).—An investigation of compounds formed in the bead reactions of the rare earths. The *borates* $M_2B_6O_{12}$ ($M_2O_3,3B_2O_3$), $M_2B_4O_9$ ($M_2O_3,2B_2O_3$), and $M_2B_2O_6$ (M_2O_3,B_2O_3), and the *phosphates*, MPO_4, of cerium, lanthanum, neodymium, praseodymium, and yttrium were prepared. The salts of neodymium are rose to violet in colour, and those of praseodymium green; all are insoluble in water or dilute acid. E. W. WIGNALL.

Complex compounds of tervalent thallium. E. KRAUSE and A. VON GROSSE (Ber., 1926, **59**, [*B*], 1712—1717).—Stable, complex compounds of thallium are prepared by the action of bromine on thallium dialkyl halides in the presence of pyridine or, more conveniently, by the action of halogen on thallous halide in pyridine in presence of the requisite alkyl halide. Pyridine may be replaced by quinoline. The following compounds are described: *n-butylpyridinium tetrabromothalliate*, $[C_5H_5N{\cdot}C_4H_9][TlBr_4]$, m. p. 119·2°, and thence by means of alcoholic sodium iodide the corresponding *tetraiodo*-compound, m. p. 193·5°; *n-propylpyridinium tetrabromothalliate*, m. p. 118°, and *n-propylpyridinium tetraiodothalliate*, m. p. 127·5°; *ethylpyridinium tetrabromothalliate*, m. p. 119°, and *ethylpyridinium tetraiodothalliate*, m. p. 129·5—130°; *methylpyridinium tetrabromothalliate*, m. p. 171—171·5°, and *methylpyridinium tetraiodothalliate*, phosphorus-red crystals, m. p. 131·5—132°, and an unstable, pale red *modification*. H. WREN.

Action of silica on electrolytes. J. N. MUKHERJEE (Nature, 1926, **118**, 517).—Polemical (cf. Joseph, J.C.S., 1923, **123**, 2027; A., 1925, ii, 383; this vol., 132). A. A. ELDRIDGE.

Silica and its hydrates. R. SCHWARZ (Z. Elektrochem., 1926, **32**, 415—419).—Preparations of silicic acid obtained from various sodium silicates as previously described (A., 1924, ii, 753; 1925, ii, 222) lose water under the vacuum pump and yield definite hydrates of silica. A preparation from $Na_2Si_2O_5$ yields at 17° $H_2Si_2O_5$, whilst preparations from Na_2SiO_3 and Na_4SiO_4 both yield at 0° H_2SiO_3. The compound H_4SiO_4 has not been isolated. At about 45°, H_2SiO_3 undergoes irreversible decomposition, giving $H_2Si_2O_5$, and the latter at about 80° yields irreversibly $H_2Si_3O_7$. This dehydration in well-defined stages confirms previous conclusions (*loc. cit.*). The degree of hydrolysis of aqueous Na_2SiO_3 solutions has been determined at three different concentrations.

H. J. T. ELLINGHAM.

Pyrogenic preparation of sulphides, particularly silicon disulphide and boron sulphide, by means of aluminium sulphide. E. TIEDE and M. THIMANN (Ber., 1926, **59**, [*B*], 1703—1706; cf. Biltz, A., 1925, ii, 986).—Silicon disulphide, m. p. 1090°, *d* 2·02, is prepared by heating a mixture of aluminium sulphide and excess of quartz sand in a current of nitrogen at 1200—1300°; silicon monosulphide is simultaneously produced and separated from the disulphide by taking advantage of its different volatility. Boron sulphide is similarly pro-

duced from boron trioxide and separated from silicon disulphide (derived from the apparatus) by its greater volatility. Lead sulphide is formed at 1150°. Zinc sulphide, produced in this manner at 1400°, is invariably mixed with silicon disulphide, from which it cannot be separated by fractional sublimation.

H. WREN.

Silicon and nitrogen. L. WÖHLER (Z. Elektrochem., 1926, **32**, 420—423).—Mainly a review of existing knowledge concerning calcium and magnesium silicides (cf. A., 1922, ii, 293; this vol., 368), silicon nitrides and silicon analogues of cyanamide, calcium cyanamide, and calcium cyanide (cf. A., 1924, ii, 473). The dissolution of calcium silicocyanamide in hot, dilute hydrochloric acid is believed to proceed according to the equations: $CaSiN_2+2HCl=CaCl_2+SiN\cdot NH_2$ and $SiN\cdot NH_2+4H_2O=2NH_3+H_4SiO_4$. Silicamide, $SiO(NH_2)_2$, is a probable intermediate product. H. J. T. ELLINGHAM.

Additive compounds of tin and titanium halides with organic bases. II. G. SCAGLIARINI and M. MONTI (Atti R. Accad. Lincei, 1926, [vi], **4**, 210—214; cf. A., 1925, i, 890; this vol., 310).—The following additive compounds containing hexamethylenetetramine are described: $SnI_4,6C_6H_{12}N_4,3C_2H_2Cl_4$; $SnI_4,2C_6H_{12}N_4$; $SnBr_4,4C_6H_{12}N_4,C_2H_2Cl_2$; $SnBr_4,4C_6H_{12}N_4,C_2H_2Cl_4$; $SnBr_4,6C_6H_{12}N_4,CHCl_3$; $SnBr_4,C_6H_{12}N_4,CHCl_3$; $2TiBr_4,7C_6H_{12}N_4$; $2TiCl_4,7C_6H_{12}N_4,C_2H_2Cl_2$. Werner's co-ordination theory furnishes no satisfactory interpretation of these compounds. In accordance with Debye and Hückel's views (Physikal. Z., 1925, **26**, 96), those compounds in which the halide or the halogenated solvent preponderates over the organic base are usually the more intensely coloured.

T. H. POPE.

Cerous thallous sulphates. F. ZAMBONINI and S. RESTAINO (Atti R. Accad. Lincei, 1926, [vi], **4**, 175—181).—Investigation of the system $Ce_2(SO_4)_3$–Tl_2SO_4–H_2O shows the existence of the compound $Ce_2(SO_4)_3,4{\cdot}5Tl_2SO_4$ (cf. Fernandes, A., 1924, ii, 861), which is stable in contact with solutions containing more than 2·5% of thallous sulphate and corresponds in form with the analogous lanthanum thallous sulphate (A., 1925, ii, 579). T. H. POPE.

Tetraphosphorus triselenide. J. MAI (Ber., 1926, **59**, [*B*], 1888—1889).—Tetraphosphorus triselenide, m. p. 242°, is readily prepared by the action of yellow phosphorus on powdered selenium in boiling tetrahydronaphthalene. The crude substance crystallises from the solution and is purified by extraction with a mixture of carbon disulphide and light petroleum. The selenide appears to exist in two modifications, but the tetrahydronaphthalene reduces the temperature of reaction to such an extent that only the form stable at the lower temperature is obtained.

H. WREN.

[Hydrides of bismuth and tin.] W. STRECKER and W. DANIEL (Ber., 1926, **59**, [*B*], 1691—1695).—The product obtained by Weeks and Druce (A., 1925, ii, 988) by the action of zinc and hydrochloric acid or aluminium and excess of potassium hydroxide on bismuth chloride is not a bismuth hydride and does not appear to be an unstable adsorption compound or to contain occluded hydrogen. When heated, it does not evolve gaseous bismuth hydride. Analogously, the existence of a solid tin hydride (cf. Weeks and Druce, *loc. cit.*) could not be confirmed.

H. WREN.

Solid hydrides of bismuth and tin. J. G. F. DRUCE and E. J. WEEKS (Chem. News, 1926, **133**, 243—244).—A reply to Strecker and Daniel (see preceding abstract).

Influence of a current of inert gas on the decomposition of sulphuretted solutions; application to mineral waters. A. DESGREZ, L. LESCŒUR, and (MLLE.) S. MANJEAN (Compt. rend., 1926, **183**, 537—540).—Free gaseous hydrogen sulphide may be removed from solutions by bubbling through them a regular stream of an inert gas such as hydrogen or nitrogen. The gas evolved in successive intervals of time may be measured from the iodometric titration of the zinc sulphide precipitated when the mixture is bubbled through zinc acetate solution. Experiments with simple solutions of hydrogen sulphide, and with solutions to which sufficient sodium hydroxide had been added to produce sodium hydrosulphide and sodium sulphide, indicate that the free gas is removed from solution quickly, whilst in the case of the hydrosulphide it is evolved more slowly as a result of hydrolysis according to the equation $NaHS+H_2O=NaOH+H_2S$. Sodium sulphide decomposes at a still slower rate, the above reaction being preceded by the following, $Na_2S+H_2O=NaOH+NaHS$. A method is thus suggested for the determination of the nature of mineral waters.

J. GRANT.

Pyrosulphuryl chloride. V. GRIGNARD and P. MURET (Compt. rend., 1926, **183**, 581—585).—Pyrosulphuryl chloride has been prepared by the action on sulphuric or chlorosulphonic acid of carbon tetrachloride at 80°. A little pyrosulphuryl chloride may be added to start the reaction, since it acts as a solvent for the carbon tetrachloride. The chlorosulphonic acid is destroyed by the addition of excess of carbon tetrachloride at the end of the reaction. The pyrosulphuryl chloride is then purified by distillation under reduced pressure (b. p. 57°/30 mm. and 52°/15 mm.), and is a hygroscopic substance with a characteristic odour; d^{19} 1·834 and n_D^{19} 1·449. Vapour-density determinations at various temperatures indicate that decomposition follows the irreversible equations, $S_2O_5Cl_2=SO_3+SO_2+Cl_2$ and $S_2O_5Cl_2=SO_3+SO_2Cl_2$, and this is confirmed by the analysis of the decomposition products. At 200°, in the presence of sulphur dioxide and chlorine, the first reaction occurs to a small extent, and gives place to the second reaction above this temperature. The reaction $SO_2Cl_2 \rightleftharpoons SO_2+Cl_2$ then occurs, and decomposition is complete at 360°. J. GRANT.

Solutions of the electronegative elements in liquid ammonia. I. Action of selenium, tellurium, arsenic, and a solution of sulphur in liquid ammonia on cyanides. F. W. BERGSTROM (J. Amer. Chem. Soc., 1926, **48**, 2319—2327).—Cyanides of potassium, aluminium, and magnesium react with sulphur in liquid ammonia to form the corresponding

thiocyanates; by-products are not formed in appreciable quantities. Experiments indicate that the sulphur nitride and ammonium sulphide in the ammonia solution of sulphur (Ruff and Geisel, A., 1905, ii, 699) react to give sulphur, which then reacts with the cyanides: $6(NH_4)_2S+N_4S_4=16NH_3+10S$. Silver and mercuric cyanides form thiocyanates together with considerable amounts of sulphide: the mercuric sulphide is not precipitated immediately, indicating that the ammonia solution contains ammonium polysulphide. Selenium is only slightly soluble in ammonia; the solution contains selenium nitride and ammonium selenide and reacts with metal cyanides in the same way as the sulphur solution. Tellurium dissolves very slowly in solutions of aluminium and potassium cyanides; arsenic will not react at all. Sulphur and selenium behave in liquid ammonia as weak nitridising ("de-electronising") agents. The following new *compounds* were obtained: $Al(SCN)_3,5NH_3$; $Mg(SCN)_2,4NH_3$; $Mg(SeCN)_2,xNH_3$, where $x=4$ and (?) 6; $Zn(SeCN)_2,4NH_3$; $Al(SeCN)_3,5NH_3$. S. K. Tweedy.

Reduction of chromic compounds by hydrogen under pressure and at high temperatures. V. N. Ipatiev and B. A. Mouromtsev (Compt. rend., 1926, **183**, 505—507).—Potassium chromate, chromium trioxide, chromic sulphate, and chromic chloride have been reduced by hydrogen in neutral, acid, or alkaline solution. At 280—300°, and under a pressure of hydrogen of 200 atm., crystals of chromic oxide hydrate, Cr_2O_3,H_2O, are obtained. By reduction in presence of free sulphuric acid at 300° and 80 atm., small violet-grey crystals, soluble in neither acid nor alkali, are formed and appear to have the composition $K_2O,2Cr_2O_3,3SO_3,H_2O$. At 280° and 150—200 atm., the compound $2Cr_2O_3,3SO_3,6H_2O$ is obtained as dark green cubic crystals. In the presence of ferrous or ferric sulphate, complex isomorphous mixtures containing iron and chromium are obtained in the form of dark green cubic crystals. Iron pyrites frequently accompanies such mixtures.

M. S. Burr.

Constitution of the molybdates. A. Travers and Malaprade (Compt. rend., 1926, **183**, 533—535).—The acid molybdates are considered to be derivatives of the tetramolybdic ion, $[4MoO_3,O]$, and of the normal ion, $[MoO_4]$, only. Salts of the former are prepared by the neutralisation of the acid $4MoO_3,H_2O$ (this vol., 925) under conditions which limit the reversal of the reaction by hydrolysis. The trimolybdates and paramolybdates are derived from the ions $[3MoO_3,O]$ and $[7MoO_3,3O]$, respectively. These ions are considered to exist in equilibrium with the normal and tetramolybdic ions. Ammonium paramolybdate appears to have the composition $12MoO_3,4(NH_4)_2O$, but is probably composed of mixed crystals of tri- and para-molybdate in equilibrium with a mother-liquor of the same composition.

J. Grant.

Formation of normal uranates by heating uranium trioxide with metal oxides. G. Tammann and W. Rosenthal (Z. anorg. Chem., 1926, **156**, 20—26).—An attempt was made to prepare normal uranates of the type M'_2UO_4 and $M''UO_4$ by heating a powdered mixture of the metal oxide with uranium trioxide in molecular proportions at 600°. Under the most favourable conditions, an 80% yield was obtained. Mixtures of uranium trioxide with lithium carbonate and oxides of the following metals were examined and the results were tabulated: silver, calcium, barium, strontium, beryllium, magnesium, zinc, cadmium, mercury, copper, lead, cobalt, manganese, nickel, aluminium, chromium, iron, and vanadium. The normal uranates are either yellow, orange, red, or brown in colour; nickel, cobalt, and manganese uranates are green. Comparisons between molybdenum, tungsten, and uranium trioxides show that molybdenum is more reactive than tungsten and this more than uranium. With the latter, heating must not be above 600°, whilst molybdenum and tungsten may be heated at 800°. Exceptions are aluminium oxide and ferric oxide, which show practically no action with molybdenum and tungsten trioxide, but at 550° gives 35% and 15% yields, respectively, with uranium. Cerium trioxide reacts vigorously with molybdenum and tungsten trioxides, but there is no action with uranium trioxide.

M. Carlton.

System uranyl nitrate-nitric acid-water. A. Colani (Bull. Soc. chim., 1926, [iv], **39**, 1243—1245).—The system uranyl nitrate–nitric acid–water was studied at 25°; the curve obtained shows the existence of three hydrates: $UO_2(NO_3)_2,6H_2O$; $UO_2(NO_3)_2,3H_2O$; $UO_2(NO_3)_2,2H_2O$. These results agree with those of earlier experimenters.

M. Carlton.

Beryllium. A. C. Vivian (Trans. Faraday Soc., 1926, 22, 211—225).—A method for the preparation of compact masses of beryllium is described, and some properties of this metal are recorded. The electrolyte consists of the double fluoride of beryllium and sodium, BeF_2,NaF, mixed with sufficient barium fluoride to give a barium content of from 10 to 15%; the barium fluoride reduces the ebullition and convection round the electrode. The anode pot is of graphite, and auxiliary graphite anodes are used; all graphite parts must be specially impregnated with salt, and this treatment is described. The cathode is a water-cooled holder for a beryllium metal tip on which the deposition takes place, whilst a rotating cathode improves the stability and continuous running; in either case, the cathode is slowly raised during the electrolysis and a rod of metal obtained. The anode crucible was heated to dull redness in a nichrome furnace and an alternating current passed between the auxiliary anodes until a temperature of 1200° was reached, when the electrolysis was started, the temperature being maintained chiefly by the "anode effect." Electrolysis was continuous, the furnace being fed with fluorides from time to time. The metal thus obtained was free from impurities except iron, carbon, aluminium, and magnesium as low as 0·05% each, and nitrogen as low as 0·005%. By melting and subliming the cathode metal in beryllia pots, carbide-free metal containing less than 0·02% of iron was obtained. All specimens are non-ductile and most have a Brinell hardness of about 140, but an annealed sublimate gave a value as low

as 90; *d* 1·84, m. p. about 1280°. It resists atmospheric corrosion very well, takes a high polish, and does not readily ignite. W. HUME-ROTHERY.

Absolute colorimetry. R. DEFAY (Bull. Soc. Chim. biol., 1926, **8**, 733—745; cf. below).—The method consists in comparing the ratio of the colorimetric readings obtained by matching two different concentrations of the unknown solution against each other, with figures obtained by the same method applied to the pure substance.

H. J. CHANNON.

Potentiometer for the measurement of hydrogen-ion concentration. R. SHOJI (J. Biophys., 1924, **1**, xliv). CHEMICAL ABSTRACTS.

Glass electrodes. (MISS) P. M. T. KERRIDGE (J. Sci. Instr., 1926, **3**, 404—409).—The theory and practice of the electrometric method of determining hydrogen-ion concentrations with the aid of glass electrodes are described. S. K. TWEEDY.

Buffers. II. Titre of buffer solutions. A. AUGSBERGER (Helv. Chim. Acta, 1926, **9**, 823—826).—Theoretical. The p_H of an acetate, phosphate, or ammonia–ammonium chloride buffer in which the proportion of the constituents is incorrect will differ from the desired p_H by the logarithm of the correction factor of this proportion. No correction of this kind can be applied to incorrect citrate, borate, or glycine buffers. E. W. WIGNALL.

Umbelliferone as fluorescent indicator. R. ROBL (Ber., 1926, **59**, [*B*], 1725—1726).—An aqueous solution of umbelliferone (0·1 g. in 500 c.c.) is recommended as indicator in the titration of acids by alkali hydroxide; the addition of a slight excess of alkali causes the appearance of a sky-blue fluorescence in the solution illuminated by the analytical quartz lamp (cf. Robl, this vol., 701). The method is particularly adapted for coloured solutions. The sensitiveness of the indicator is approximately the same as that of neutral-red. H. WREN.

Reagent and standard for borax. L. S. WEATHERBY and H. H. CHESNY.—See B., 1926, 820.

Titration of solutions of iodine by means of hydrazine sulphate. E. CATTELAIN (Bull. Soc. chim., 1926, [iv], **39**, 1279—1280; Ann. Chim. analyt., 1926, [ii], **8**, 289—290).—By addition of a large excess of iodine to a solution of hydrazine sulphate in presence of sodium acetate, the hydrazine sulphate is quantitatively oxidised according to the equation $(NH_2)_2,H_2SO_4 + 2I_2 + 2H_2O = 4HI + N_2 + 2H_2O + H_2SO_4$. This method is stated to be precise and more convenient than those in general use for the titration of iodine; moreover, hydrazine sulphate is readily obtained pure. M. CARLTON.

Determination of oxygen in iron. P. OBERHOFFER, J. KEUTMANN, W. HESSENBRUCH, and E. AMMON.—See B., 1926, 790.

Analysis of sulphur chloride. E. BENESCH.—See B., 1926, 787.

Quantitative analysis using bromine. I. Determination of thiocyanic acid, arsenious acid, and antimony. T. NAKASONO and S. INOKO (J. Chem. Soc. Japan, 1926, **47**, 20—27).—The authors have studied the effect of acidity of the solution by hydrochloric acid on the titration of thiocyanic acid (*A*), arsenious acid (*B*), and antimony (*C*) with potassium bromate, the end-point having been determined by methyl-orange or the sudden change of the *E.M.F.* of the solution. The concentration of the hydrochloric acid should be 0·3—0·6*N* (*A*), 0·3—2*N* (*B*), or 1·3—2*N* (*C*) when methyl-orange is used, and 0·3—3*N* (*A*), 0·3—6*N* (*B*), or 1·3—6*N* (*C*) in the *E.M.F.* method. The methyl-orange method is inferior to the *E.M.F.* method by reason of the restricted range of concentration of the acid. In (*B*) and (*C*), the differences of the *E.M.F.* at the end-point decrease as the concentrations of the acid increase; these are defects in the *E.M.F.* method. 20—40 C.c. of 2*N*-hydrochloric acid and 10 c.c. of 5% potassium bromide solution are added to the sample; after dilution to 100 c.c., the liquid is titrated with 0·1*N*-potassium bromate at the ordinary temperature. With antimony, there is no need to warm the solution (cf. Cumming and Kay, "Quantitative Chemical Analysis," 2nd ed., 117). K. KASHIMA.

Determination of selenium and tellurium by means of potassium permanganate. W. T. SCHRENK and B. L. BROWNING (J. Amer. Chem. Soc., 1926, **48**, 2550—2553).—To a dilute solution of selenious or tellurous acid, free from hydrochloric acid, disodium phosphate is added and a known amount of standard potassium permanganate solution; the excess of the latter is then determined by electrometric titration with ferrous sulphate solution after 10—30 min. In a mixed sample, the tellurium may be determined by potassium dichromate (cf. this vol., 261) and the selenium by permanganate; or both may be determined by the latter and the tellurium by dichromate in a separate sample.

S. K. TWEEDY.

Micro-determination of nitrogen. H. J. FUCHS (Biochem. Z., 1926, **176**, 32—37).—By reducing possible errors, by using Jena glass and replacing rubber stoppers with ground-glass joints, the limit of error of Bang's micro-Kjeldahl method becomes 0·007 mg. of nitrogen. A similar improvement of the Van Slyke apparatus is described.

P. W. CLUTTERBUCK.

Chloroamine. P. N. VAN ECK (Pharm. Weekblad, 1926, **63**, 1117—1121).—The oxidising properties of "chloramine-*T*" (the sodium compound of *p*-toluenesulphochloroamide) may be employed in titration of nitrites, sulphites, etc. The solution is standardised by means of potassium iodide and sodium thiosulphate, and the excess after oxidation determined in the same way. Control analyses show that accurate results are readily obtained. S. I. LEVY.

Correction of colorimetric determinations. R. DEFAY (Bull. Soc. Chim. biol., 1926, **8**, 715—732).—The colorimetric determination of cystine by the method of Folin and Looney, and of ammonia by Nessler's reagent has been studied in detail. The magnitude of the errors caused by assuming that the colorimetric readings are proportional to the concentrations has been determined, and correction curves are plotted. H. J. CHANNON.

Sliding scale colorimeter and determination of traces of ammonia, nitrite, lead, and iron. A. L. BERNOULLI (Helv. Chim. Acta, 1926, **9**, 827—840).—A description of apparatus depending for its application on equalising the intensity of colour of two beams of light, one passing direct through a standard colorimetric cell, whilst the other is reflected by prisms through the liquid to be examined. The prisms are immersed in the liquid, contained in any vessel, and one of them is attached to a sliding scale provided with a vernier; in this way the length of path of the beam through the liquid can be changed and measured very delicately. The apparatus is standardised to correct for loss of light on reflexion. 5×10^{-5} Mg. of nitrite-nitrogen per c.c. can be measured to 1%, using the Griess reagent.

The violet colour produced by pyrocatechol and very dilute ferric iron enables the latter to be determined to 0·5% at 0·0062 mg. per c.c. Lead is determined by sulphide and ammonia by phenol and hypochlorite. For micro-analysis, the "inversion method" is employed, using the solution to be examined in a standard micro-cell, and the standard solution in the measuring vessel. In this way, by pyrocatechol, 0·002 mg. of iron can be determined in 0·1 c.c. to 0·4%. The new colorimeter is particularly suitable for the determination of reaction velocity, and for colorimetry at high temperatures.

E. W. WIGNALL.

Use of liquid amalgams in volumetric analysis. V. Determination of phosphoric acid by means of a uranyl salt. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 417—420; cf. this vol., 1117).—The reducing action of bismuth amalgam is applied to the determination of phosphoric acid. The phosphate is precipitated as uranyl ammonium phosphate, which must be obtained in a crystalline form by a special method. The crystals are dissolved in hydrochloric acid, reduced with zinc amalgam or bismuth amalgam, and titrated with potassium dichromate, using diphenylamine as an internal indicator.

E. S. HEDGES.

Simple comparison electrodes for electrometric determinations with permanganate. R. LANG (Z. Elektrochem., 1926, **32**, 454—460).—Solutions of reducing substances such as arsenious oxide and ferrous and vanadyl salts can be electrometrically titrated with potassium permanganate solutions by the method of Treadwell and Weiss (A., 1920, ii, 119), and comparison electrodes have been devised for this purpose. The following schemes are developed: Pt (working electrode)|solution of reducing substance containing HCl or H_2SO_4 being titrated with 0·1*N*-$KMnO_4$:*N*—3*N*-HCl containing 1 drop (0·03 c.c.) of 0·1*N*-$KMnO_4$ per 50 c.c.|Pt (comparison electrode); Pt|solution of reducing substance containing H_2SO_4 being titrated with 0·01*N*-$KMnO_4$:2*N*-H_2SO_4 containing 1 drop of 0·01*N*-$KMnO_4$ and 1—2 g. NaCl per 50 c.c.|Pt; Pt|solution of reducing substance containing HCl being titrated with 0·01*N*-$KMnO_4$:*N*-HCl containing 1 drop of 0·01*N*-$KMnO_4$ and about 0·05 g. of Mn as $Mn^{\cdot\cdot}$ salt per 50 c.c.|Pt; Pt|$KMnO_4$ solution in *N*—2*N*-Na_2CO_3 being titrated with 0·1—0·01*N*-As_2O_3 in $NaHCO_3$ solution:*N*-Na_2CO_3 containing 1 drop of 0·1*N*-$K_3Fe(CN)_6$ and 1 drop of 0·01*N*-$K_4Fe(CN)_6$|Pt. These determinations are capable of great exactitude, the addition of the last drop of solution causing the voltage to change sign by a notable jump. The conditions governing the accuracy of the method are discussed.

H. J. T. ELLINGHAM.

Carbonic acid content of distilled water and its accurate determination. I. M. KOLTHOFF (Biochem. Z., 1926, **176**, 101—108).—The carbonic acid content of water in equilibrium with normal air is shown to be $1\cdot5$—$1\cdot6\times10^{-5}M$ by titration with neutralised indicator solutions of such a composition that they have the same p_H in pure water as the solution to be titrated when at its equilibrium point. The titration should be carried out in flasks which are almost filled with fluid. Distilled water obtained from tap water contains considerable amounts of carbonic acid. Water placed in contact with air comes into equilibrium with it in just over a week, the equilibrium being more easily reached by sucking washed air through the water for 10 hrs. By one distillation of tap water a distilled water is obtained which, when brought into equilibrium with air, has a conductivity of 0·75—0·8 reciprocal ohm at 18°.

P. W. CLUTTERBUCK.

Detection of barium chloride in calcium chloride. F. RICHARD.—See B., 1926, 786.

Test for cadmium in presence of copper. G. M. KARNS (J. Amer. Chem. Soc., 1926, **48**, 2626—2627).—The ammoniacal filtrate from the bismuth separation is neutralised with acid and treated with an equal volume of saturated sodium hydrogen carbonate solution. A turbid, white precipitate, easily seen in the blue copper solution, indicates the presence of cadmium. The test, which is sensitive to 0·1 mg./c.c., is not vitiated by the presence of mercury or lead.

S. K. TWEEDY.

Rapid volumetric determination of large quantities of manganese in technical iron alloys. T. HECZKO.—See B., 1926, 791.

Colorimetric determination of ferric iron in acid solution. H. W. VAN URK (Pharm. Weekblad, 1926, **63**, 1121—1123).—The colour obtained by addition of a 1% pyramidone solution to a dilute acid solution of a ferric salt is independent of the concentration of the acid between the limits 0·1 and 0·2*N*. The most suitable concentrations of ferric iron for quantitative determinations are between 0·05 and 0·3 mg. per 100 c.c.

S. I. LEVY.

Microscopical examination of borax beads. J. MIKA (Koll.-Chem. Beih., 1926, **23**, 309—312).—A method is described by means of which minute borax beads may be examined under the microscope. Sensitivity data are worked out for the case of the detection of cobalt. An absolute amount of 5×10^{-6} mg. of cobalt can be detected by this means.

E. S. HEDGES.

Use of liquid amalgams in volumetric analysis. VI. Determination of chromic acid, ferric iron, and ferricyanide by a titanous salt. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 421—426; cf. following abstract).—In presence of diphenylamine as an internal indicator, titanous sulphate,

prepared by the amalgam method, may be used for the titration of ferricyanide, chromic acid, and a mixture of ferric iron and chromic acid. The last case is suited to the analysis of chromium steels. The diphenylamine indicator may be used for the titration of ferrocyanide with stannous chloride.

E. S. HEDGES.

Use of liquid amalgams in volumetric analysis. IV. Reducing action of bismuth amalgam, reduction of uranium, and the application of dichromate titration. K. SOMEYA (Sci. Rep. Tôhoku Imp. Univ., 1926, **15**, 399—415).—In presence of sufficient excess of free sulphuric acid or hydrochloric acid, bismuth amalgam quantitatively reduces quadrivalent titanium to the tervalent condition. The reducing action of bismuth amalgam on vanadic and molybdic acids depends on the concentration of free acid present, but by suitably regulating the amount of hydrochloric acid molybdenum may be reduced quantitatively to the quinquevalent or tervalent state, and similarly in sulphuric acid solution, vanadium may be reduced quantitatively to the quadrivalent state. Uranium is reduced quantitatively by bismuth amalgam in hydrochloric acid or sulphuric acid solution to the quadrivalent stage, whilst zinc amalgam in hydrochloric acid reduces it to the tervalent stage. Solutions of tervalent and quadrivalent uranium, tervalent titanium, and hydrochloric acid solutions of ferrous acetate may be determined by titration with potassium dichromate, using diphenylamine as an internal indicator. By utilising these observations, methods are worked out for the differential determination of iron and titanium and of uranium and titanium. Also, by using an excess of a titanous salt, chloric and chromic acids may be determined. The reduced molybdenum solution may be used for the determination of phosphoric acid, and the method is suitable for examining the phosphorus content of metals. E. S. HEDGES.

Separation of zirconium and hafnium. D. H. DROPHY and W. P. DAVEY (Physical Rev., 1925, [ii], **25**, 882—883).—Zirconium citrate, which is soluble in ammonium hydroxide or citric acid solution, is sparingly soluble in water, whilst hafnium citrate is readily soluble. A. A. ELDRIDGE.

Attempted separation of hafnium and zirconium by the ionic migration method. J. KENDALL and W. WEST (J. Amer. Chem. Soc., 1926, **48**, 2619—2626).—Prolonged electrolysis of an agar gel containing zirconium and hafnium in the form of complex oxalates produced only a very slight separation of these anions. Consideration of some of the properties of these metals (*e.g.*, electronic configuration, ionic volume) shows that only a very small separation is to be expected. S. K. TWEEDY.

Potentiometric determination of gold. E. MÜLLER and F. WEISBROD (Z. anorg. Chem., 1926, **156**, 17—19).—Solutions of gold chloride are titrated, using a solution of ferrous sulphate which had been standardised against potassium permanganate (cf. Zintl and Rauch, Z. Elektrochem., 1925, **31**, 429; A., 1925, ii, 1005). Any aurous chloride present in the original solution is first oxidised by addition of chlorine water. The end-point is determined potentiometrically, using a platinum electrode against the normal calomel electrode. There are two breaks in the curve; the first shows the end of the reaction $Cl_2+2Fe^{\cdot\cdot} \rightarrow 2Cl'+2Fe^{\cdot\cdot\cdot}$, the second $Au^{\cdot\cdot\cdot}+3Fe^{\cdot\cdot} \rightarrow Au+3Fe^{\cdot\cdot\cdot}$. The difference gives the gold content.

A degree of accuracy of 0·25% is claimed for 0·01*M*-solutions. The presence of copper does not interfere with the titration; the influence of other metals is not yet determined. M. CARLTON.

New analytical reactions of the platinum metals. S. C. OGBURN, jun. (J. Amer. Chem. Soc., 1926, **48**, 2493—2507).—The reactions under various conditions between a large number of typical organic and inorganic compounds and dilute solutions of the chlorides of ruthenium, rhodium, palladium, osmium, iridium, and platinum are tabulated. The most reactive substances include sulphides, thiosulphates, hydrazine (preferably in alkaline solution), magnesium, alkaloids, oximes, aromatic amines, etc. The observations indicate that, with the exception of iridium, the nearer the platinum metal approaches electron saturation in its penultimate orbit the more readily does it form co-ordinated salts. The following new colour reactions were observed amongst others. Ruthenium chloride solutions after being rendered alkaline with potassium nitrite become deep violet on boiling with phloroglucinol. On warming with aniline sulphate solution, potassium osmate solution turns deep rose, potassium chloro-osmate solution violet, iridium chloride solution deep blue, and platinum chloride solution blood-red, the latter turning dark reddish-brown when boiled with pyrocatechol. S. K. TWEEDY.

Qualitative separation of the platinum metals. S. C. OGBURN, jun. (J. Amer. Chem. Soc., 1926, **48**, 2507—2512).—To a solution of the metallic chlorides containing the equivalent of 7—8 c.c. of concentrated hydrochloric acid per 100 c.c., a 1% alcoholic solution of dimethylglyoxime is added. Palladium is precipitated as the compound $Pd(C_4H_7O_2N_2)_2$ and on boiling the filtrate with 2% alcoholic α-furildioxime solution the platinum is removed as $Pt(C_{10}H_7O_4N_2)_2$. The concentrated filtrate, after warming with hydrochloric acid and sodium chlorate, is boiled with alcoholic potassium nitrite solution, when the rhodium is precipitated as $K_3Rh(NO_2)_6$ on keeping over-night. The acidified filtrate is evaporated nearly to dryness, diluted, and ruthenium precipitated as $Ru_2O_3,3H_2O$ by boiling with alcoholic sodium hydroxide. Reduction of the filtrate with zinc and acid precipitates mixed osmium and iridium; the osmium is separated by treating the mixture with sodium hypochlorite solution and reprecipitated by reducing the latter with zinc and acid. By following the details given, the separation can be made quantitative to within 2%.

S. K. TWEEDY.

Spectral filters. K. S. GIBSON (J. Opt. Soc. Amer., 1926, **13**, 267—280).—Data are given relating to the nature, thickness, and transmissive power of the different types of spectral filter employed for ultra-violet, visible, and infra-red radiation. A bibliography is also included. M. S. BURR.

Application of the neutral wedge in a form of direct comparison spectrophotometer. H. C. TERRY (Physical Rev., 1925, [ii], **25**, 116).—A Brace prism or a Lummer–Brodhun cube with dispersing prism is employed, the intensity of the comparison source being varied by means of a pair of neutral wedges. A. A. ELDRIDGE.

Interferential spectroscope for accurate measurement of wave-lengths. H. NAGAOKA and T. MISHIMA (Proc. Imp. Acad. Tokyo, 1926, **2**, 110—111).—The usual double convex lens of the spectroscope collimator is replaced by a plano-convex lens with a glass plate a little way from its plane face, the plane surfaces being thinly silvered. This arrangement acts as a Fabry–Perot interferometer, and by its use wave-lengths can be measured with an accuracy of about 0·001 Å. R. CUTHILL.

Anastigmatic reflecting-condensers for dark-field illumination and microscopy. H. SIEDENTOPF (Koll.-Chem. Beih., 1926, **23**, 218—242).—A mathematical treatment of different arrangements and the corrections to be applied. E. S. HEDGES.

Automatic cryostat. H. SHINOZAKI and R. HARA (J. Soc. Chem. Ind. Japan, 1926, **29**, 262—265; Tech. Rep. Tôhoku Imp. Univ., 1926, **6**, 121—127).—The volume change of liquid pentane in the automatic regulator sets a mercury column, and hence an electrical relay, in motion, closing or breaking the circuit of a small electro-magnetic plunger valve, and sharply increasing or reducing the pressure in a liquid-air reservoir. This pressure change accelerates or retards the flow of liquid air through a vacuum-jacketed tube into the cryostat bath in a manner similar to that of Henning's hand-regulating cryostat (Z. Instrumentenkunde, 1913, **33**, 33). The temperature is kept constant to $\pm 0{\cdot}02°$ to $\pm 0{\cdot}03°$ within the range from 0° to −150°. The consumption of liquid air is small. K. KASHIMA.

Continuous and automatic apparatus for distilling mercury in a vacuum. L. HACKSPILL and A. SIGOT (Bull. Soc. chim., 1926, [iv], **39**, 1281—1284).—A mercury still made from Pyrex glass is described in detail; it gives a rapid and complete condensation by circulating water in the immediate neighbourhood of the boiling mercury. It is composed of a barometric tube enlarged at the upper end and surmounted by a refrigerator. By means of a water pump, the mercury is raised into the barometric chamber, and heated by means of a small electric furnace. The condensed mercury vapour is collected and falls down a long tube into the receiver, carrying with it air, and thus maintaining a good vacuum. A tube of phosphorus pentoxide removes traces of moisture. Only 200 c.c. of mercury are necessary for working the still, and by means of an electrical device the current to the furnace is automatically cut off when the distillation is complete. By altering the heating current, from 32 to 58 kg. of mercury may be distilled in 24 hrs. M. CARLTON.

Distillation in a high vacuum with the aid of liquid air and silica gel. L. ANSCHÜTZ (Ber., 1926, **59**, [*B*], 1791—1794).—An apparatus is figured and described which permits distillation at 0·01—0·001 mm. of mercury in a current of carbon dioxide. It is exhausted initially by a water pump, after which high vacuum is obtained by the combined use of liquid air and silica gel. H. WREN.

Micro-apparatus for the determination of mol. wt. by elevation of the b. p. A. RIECHE (Ber., 1926, **59**, [*B*], 2181—2184).—The apparatus, which permits direct heating with a flame, is figured and described. H. WREN.

Electro-ultrafilter. J. J. BRONFENBRENNER (J. Gen. Physiol., 1926, **10**, 23—26).—An apparatus is described with a diagram for carrying out simultaneously ultrafiltration and electro-dialysis of colloidal solutions. W. O. KERMACK.

Temperature control for refractometers and polarimeters. M. T. CASEY (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 263—264).—An air-jet causes the circulation of water from a large constant-temperature vessel through the instrument and back again. G. M. BENNETT.

Technique of making thin celluloid films. J. TAYLOR (J. Sci. Instr., 1926, **3**, 400—404).—The technique of preparing thin celluloid films by dropping celluloid or other solutions from narrow tubes on to water or mercury surfaces is described. Diluted commercial cellulose acetate varnishes give good results. Strong films of thickness 500—600 Å., but not vacuum-tight, are formed on water; vacuum-tight films are obtained on perfectly clean mercury surfaces. The films are non-crystalline; they are porous to water vapour and may be coloured with suitable dyes. Such films, also, may be coated in a vacuum with magnesium by evaporation of the latter from an electrically heated filament. S. K. TWEEDY.

Early history of gaseous adsorption. (SIR) J. LARMOR (Nature, 1926, **118**, 586).

Mineralogical Chemistry.

Quantity of helium and other gases contained in Japanese natural gases. III. B. YAMAGUCHI and Y. KANO (J. Chem. Soc. Japan, 1926, **47**, 13—19; cf. *ibid.*, **43**, 885; **44**, 1018).—Percentages of helium, carbon dioxide, hydrogen sulphide, hydrocarbons, oxygen, carbon monoxide, methane, ethane, nitrogen, and other inactive gases in 43 natural gases from hot springs, cold springs, water wells, gas wells, petroleum wells, and coal mines were determined. No carbon monoxide was detected in any gas. Gases other than those from petroleum wells contained hydrocarbons absorbed by fuming sulphuric acid in amount less than 0·2%. The amount of oxygen was less than 1%. Gases, other than volcanic, contained

no hydrogen. A group of gases rich in carbon dioxide is evolved from volcanoes and hot springs; another, rich in methane, is evolved from coal mines, petroleum wells, mineral waters, and layers of new quaternary period; a third, rich in nitrogen, is evolved from hot and cold springs. Helium was mainly found in the third and sometimes in the second group. Generally in hot springs, the amount of helium was proportional to that of emanation; some cold mineral waters contained emanation, but no helium. K. KASHIMA.

Presence of sodium and potassium fluosilicates among the products of the present-day activity of Vesuvius. F. ZAMBONINI and G. CAROBBI (Atti R. Accad. Lincei, 1926, [vi], **4**, 171—175).—Malladrite occurs among the products of fumarole activity on Vesuvius. T. H. POPE.

Thermal analysis of chlorites. J. ORCEL (Compt. rend., 1926, **183**, 565—567; cf. *ibid.*, 1924, **179**, 1056).—The chlorites are classified as follows, according to the amounts of heat absorbed when water is driven off from them at various temperatures: (1) those absorbing heat at 600°; (2) those absorbing heat at 600° and 800°, absorption at the former temperature being greatest; (3) those absorbing equal amounts of heat at 600° and 800°; (4) those absorbing heat at other temperatures. An attempt is made to correlate these phenomena with the compositions of the chlorites. J. GRANT.

Origin of phosphate deposits. W. A. P. GRAHAM (Econ. Geol., 1925, **20**, 319—334).—Humic acids are probably the best natural solvents of phosphorus, although other solutions have a sufficiently solvent action to form phosphate deposits. Carbon dioxide solutions dissolve phosphorus and calcium oxides in the ratio 1/100. Solutions free from carbon dioxide leach a larger proportion of phosphorus than lime from a lean phosphate rock; with a rich phosphate rock the reverse obtains.

CHEMICAL ABSTRACTS.

Japanese volcagenous ash-loams. T. SEKI (Proc. Imp. Acad. Tokyo, 1926, **2**, 61—66).—Many specimens of the above have been analysed. The argillaceous substances present in them seem to consist of clays resembling allophane, along with colloidal ferric and aluminium hydroxides. It is apparently owing to the difference in properties of these compounds that the loams possess a high absorptive power for both ammonia and phosphoric acid. The colloidal substances retain large quantities of water, and so exercise a deleterious effect on crops in wet seasons. R. CUTHILL.

Chloritic minerals in the basaltic rocks of Derbyshire. S. I. TOMKEIEV (Min. Mag., 1926, **21**, 73—82).—A pale green chlorite forming nodules (*d* 2·393) which consist of an aggregate of fibrous spherulites occurs in vesicles in the basalt of Calton Hill. Analysis gave SiO_2 35·92, Al_2O_3 12·20, Fe_2O_3 7·59, FeO 4·66, MgO 21·82, CaO 1·82, CO_2 0·13, H_2O at 105° 6·50, H_2O ign. 9·20, total 99·84, agreeing with $10R''O,2{\cdot}5R'''_2O_3,9SiO_2,13H_2O$ (or, neglecting water lost at 105°, $7{\cdot}5H_2O$). A comparison with various chlorites suggests that this is near delessite. It was evidently formed during the post-volcanic phase (autopneumatolitic). Another chlorite, resembling palagonite, fills spaces between fresh crystals of felspar and augite, and is evidently of primary origin. Other chloritic material is secondary and has been produced by atmospheric weathering. L. J. SPENCER.

Identity of the Cobija and Lampa meteoric stones. E. D. MOUNTAIN (Min. Mag., 1926, **21**, 87—93).—A detailed analysis is given of the chondritic stone found in 1892 near Cobija in Chile. A partial analysis of the Lampa stone and the history of the masses suggest that they belong to the same meteoric fall. L. J. SPENCER.

Nature of berthierite. F. L. STILLWELL (Min. Mag., 1926, **21**, 83—86).—Analysis by W. A. GRIEG of a steel-grey columnar specimen from Nullamanna, New South Wales, gave Sb 58·63, Fe 10·08, S 28·71, insol. 1·44, H_2O 1·14, total 100·00, agreeing with the formula $3FeS,4Sb_2S_3$. Polished sections examined in reflected polarised light show, however, an intergrowth of about 16% of stibnite with the berthierite. Deducting this, the formula for berthierite becomes FeS,Sb_2S_3. L. J. SPENCER.

Organic Chemistry.

Thermal decomposition of methane at a glowing filament. G. M. SCHWAB and E. PIETSCH. —See this vol., 1109.

Catalytic oxidation of methane. II. S. S. MEDVEDEV.—See this vol., 1012.

Non-acidic oxidation products of paraffin wax. F. FRANCIS and H. F. GAUNTLETT (J.C.S., 1926, 2377—2384).—The non-acidic oxidation products obtained from paraffin wax (cf. *ibid.*, 1922, **121**, 496) consist of secondary alcohols and ketones having a carbon-chain length of 26—29 atoms, with the ketonic oxygen situated on the third or fourth carbon atom, and probably dihydric alcohols, hydroxyketones, and diketones. The quantity of non-acidic products formed diminishes as the oxidation proceeds owing to the formation of acidic substances.

H. BURTON.

Substitution processes with butadiene derivatives. P. W. NEBER and S. PAESCHKE (Ber., 1926, **59**, [*B*], 2140—2150).—α-Cyano-αδ-diphenyl-$\Delta^{\alpha\gamma}$-butadiene is converted by nitrogen peroxide in anhydrous ether at 0° into *γδ-dinitro-α-cyano-αδ-diphenyl-*Δ^{α}*-butene*, $CN{\cdot}CPh{:}CH{\cdot}CH(NO_2){\cdot}CHPh{\cdot}NO_2$, m. p. 126°, which is transformed by cautious treatment with water at 40—45° and subsequently with alcohol into *γ-nitro-α-cyano-αδ-diphenyl-*$\Delta^{\alpha\gamma}$*-butadiene*, m. p. 85°. When treated with nitrogen peroxide in cold chloroform, the latter substance affords *γδ(?)-di-*

nitro-α-cyano-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene, m. p. 198°, identical with a by-product of the action of nitrogen peroxide on α-cyano-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene. Elucidation of the constitution of the mononitro-compound by ozonisation is rendered difficult by the simultaneous attack of the reagent at both double linkings. Successive treatment with alcoholic potassium methoxide and sodium hypobromite, however, affords *γ-bromo-γ-nitro-α-cyano-δ-methoxy-αδ-diphenyl-Δ$^{\alpha}$-butene*, CN·CPh:CH·CBr(NO_2)·CHPh·OMe, m. p. 129°, from which hydrogen bromide could not be satisfactorily removed by means of methyl-alcoholic potassium hydroxide; when treated with potassium methoxide and a mixture of methyl alcohol and ether, the bromide yields *γ-nitro-α-cyano-δ-methoxy-αδ-diphenyl-Δ$^{\alpha}$-butene*, m. p. 110°. If, however, γ-nitro-α-cyano-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene is dissolved in potassium methoxide solution and the solution is treated with moderately concentrated sulphuric acid, the nitromethoxybutadiene, CN·CPh:CH·C(NO_2):CPh·OMe, is almost quantitatively decomposed into benzaldehyde, methyl alcohol, and γ-nitro-α-phenylcrotonamide, whence *β-carboxylamidocinnamylhydroxamic acid*, NH_2·CO·CPh:CH·C(OH):N·OH, decomp. 180—185° after darkening at 170° (also *monohydrate*), is derived. The latter compound is transformed by sodium carbonate solution into *β-carboxycinnamylhydroxamic anhydride*, m. p. 165°. The amide and anhydride are converted by sodium hydroxide into phenylmaleic anhydride, m. p. 119°. Addition of nitrogen tetroxide to α-cyano-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene therefore occurs in the γδ-position and the nitro-group is subsequently lost from the δ-carbon atom.

If α-phenylcinnamenylacrylic acid is treated with nitrogen peroxide in presence of ether and light petroleum, carbon dioxide is lost and βγ(?)-dinitro-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene, m. p. 223°, is obtained identical with the product described by Wieland and Stenzl (A., 1908, i, 517). If, however, the methyl ester is used in place of the free acid, *methyl γ(?)-nitro-αδ-diphenyl-Δ$^{\alpha\gamma}$-butadiene-α-carboxylate*, m. p. 154°, is produced.

The presence of a substituent in the benzene nucleus appears to render the dinitro-compounds less stable. Thus, *p*-nitrophenylcinnamenylacrylonitrile and nitrogen peroxide in chloroform yield an unstable, colourless compound, m. p. 152°, which readily loses nitrous acid and passes into *γ(?)-nitro-α-cyano-δ-phenyl-α-p-nitrophenyl-Δ$^{\alpha\gamma}$-butadiene*, m. p. 200°. *p*-Bromophenylacetonitrile and cinnamaldehyde condense to the *nitrile*, C_6H_4Br·C(CN):CH·CH:CHPh, m. p. 151°, which yields *γδ(?)-dinitro-α-cyano-δ-phenyl-α-p-bromophenyl-Δ$^{\alpha}$-butene*, m. p. 128°, readily passing into *γ(?)-nitro-α-cyano-δ-phenyl-α-p-bromophenyl-Δ$^{\alpha\gamma}$-butadiene*, m. p. 150°. Similarly, *α-m-bromophenylcinnamenylacrylonitrile*, m. p. 124°, from cinnamaldehyde and *m*-bromophenylacetonitrile, affords *γδ(?)-dinitro-α-cyano-δ-phenyl-α-m-bromophenyl-Δ$^{\alpha}$-butene*, which is very readily converted into *γ(?)-nitro-α-cyano-δ-phenyl-α-m-bromophenyl-Δ$^{\alpha\gamma}$-butadiene*, m. p. 108°. H. Wren.

Diethylenic hydrocarbons. II. R. Escourrou (Bull. Soc. chim., 1926, [iv], **39**, 1249—1254).—On dehydration with excess of metaphosphoric acid, the methylheptenols previously described (this vol., 1022) afford the corresponding diolefines, in yields which decrease regularly with the mol. wt. of the alcohol. Pyrophosphoric acid induces formation of cyclic compounds. The new diolefines combine with bromine in chloroform, but crystalline bromine derivatives could not be obtained. The action of ozone indicates that in some cases the products are mixtures of isomerides. Thus dimethylheptenol at 140—150° affords (yield 90%) βζ-dimethyl-Δ$^{\alpha\epsilon}$-heptadiene, b. p. 140—143°/745 mm., d^{11} 0·7750, n_D^{11} 1·44707. *βζ-Dimethyl-Δ$^{\beta\zeta}$-octadiene*, b. p. 89°/52 mm., 165—166°/737 mm., d^{12} 0·7918, n_D^{15} 1·45245, and *βζ-dimethyl-Δ$^{\beta\zeta}$-nonadiene*, b. p. 181—183°/746 mm., d^{10} 0·8007, n_D^{10} 1·45807, are similarly prepared. Methyl*iso*propylheptenol at 130° and then at 170° gives a 20% yield of *βζη-trimethyl-βζ-octadiene*, b. p. 182—183°/756 mm., *d* 0·8100, n_D^{11} 1·46085, probably contaminated with traces of a cyclic derivative. *βζ-Dimethyl-Δ$^{\beta\zeta}$-decadiene* has b. p. 82—84°/10 mm., 201—202°/747 mm., d^{10} 0·8034, $n_D^{19\cdot5}$ 1·45937, and *βζι-trimethyl-Δ$^{\beta\zeta}$-decadiene*, b. p. 214°/742 mm., d^{11} 0·8037, n_D^{11} 1·45967; the product obtained on dehydration with acetic anhydride in the presence of sodium acetate has n_D^{19} 1·45617, probably owing to isomerisation. Similarly, *ζ-phenyl-β-methyl-Δ$^{\beta\zeta}$-heptadiene* obtained from phenylmethylheptenol by the acetic anhydride method (yield 60%) has b. p. 140—142°/22 mm., d^{10} 0·9205, n_D^{19} 1·53619, whilst the phosphoric acid method affords a product b. p. 126—128°/10 mm., 245—247°/745 mm., d^{10} 0·9296, n_D^{19} 1·54346. *β-Methyl-ζ-benzyl-Δ$^{\beta\zeta}$-heptadiene*, b. p. 136—138°/12 mm., d^{11} 0·9289, n_D^{11} 1·53245, cannot be obtained by the acetic anhydride method. R. Brightman.

Diacetylene. F. Straus and L. Kollek (Ber., 1926, **59**, [*B*], 1664—1681; cf. Lespieau and Prévost, A., 1925, i, 493; Müller, this vol., 44).—Diacetylene, C_4H_2, b. p. +9·5° to +10°/749·2 mm., d_4^0 0·7364, $n_D^{0\cdot8}$ 1·43862, is conveniently prepared by the action of cupric chloride solution on cuprous acetylide, followed by treatment of the copper diacetylide thus formed with dilute hydrochloric acid; the gas is purified in the Stock vacuum apparatus. Increase in the relative proportion of cupric chloride up to a point increases the purity of the diacetylene produced, but also diminishes the total yield of gas owing to increased oxidation of the copper compounds. Reaction proceeds more smoothly with the copper compounds of monosubstituted acetylenes. Liquid diacetylene readily polymerises to dark-coloured, solid products, the change appearing to be induced by the glass surfaces; when heated, it forms liquid polymerides. Di-iododiacetylene, m. p. 100° after softening at 97—98°, is prepared by the action of iodine on the silver salt, or, more conveniently, by treatment of diacetylene with iodine and hypoiodous acid; impure specimens are violently explosive. It is transformed by iodine in ethereal solution into ααβγδδ-hexaiodobutadiene, m. p. 165·5—166·5° (decomp.) after darkening at 140° (cf. Lespieau and Prévost, *loc. cit.*). With iodine in chloroform solution, diacetylene affords *diacetylene tetraiodide*, $C_4H_2I_4$, m. p. 58—59°. Addition of bromine to diacetylene

occurs with unexpected slowness, the main product being the hexabromide, m. p. 183·5°; its production is invariably accompanied by that of an *isomeride*, m. p. 114°. Removal of the bromine from the hexabromide is readily effected by zinc in the presence of alcohol or acetone, but does not lead to a smooth regeneration of diacetylene. The acetylenic hydrocarbons evolved contain, at the most, traces of diacetylene. The main products are a monosubstituted acetylene of unknown structure and butadiene.

H. WREN.

Law of periodicity. I. Activity of organic halides. P. PETRENKO-KRITSCHENKO and V. OPOTZKY (Ber., 1926, **59**, [*B*], 2131—2140).—Further evidence is adduced which confirms the hypothesis that the accumulation and approximation of certain atoms and groups within the molecule cause a change in their mutual relationships (cf. A., 1923, ii, 749). The rates of reaction of all the chloro-, bromo-, and iodo-derivatives of methane (with exception of carbon tetraiodide), the mono- and di-αα- and di-αβ-chloro-, bromo-, and iodo-derivatives of ethane, the chloro-derivatives of toluene, and acetic acid have been examined with (*a*) potassium, tetramethylammonium, tetraethylammonium, barium, and thallium hydroxides and sodium ethoxide, and (*b*) with ammonia, piperidine, water, alcohol, silver nitrate, potassium acetate, and potassium thiocyanate. With reagents of group (*a*), a distinct periodicity is observed, which is particularly marked with the chloro-derivatives. With reagents of the group (*b*), the transition from mono- to di-substituted derivatives proceeds similarly to that with group (*a*), but, in general, there is no evidence of periodicity. In all cases, decrease of activity is observed when two halogen atoms become concentrated at the same carbon atom and in the transition from αα- to αβ-disubstituted compounds. Monosubstituted derivatives of ethane are almost invariably less active than those of methane, but this is not the case with αα-dihalogeno-derivatives, with which the usual effect of homology is not obvious. Whereas the accumulation of similar groups results in a diminution of activity, the similar accumulation of dissimilar groups causes increase in activity which is the more pronounced as the likeness between the groups diminishes. This is illustrated by the increasing sequence of activity in the compounds $CH_2(Hal)_2$, $CH_2Ph{\cdot}OH$, $CH_2{:}CH{\cdot}CH_2{\cdot}OH$, $CO_2H{\cdot}CH_2Cl$, CH_2PhCl, $CH_2{:}CH{\cdot}CH_2Cl$. H. WREN.

Similar behaviour of persubstituted halogen compounds and halogenoacylamines. E. SCHMIDT, A. ASCHERL, and W. VON KNILLING (Ber., 1926, **59**, [*B*], 1876—1888).—The ability to add the esters of hypobromous acid to olefinic double linkings in alcoholic solution is shown by bromotrinitromethane, tribromonitromethane, dibromodinitromethane, and bromonitromalonic esters, but not by carbon tetrabromide. Tribromoacetic esters do not add methyl hypobromite to *cyclo*hexene, but this reaction is effected by dibromomalonic esters and, more readily, by bromomethanetricarboxylic esters. Enhanced activity is observed when the group $-CO{\cdot}CBr_2{\cdot}CO-$ is present in cyclic form, as in dibromodimethyldihydroresorcinol, dibromodiketohydrindene, or dibromobarbituric acid, and also with the group $-C{:}C{\cdot}CBr_2{\cdot}C{:}C-$ as in 2 : 4 : 6 : 6-tetrabromo-$\Delta^{1:4}$-*cyclo*hexadien-3-one. According to previous experience, addition of alkyl hypobromite occurs only when the reactive bromine atom attached to the persubstituted carbon can be considered replaceable by a tautomeric hydrogen atom. Halogenoacylamines are decomposed by water and alkali hydroxides into acid amides and hypohalogenous acid; hence, in them, as in persubstituted bromo-compounds, the halogen is replaced by hydrogen by means of alkali hydroxide. In solvents containing the hydroxyl group an equilibrium is set up thus: $Ac{\cdot}NH{\cdot}Hal+H_2O$ [$R{\cdot}OH$, $R{\cdot}CO{\cdot}OH$] $\rightleftharpoons AcNH_2+Hal{\cdot}OH$ [$Hal{\cdot}OR$, $Hal{\cdot}O{\cdot}CO{\cdot}R$]. This is precisely similar to the equilibrium $CBr(NO_2)_3+R{\cdot}OH \rightleftharpoons CH(NO_2)_3+R{\cdot}OBr$ with polynitroparaffins. In consequence, the reactive halogen in persubstituted bromo-derivatives and halogenoacylamines functions as buffered hypohalogenous acid and one nitro-group of tetranitromethane as "buffered" nitric acid. Such "buffered" acids add as such in the presence of water, as esters in alcoholic solution, and as mixed acid anhydrides in the presence of organic acids. Further analogies between the actions of persubstituted bromo-, bromonitro-, or polynitro-compounds and halogenoacylamines exist in absence of hydroxylated solvents, *e.g.*, in their halogenating action towards the aromatic and heterocyclic nucleus. H. WREN.

Action of phosphorus halides or halogen acids on acetylenic γ-glycols. W. KRESTINSKY (Ber., 1926, **59**, [*B*], 1930—1936).—The stability of the compound towards bromine or permanganate and the firmness with which the halogen atoms are retained are not in harmony with the structure, $CMe_2Br{\cdot}C{:}C{\cdot}CMe_2Br$, assigned by Dupont (A., 1911, i, 174) to the product, m. p. 39°, of the action of hydrogen bromide on βε-dimethyl-Δγ-hexinene-βε-diol. The mol. refraction in alcohol or toluene, the positive reaction towards tetranitromethane, and the oxidation by permanganate to acetone, oxalic acid, and α-hydroxy*iso*butyric acid indicate the formula $CMe_2{:}CBr{\cdot}CBr{:}CMe_2$. The apparently saturated nature of the compound is ascribed to the presence of a conjugated system with two ethylenic linkings which in themselves are already partly saturated. Zinc dust in the presence of boiling alcohol reduces the dibromide to a very unstable hydrocarbon, m. p. 35°, which rapidly becomes amorphous. Phosphorus tribromide converts βε-dimethyl-Δγ-hexinene-βε-diol in the presence of cold benzene into a mixture of at least three *dibromides*. One of these, to which the constitution $CMe_2Br{\cdot}C{:}C{\cdot}CMe_2Br$ is ascribed, has m. p. 46—48°. The remaining two have b. p. 111—113°/13 mm. and 116—118°/13 mm., respectively; the latter is converted by zinc dust into an unstable *hydrocarbon*, (?)C_8H_{12}, b. p. 126—127°, d_4^{20} 0·7680, n_D^{20} 1·48143. H. WREN.

Action of hydrogen bromide on a glycol of the acetylenic series. J. SALKIND and A. KRUGLOW (Ber., 1926, **59**, [*B*], 1936—1941; cf. preceding abstract).—The action of a saturated solution of hydrogen bromide in glacial acetic acid on αδ-diphenyl-Δ^{β}-butinene-αδ-diol, m. p. 140°, leads to the production

of the *monobromo-oxide*, $\begin{matrix}CBr\cdot CHPh\\ \|\\ CH-CHPh\end{matrix}>O$; this is oxidised by permanganate in acetone to benzoic acid and *αβδ-tribromo-αδ-diphenyl-Δ$^{\beta}$-butene*, m. p. 155°, which does not add bromine, is scarcely oxidised by permanganate in alkaline solution, is hydrolysed with great difficulty, and affords benzoic acid as sole isolable product of oxidation. When slightly aqueous acetic acid is used the main product at the atmospheric temperature is a very stable *dibromide*, m. p. 114°, (converted by alcoholic potassium hydroxide into diphenyldiacetylene); the liquid monobromo-oxide is also formed in small amount. At 0° a second *dibromide*, m. p. 92—95°, is produced which is readily transformed into the isomeride, m. p. 114°. When the latter compound is subjected to the protracted action of hydrogen bromide and glacial acetic acid the tribromide, m. p. 155°, is obtained together with a liquid *dibromide*. H. WREN.

Preparation of glycerol monochlorohydrin. J. BÖESEKEN and P. H. HERMANS (Bull. Soc. chim., 1926, [iv], **39**, 1254).—The method of preparing glycerol monochlorohydrin recently described by Fourneau and Marquès (this vol., 711) has already been given by the authors (A., 1924, i, 257).

R. BRIGHTMAN.

Configurational relationships of α-, β-, and γ-hydroxy-acids. II. Conversion of *d*-α-amino-γ-hydroxybutane into *d*-αγ-dihydroxybutane. P. A. LEVENE and H. L. HALLER (J. Biol. Chem., 1926, **69**, 569—574; cf. this vol., 1024).—*sym*-Di-(*l*-γ-hydroxybutyl)carbamide, $[\alpha]_D^{22}$ —45°, on hydrolysis with barium hydroxide (hydrochloric acid caused complete racemisation), gave *d-α-amino-γ-hydroxybutane, chloroplatinate*, m. p. 206°, $[\alpha]_D^{22}$ +8·6°. On deamination this gave d-αγ-*dihydroxybutane*, b. p. 103—107°/14 mm., $[\alpha]_D^{22}$ +18·5° in alcohol, *diphenylcarbimide*, m. p. 122—123°, $[\alpha]_D^{22}$ +54·8° in alcohol. The above results confirm the authors' previous conclusion (*loc. cit.*) regarding the configurational relationship of β-hydroxybutyric and γ-hydroxyvaleric acids. C. R. HARINGTON.

α-Oxides from aldehydes and carboxylic acids. III. J. VON BRAUN and W. MÜNCH (Ber., 1926, **59**, [*B*], 1941—1950; cf. A., 1923, i, 1186).—*Ethyl α-bromo-δ-phenyl*-n-*valerate*, b. p. 203—205°/28 mm., is smoothly converted by dimethylamine in benzene into *ethyl α-dimethylamino-δ-phenyl*-n-*valerate*, b. p. 171°/16 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 78°; *methiodide*, m. p. 144°), which is reduced by sodium and alcohol to β-*dimethylamino-ε-phenyl*-n-*amyl alcohol*, b. p. 188°/22 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 133°; *methiodide*, m. p. 110°). The quaternary hydroxide is decomposed by heat, giving trimethylamine, a strongly unsaturated base, (?) polymeric γ-*phenyl*-n-*propylethylene oxide*, α-*phenylpentane-δε-diol*, b. p. 220—225°/17 mm., and γ-*phenyl*-n-*propylethylene oxide*, b. p. 122°/16 mm., d_4^{17} 0·9984, n_D^{17} 1·5144. The latter compound is converted by dimethylamine in benzene into α-*phenyl-ε-dimethylaminopentan-β-ol*, b. p. 155°/17 mm. (non-crystalline *hydrochloride* and *methiodide*; *picrate*, m. p. 86°).

*Ethyl α-bromo*cyclo*pentylacetate*, b. p. 108—111°/9 mm. (α-*bromo*cyclo*pentylacetic acid*, m. p. 50—51°), is converted by dimethylamine in benzene into *ethyl α-dimethylamino*cyclo*pentylacetate*, b. p. 103—104°/9 mm. (non-crystalline *picrate*; *methiodide*, m. p. 174°), which is reduced to β-*dimethylamino*-β-cyclo*pentylethyl alcohol*, b. p. 105—107°/9 mm. (*hydrochloride*, m. p. 126°; *picrate*, m. p. 88°; *methiodide*, m. p. 127°). The corresponding quaternary hydroxide is decomposed by heat into trimethylamine, cyclo*pentylethylene oxide*, b. p. 155—157°, d_4^{20} 0·9370, n_D^{20} 1·4480, and (?) the corresponding glycol, b. p. 229—233°.

Ethyl αα'-dibromoazelaate, b. p. 215°/12 mm., is converted by dimethylamine in benzene into *ethyl αα'-bisdimethylaminoazelaate*, b. p. 191—193°/11 mm., which is reduced to the corresponding *alcohol*, b. p. about 200°/12 mm., in very unsatisfactory yield. *Ethyl αα'-dipiperidinoazelaate*, b. p. 250—255°/12 mm. (slight decomp.), 220°/2 mm., is satisfactorily reduced to the *alcohol*,

$CH_2(OH)\cdot CH(NC_5H_{10})\cdot[CH_2]_5\cdot CH(NC_5H_{10})\cdot CH_2\cdot OH$,

b. p. 220—225°/1·5 mm. (non-crystalline *methiodide* and *methochloride*; corresponding *chloroplatinate*, decomp. 244°), but the oxide obtained from it was insufficient for investigation.

Ethyl *meso-αα'*-dibromoadipate, m. p. 67°, is converted in poor yield into *ethyl αα-bisdimethylaminoadipate*, b. p. 180—190°/17 mm. (*methiodide*, m. p. 189°), which gives only small yields of the corresponding alcohol. *Ethyl αα'-dipiperidinoadipate*, m. p. 99° (*hydrochloride*, m. p. 180°; *picrate*, decomp. 217—219°), is formed in relatively poor yield owing to the readiness with which it is hydrolysed to *αα'-dipiperidinoadipic acid*, m. p. 94—97° (*hydrochloride*, m. p. 208°). The ester is reduced by sodium and alcohol to a mixture of the *alkamine*, $C_{18}H_{22}O_2N_2$, m. p. 107° (*hydrochloride*, m. p. 258°; *picrate*, decomp. 222—223°; *methiodide*, m. p. 226°), and an isomeric *alkamine*, m. p. 78—79° (*hydrochloride*, m. p. 253—254°; *methiodide*, m. p. 201—202°). The quaternary hydroxide corresponding with the base, m. p. 107°, is decomposed when heated into 1-methylpiperidine, *αβ-oxido-ε-piperidino*-n-*hexan-ζ-ol*, b. p. 156—163°/12 mm., d_4^{21} 1·020, n_D^{21} 1·4857 (non-crystalline *methiodide*; *picrate*, m. p. 99°), and the *product*, $C_6H_{10}O_2$, b. p. 78—82°/12 mm., d_4^{25} 1·075, n_D^{25} 1·4750, which appears to consist of a mixture of little di-αβεζ-oxido-*n*-hexane and much αβ-oxido-Δ$^{\delta}$-hexen-ζ-ol.

H. WREN.

Reactivity of halogenated ethers. I. Halogenated diethyl ethers and zinc. F. NEHER and C. L. FLEECE (J. Amer. Chem. Soc., 1926, **48**, 2416—2425).—Dichloroacetal is obtained in 78% yield by the addition of granulated zinc to αββ-trichlorodiethyl ether, dissolved in 6 mols. of absolute alcohol, at 5°. *α-Chloro-βββ-tribromodiethyl ether*, b. p. 120—121·5°/14 mm., $d_4^{20\cdot5}$ 2·2069, obtained by the action of phosphorus pentachloride on ethereal bromal alcoholate, yields similarly *ethyl ββ-dibromovinyl ether*, b. p. 73—75°/15 mm., $d_4^{17\cdot5}$ 1·7697. When treated with bromine, the latter affords *αβββ-tetrabromodiethyl ether*, decomp. when heated, $d_4^{17\cdot3}$ 2·2432, which yields the above ethyl dibromovinyl ether when treated with zinc. ββ-Dichloro-αβ-dibromodiethyl ether, b. p. 106·5—

108°/16 mm. (slight decomp.), $d_4^{18\cdot5}$ 1·8249 (cf. Oddo and Mameli, A., 1904, i, 289), obtained by the addition of bromine to dichlorovinyl ether, yields the latter when treated with zinc. F. G. Willson.

Synthesis of a new class of mixed formals, of the formula $OR{\cdot}CH_2{\cdot}O{\cdot}CH(CH_2X){\cdot}CH_2X'$ (by additive reaction with epichlorohydrin). L. Blanchard (Bull. Soc. chim., 1926, [iv], **39**, 1263—1265).—On treatment with excess of methyl alcohol in the presence of sulphuric acid, epichlorohydrin affords "chloromethyline," *methyl γ-chloro-β-hydroxypropyl ether*, b. p. 173°/752 mm. (yield 88—90%). With 1 mol. of a halogen-substituted methyl ether, $CH_2X{\cdot}OR$, in the presence of mercuric chloride in the cold, epichlorohydrin affords a mixed formal of the type $CH_2Cl{\cdot}CH(O{\cdot}CH_2{\cdot}OR){\cdot}CH_2X$. In the absence of cooling, symmetrical formals of the type $CH_2[O{\cdot}CH(CH_2X){\cdot}CH_2Cl]_2$ are obtained. The following are described: *ethoxymethyl αγ-dichloroisopropyl ether*, b. p. 96—98°/16 mm., *amyloxymethyl αγ-dichloroisopropyl ether*, 133—135°/19 mm.; *ethoxymethyl α-chloro-γ-bromoisopropyl ether*, b. p. 115—117°/20 mm., and the corresponding *amyloxymethyl ether*, b. p. 140—150°/15 mm.; *ethoxymethyl α-chloro-γ-iodoisopropyl ether*, b. p. 130°/18 mm. All the above formals are converted into symmetrical formals when heated above 150°. R. Brightman.

Syntheses of calcium glucophosphate and glycerophosphate. S. Sabetay (Bull. Soc. chim., 1926, [iv], **39**, 1255—1263).—The action of phosphoryl chloride in cold pyridine on dextrose, followed by treatment of the reaction mixture with lime, affords a calcium glucophosphate, $[\alpha]_D^{20}$ +29·23°, composed of 52% of mono-ethers, the remainder probably consisting of a diether, $\begin{matrix}-CH{\cdot}O\\ |\\ -CH{\cdot}O\end{matrix}\!>\!PO_2{\cdot}\frac{1}{2}Ca$, and a di-glucomonophosphate. This glucophosphate reduces Fehling's solution on warming and gives a voluminous precipitate with lead subacetate, but not with lead acetate. On treatment with *N*-sodium hydroxide at the ordinary temperature, the proportion of mono-ethers is considerably increased and a glucophosphate can be isolated containing 89% of mono-ethers. Similarly, glycerol affords a calcium glycerophosphate very soluble in water; and consisting solely of mono-ethers, the poly-ethers first formed being readily hydrolysed by the lime water. Barium hydroxide affords a barium salt insoluble in water and in acetic acid. Replacement of the pyridine in these syntheses by dimethylaniline gives inferior results.

R. Brightman.

Interpretation of the acetyl value and ester transformation of glycerides by acetic anhydride. D. Holde (Ber., 1926, **59**, [*B*], 1730—1733).—The acetyl values of the unsaponifiable solid and liquid portions of lignite tar and the dry distillates of montan wax are due to the presence of small amounts of polyhydric phenols which are not removed by treatment with alkali hydroxide, and not to higher alcohols (cf. Marcusson and Picard, A., 1924, i, 387). Ester transformation does not occur during the treatment of glycerides with acetic anhydride (cf. Willstätter and Madinaveitia, A., 1912, ii, 1104); the observed acetyl values of tristearin are due to the presence in it of mono- and di-glycerides.

H. Wren.

Lengthened chain compounds of sulphur. G. M. Bennett (Nature, 1926, **118**, 555).—A criticism of the conclusions of Rây and Bose-Rây (this vol., 1023) regarding the individuality of the products of interaction of dithioethylene glycol and ethylene dibromide. Such products are probably mixtures of substances of the general formula $A{\cdot}(S{\cdot}C_2H_4)_n{\cdot}S{\cdot}B$, where *A* and *B* may be alike or different, and may be $\cdot CH_2{\cdot}CH_2{\cdot}OH$, $\cdot CH{:}CH_2$, or $\cdot CH_2{\cdot}CH_2Hal$.

A. A. Eldridge.

Alkyl hydrogen sulphates. F. Popelier (Bull. Soc. chim. Belg., 1926, **35**, 264—276).—Alkyl hydrogen sulphates are quantitatively prepared by heating sulphuric acid with a large excess of the anhydrous alcohol in such a manner that the water formed is removed as the binary mixture with the alcohol and the temperature of the reactants is not sufficiently high to induce noticeable etherification of the alcohol. The preparation of *iso*amyl, *n*-butyl, *iso*butyl, *n*-propyl, and ethyl hydrogen sulphate is described. The compounds readily form salts with amines, the following being described: the *aniline* salts of *iso*amyl (m. p. 123—123·5°), butyl (m. p. 111·5—114°), *iso*butyl (m. p. 122—122·5°), propyl (m. p. 108·5—109°), and ethyl (m. p. 106·7—107°) hydrogen sulphates; *p-toluidine* iso*amyl sulphate*, m. p. 98·2—98·8°; *o-toluidine* iso*amyl sulphate*, m. p. 86—86·5°; *o-toluidine butyl sulphate*, m. p. 68·5—69°; *α-naphthylamine ethyl sulphate*, m. p. 157·8—158°; basic *benzidine* iso*amyl sulphate*, decomp. above 200°; normal *benzidine butyl sulphate*, decomp. above 240°; *benzylamine ethyl sulphate*, m. p. 64·5—65°; *diphenylamine* iso*amyl sulphate*, m. p. 78·5—79°; *diphenylamine ethyl sulphate*, m. p. 76·5—77°; *methylaniline ethyl sulphate*, m. p. about 44°; *dimethylaniline propyl sulphate*, m. p. about 58°; *pyridine* iso*amyl sulphate*, m. p. about 46°; *pyridine butyl sulphate*, m. p. about 41°; *quinoline propyl sulphate*, m. p. about 142°. Aniline *iso*butyl sulphate is converted by an excess of aniline at 170° into aniline phenylsulphamate. *o-Toluidine phenylsulphamate*, *o-toluidine o-tolylsulphamate*, and *aniline o-tolylsulphamate* are described.

P. V. McKie.

Supposed potassium hydroxymethanesulphonate of Max Müller. F. Raschig and W. Prahl (Ber., 1926, **59**, [*B*], 2025—2028; cf. this vol., 598).—Müller's potassium hydroxymethanesulphonate is identified as *potassium s-acetonedisulphonate* by chemical and crystallographical comparison of the original preparation with that derived from *s*-dichloroacetone and potassium sulphite. The origin of the salt is obscure, since acetone, alone or in the presence of methyl alcohol, could not be converted into the disulphonate. *Potassium* and *barium acetonetetrasulphonates* are identical with the products described by Müller as potassium and barium hydroxymethanedisulphonates.

H. Wren.

Sulphoxyl compounds. XIV. Constitution of sulphoxyl compounds. A. Binz (Ber., 1926, **59**, [*B*], 1695—1698).—The formulæ $:C{\cdot}O{\cdot}S{\cdot}O{\cdot}C:$ and

$\begin{matrix}:C\\:C\end{matrix}>S<\begin{matrix}O\\O\end{matrix}$ (cf. Raschig, this vol., 598) are not completely satisfactory for sulphoxyl compounds, since neither explains why formaldehydesulphoxylic acid is converted by iodine into sulphuric acid and formaldehyde, whereas "formaldehyde bisulphite" remains unchanged, why the condensation products from "formaldehyde bisulphite" and amines are transformed by potassium cyanide into sulphite and nitriles, whereas the analogous reaction occurs, at most, to a minimal extent with sulphoxyl compounds, and why formaldehyde- and benzaldehyde-sulphoxylic acids are dibasic. The differences between the properties of the two classes of compounds are so pronounced that the application of observations on the constitution of "aldehyde bisulphite" compounds to sulphoxyl derivatives appears scarcely justified.

H. WREN.

Catalytic transformation of fatty acids into hydrocarbons. G. A. STADNIKOV and E. E. IVANOVSKII.—See this vol., 1110.

Decomposition of formic acid by ultra-violet light. E. MÜLLER and H. HENTSCHEL (Ber., 1926, **59**, [*B*], 1854—1855).—The catalytic decomposition of formic acid into carbon dioxide and hydrogen in the presence of platinum metals is very greatly influenced by the dispersivity of the latter and falls rapidly as the catalyst becomes aggregated. In boiling aqueous solution, formic acid is decomposed by the action of ultra-violet light into carbon dioxide and hydrogen (of which a portion is used for reduction) and also into water and carbon monoxide. The intermediate production of methyl alcohol or formaldehyde could not be established. Decomposition is accompanied by the production of a non-crystalline solid in the solution which could not be identified.

H. WREN.

Nervonic acid. E. KLENK (Z. physiol. Chem., 1926, **157**, 283—290).—"Nervonic acid," $C_{24}H_{46}O_2$, obtained by hydrolysis of the cerebroside isolated from human brain (A., 1925, i, 1346), when shaken, in ethereal solution, with colloidal palladium in an atmosphere of hydrogen takes up two atoms of hydrogen, giving a saturated fatty acid, m. p. 85°. This appears to be identical with lignoceric acid derived from beechwood tar, which has itself been shown to be identical with *n*-tetracosoic acid.

H. D. KAY.

New acid from cerebroside of brain. E. KLENK (Z. physiol. Chem., 1926, **157**, 291—298).—An *acid*, $C_{24}H_{46}O_3$, m. p. 65°, $[\alpha]_D^{20}$ +2·87°, has been isolated from the products obtained by hydrolysis with 10% methyl-alcoholic sulphuric acid of certain cerebroside fractions derived from human brain. The acid is separated from nervonic acid and certain other impurities by precipitation with magnesium acetate followed by fractional precipitation with lead acetate. It is probably a hydroxy-acid with a double linking in the molecule.

H. D. KAY.

Propiolic acid and propiolic anhydride. F. STRAUS and W. VOSS (Ber., 1926, **59**, [*B*], 1681—1691).—Propiolic acid, b. p. 52°/18 mm., m. p. +9°, is conveniently prepared by the action of carbon dioxide under pressure on sodium acetylide mixed with sand. Similarly, disodium acetylide affords acetylenedicarboxylic acid, m. p. 171°. Propiolic acid appears indefinitely stable, polymerisation to trimesic acid in the presence of active charcoal or spongy platinum under varied conditions not being observed. Baeyer's observation that ethyl propiolate is converted by zinc and hydrochloric acid into ethyl propargyl ether could not be confirmed, the main products of the action being ethyl acrylate and propionate mixed with chlorinated compounds. Attempts to prepare ethyl propiolate by the action of anhydrous copper sulphate on a boiling, ethyl-alcoholic solution of propiolic acid yielded carbon dioxide, acetylene, copper acetylide, and *ethyl ββ-diethoxypropionate*, b. p. 93°/22 mm., in varying proportions. *Sodium propiolate* is described. *Propiolic anhydride*, b. p. 56°/16 mm., d_4^{21} 1·1432, $n_D^{23\cdot4}$ 1·4358, prepared by the action of thionyl chloride on sodium propiolate in dry ether, is converted by the requisite bases into the following compounds: *ammonium propiolate*, m. p. 135° (decomp.) after darkening at 130°, and propiolamide, m. p. 60·5—61°; *aniline propiolate* (+0·5H_2O), m. p. 71—72° (decomp.), and *propiolanilide*, m. p. 86—87°; p-*phenetidine propiolate*, m. p. 117° (decomp.), and *propiol*-p-*phenetidide*, m. p. 99—100·5°. Ethyl propiolate and diethylamine afford *ethyl* β-*diethylaminoacrylate*, b. p. 90—91°/0·15 mm. *Ethyl* β-*piperidinoacrylate*, b. p. 115—116°/0·3 mm., 152°/14 mm., and *ethyl* β-*anilinoacrylate*, colourless needles, m. p. 114—114·5°, or yellow platelets, m. p. 116° after softening at 114°, are similarly prepared.

H. WREN.

Preparation of glyoxylic acid from oxalic acid. W. MOHRSCHULZ.—See this vol., 1110.

Oxidation of pyruvic acid by metallic ions. Determination of ketonic and enolic forms. C. FROMAGEOT (Bull. Soc. chim., 1926, [iv], **39**, 1207—1222).—A more detailed account of work already published (this vol., 820).

Condensation of lactic acid to methylsuccinic acid under the influence of the combined action of catalysts at high pressures and temperatures. W. IPATIEV and G. RASUVAJEV (Ber., 1926, **59**, [*B*], 2031—2034).—Treatment of sodium lactate in aqueous solution in the presence of nickel oxide and aluminium oxide with hydrogen at 270° and 70 atm. gives methylsuccinic acid (*methyl* ester, b. p. 196—198°, $d_D^{18\cdot5}$ 1·4221; *ethyl* ester, b. p. 217—218°, $d_4^{18\cdot5}$ 1·0154, n_D^{18} 1·4210), propionic, *n*-butyric, and α-methylbutyric acids. The initial formation of dimethylmalic acid is postulated. Methane and sodium carbonate are also formed in considerable proportions.

H. WREN.

Electrolytic synthesis of tetramethyladipic acids. E. H. FARMER and J. KRACOVSKI (J.C.S., 1926, 2318—2323).—Electrolysis of sodium ethyl *as*-dimethylsuccinate ($CO_2Et\cdot CMe_2\cdot CH_2\cdot CO_2Na$) yields a mixture of esters from which *αα'α'-tetramethyladipic acid*, m. p. 191°, and methoxypivalic acid (?) were obtained. The isomeric sodium ethyl *as*-dimethylsuccinate gave *ββββ'β'-tetramethyladipic acid*, m. p. 207—208°, ββ-dimethylacrylic acid, and β-*methoxyisovaleric acid*, b. p. 118°/14 mm.

H. BURTON.

Conditions underlying the formation of unsaturated and of cyclic compounds from halogenated open-chain derivatives in relation to the atomic volume tetrahedral theory. II. Products derived from α-halogenated adipic acids. Halogenated glutaconic acids and a synthesis of the aromatic nucleus. R. F. HUNTER (Chem. News, 1926, **133**, 209—213).—A theoretical paper concerned mainly with Ingold's work.

H. WREN.

[Attempted] synthesis of *apo*fenchocamphoric acid. Preparation of αα-dimethyl-γ-carboxyadipic acid. K. C. ROBERTS (J. Amer. Chem. Soc., 1926, **48**, 1975—1977).—The monosodium derivative of ethyl αα-dimethylacetone-γγ-dicarboxylate condenses with ethyl chloroacetate, giving *ethyl β-keto-αα-dimethylbutane-αγδ-tricarboxylate*, b. p. 150—160°/14 mm., n_D 1·4400, a little of the *ester*, $CO_2Et{\cdot}CMe_2{\cdot}CO{\cdot}C(CH_2{\cdot}CO_2Et)_2{\cdot}CO_2Et$, b. p. 170—180°/14 mm., n_D 1·4458, being also formed in one experiment. Reduction with sodium amalgam and aqueous alcohol yields *ethyl β-hydroxy-αα-dimethylbutane-αγδ-tricarboxylate*, from which *αα-dimethylbutane-αγδ-tricarboxylic acid*, m. p. 139—141°, was obtained, using red phosphorus and hydriodic acid (*d* 1·93). With hydriodic acid of *d* 1·69, crystals of the *γ-lactone*, $C_9H_{12}O_6$, m. p. 146°, were isolated. Improved yields of ethyl αα-dimethylacetone-γγ-dicarboxylate are obtained by using a mixture of absolute alcohol and anhydrous ethyl acetate and passing a stream of carbon dioxide through the reaction mixture. R. BRIGHTMAN.

Pectic acids. E. K. NELSON (J. Amer. Chem. Soc., 1926, **48**, 2412—2414).—The pectic acid obtained in the determination of pectin in fruit products by the method of Wichmann and Chernoff (J. Assoc. Off. Agric. Chem., 1924, **8**, 129), is identical with Ehrlich and Sommerfeld's digalacturonic acid (this vol., 441), of which the *barium* salt is described.

F. G. WILLSON.

Products of the action of chlorosulphonic acid on acetyl chloride. M. KRAČJINOVIĆ (Ber., 1926, **59**, [*B*], 2117—2119).—The primary reaction at 20° occurs according to the scheme, $CH_3{\cdot}COCl + HO{\cdot}SO_2Cl = CH_3{\cdot}CO{\cdot}O{\cdot}SO_2Cl + HCl$. Above 45°, the product $CH_3{\cdot}CO{\cdot}O{\cdot}SO_2Cl$ becomes transformed into sulphoacetyl chloride, which with more chlorosulphonic acid at temperatures above 60° is converted into sulphomethanesulphonyl chloride, carbon dioxide, and hydrogen chloride. The substance, $C_8H_8O_4$, m. p. 99°, obtained at temperatures above 60°, is identified as 2-methylpyrone-6-acetic acid (cf. Collie and Hilditch, J.C.S., 1907, **91**, 789).

H. WREN.

Decomposition of formaldehyde by heat. S. S. MEDVEDEV and E. A. ROBINSON.—See this vol., 1010.

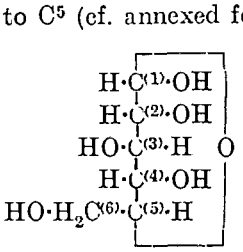
Iodoform reaction for acetone and ethyl alcohol. J. VAN DER LEE (Chem. Weekblad, 1926, **23**, 444—445).—Tests under the same conditions show that iodoform is formed more quickly, and in solutions of lower p_H values, from acetone than from alcohol. S. I. LEVY.

Synthesis of mesityl oxide from acetone. I. GASOPOULOS (Ber., 1926, **59**, [*B*], 2188).—Mesityl oxide, with a little phorone, is conveniently prepared by the action of phosphoryl chloride on acetone if rise of temperature above the atmospheric is avoided.

H. WREN.

Acetylacetonate of zirconium and hafnium. G. VON HEVESY and M. LÖGSTRUP (Ber., 1926, **59**, [*B*], 1890—1893).—*Hafnium acetylacetonate*, $Hg(C_5H_7O_2)_4{,}10H_2O$, is prepared by the addition of acetylacetone and sodium carbonate to an aqueous solution of hafnium oxychloride and converted into the anhydrous compound by two crystallisations from acetylacetone. Zirconium acetylacetonate (cf. Biltz and Clinch, A., 1904, i, 715) is slowly decomposed by hot alcohol. The crystalline forms of the anhydrous acetylacetonates are closely similar, whilst the refractive index of the zirconium compound is slightly greater than that of the hafnium derivative. The data d_4^{25} 1·415 and 1·670 are recorded. Both compounds have m. p. 193—195° (slight decomp.) and behave similarly when sublimed. Neither compound adds ammonia. The solubilities in ethylene bromide are 0·0907 mol. per litre at 25° for the zirconium and 0·620 mol. for the hafnium compound. Each compound forms a cherry-red solution in carbon disulphide after some time; the change appears characteristic for the elements. H. WREN.

Ring structure in sugar group. H. D. K. DREW and W. N. HAWORTH (J.C.S., 1926, 2303—2310).—The rotation of an equimolecular mixture of the α- and β-forms of a sugar, thus eliminating the effect of the C^1 atom, should be dependent on the sign of the ring-forming carbon atom situated lower in the chain. When the hydrogen atom attached to C^5 (cf. annexed formula for α-*d*-glucose) is on the right of the formula, provided C^5 is asymmetrical, the sign of this carbon atom is positive. If a 1 : 5 ring is persistently formed in ascending to the higher series from a given sugar, the successive rotations of the equimolecular mixture will be the same as the successive signs of the C^4, C^3, C^2 atoms in the parent sugar. Examination of the specific rotations of equimolecular mixtures of the α- and β-forms in different series of aldoses indicates the correctness of the amylene oxide formula.



H. BURTON.

Mercaptals of sugars. I. *n*-Butyl mercaptals. II. *n*-Propyl mercaptals. Y. UYEDA (Bull. Chem. Soc. Japan, 1926, **1**, 179—182).—*n*-Butyl and *n*-propyl mercaptans combine with sugars, forming mercaptals similar to those obtained by Fischer (A., 1894, i, 269) using ethyl mercaptan.

I. [With J. KAMON.]—The n-*butyl mercaptals* of dextrose, m. p. 124°, $[\alpha]_D^{12}$ +27·00°; galactose, m. p. 123°, $[\alpha]_D^{12}$ +12·67°; mannose, m. p. 117°, $[\alpha]_D^{3}$ +16·45°; rhamnose, m. p. 119°, $[\alpha]_D^{3}$ +16·49°; arabinose, m. p. 111·5°, $[\alpha]_D^{3}$ +14·00°; maltose, m. p. 126°, $[\alpha]_D^{3}$ +12·00°; lactose, m. p. 106°, $[\alpha]_D^{3}$ +23·55°; and sucrose, m. p. 123°, $[\alpha]_D^{3}$ +3·71°, are described.

II. [with Y. MAEDA.]—The n-*propyl mercaptals* of

dextrose, m. p. 147°, $[\alpha]_D^{17}$ +41°; galactose, m. p. 129°, $[\alpha]_D^{17}$ +27·5°; mannose, m. p. 125°, $[\alpha]_D^{17}$ +31°; rhamnose, m. p. 130°, $[\alpha]_D^{17}$ +10°; arabinose, m. p. 128°, $[\alpha]_D^{17}$ +29°; maltose, m. p. 146°, $[\alpha]_D^{17}$ +25°; and sucrose, m. p. 146°, $[\alpha]_D^{17}$ +13·5°, are described. H. E. F. NOTTON.

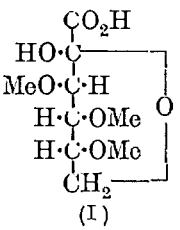
Activity of the fourth hydroxyl group of dextrose. H. H. SCHLUBACH and H. FIRGAU (Ber., 1926, **59**, [*B*], 2100—2102).—The fourth hydroxyl group of dextrose is not characterised by particular activity, and its preferential use in the formation of natural polysaccharides is due to some mechanism other than simple etherification. βγζ-Trimethylglucose is prepared in 75% yield by treatment of octamethyl-lactose with methyl-alcoholic hydrogen chloride, benzoylation of the product, and removal of pentamethylgalactose followed by debenzoylation and hydrolysis of the residue with 8% hydrochloric acid. It is converted by treatment with hydrogen chloride in chloroform, followed by the use of methyl alcohol and silver carbonate, into 2 : 3 : 6-trimethyl-β-methylglucoside. The latter substance is converted by potassium in the presence of benzene into the *potassium* derivative, $C_{10}H_{19}O_6K$, converted by methyl iodide into tetramethyl-β-methylglucoside, but unaffected by propyl iodide, benzyl chloride, or acetobromoglucose. H. WREN.

Acetone compounds of sugars and their derivatives. VII. Constitution of some monoacyl derivatives of monoacetoneglucose [glucose *iso*propylidene ether] and the ring structure of dextrose. H. OHLE and K. SPENCKER (Ber., 1926, **59**, [*B*], 1836—1848).—In attempts to establish the constitution of the products obtained by the action of acyl chlorides on glucose *iso*propylidene ether, β-glucosan triacetate is found to react with acid chlorides only under such drastic conditions that the primary products are decomposed. 6-Bromotriacetyl-β-methylglucoside and silver benzoate in boiling pyridine yield *6-benzoyltriacetyl-β-methylglucoside*, m. p. 127°, $[\alpha]_D^{19}$ +15·15° in chloroform, in very poor yield; this substance is also obtained by successive treatment of ζ-benzoylglucose *iso*propylidene ether with hydrogen bromide and glacial acetic acid and methyl alcohol and silver carbonate. 6-Bromotriacetyl-β-methylglucoside and silver *p*-toluenesulphonate in boiling pyridine yield exclusively *triacetyl-β-methylglucoside-ζ-pyridinium* p-*toluenesulphonate*, m. p. 169—170° (decomp.), $[\alpha]_D^{19}$ −17·9° in water. The probability that *p*-toluenesulphonylglucose *iso*propylidene ether has the acyl group in the ζ-position is strengthened by the observation that it is converted by hydrogen bromide and glacial acetic acid into a non-crystalline bromo-derivative (giving with silver carbonate and methyl alcohol 6-p-*toluenesulphonyltriacetyl-β-methylglucoside*, m. p. 155°, $[\alpha]_D^{20}$ +12·03° in chloroform, differing from 3-p-*toluenesulphonyltriacetyl-β-methylglucoside*, m. p. 131—132°, $[\alpha]_D^{19}$ −18·13° in chloroform. Acetobromoglucose and silver *p*-toluenesulphonate in pyridine afford β-*tetra-acetylglucosido*-1-*pyridinium* p-*toluenesulphonate*, m. p. 184° (decomp.), $[\alpha]_D^{20}$ −22·5° in water. *Triacetylglucose* iso*propylidene ether*, m. p. 75°, $[\alpha]_D$ +24·6° in chloroform, is readily prepared from glucose *iso*propylidene ether and acetic anhydride in pyridine.

The action of hydrogen bromide in acetic acid on glucose mono- and di-*iso*propylidene ethers and on some of their monoacyl derivatives is accompanied by characteristic colour changes and by the formation of products which retain bromine firmly; these characteristics are not shown by 3-*p*-toluenesulphonylglucose *iso*propylidene ether, which, on other grounds, has been assigned a ring structure differing from that of glucose *iso*propylidene ether. Triacetylglucose *iso*propylidene ether, to which the butylene oxide structure has been assigned, shows characteristic colour changes with the reagent, but does not yield acetobromoglucose. It is therefore assumed that the latter substance must have some other ring structure, probably the amylene oxidic. Hence β-glucose and β-methylglucoside, which are closely allied to acetobromoglucose, are also considered to contain the amylene oxide ring (cf. Charlton, Haworth, and Peat, this vol., 273; Hirst, *ibid.*, 385). H. WREN.

Effect of disodium phosphate on dextrose and lævulose. H. A. SPOEHR and P. C. WILBUR (J. Biol. Chem., 1926, **69**, 421—434).—Long preservation of solutions of dextrose containing disodium phosphate led to the formation of some lævulose; the latter, under similar conditions, was partly converted into dextrose. In both cases, the reducing power of the solution was diminished owing to the formation of some glutose, but no acidic products were detected. Glutose may be conveniently prepared by heating a solution of invert-sugar with disodium phosphate at 75° for 24 hrs., the yield being 50% of the sucrose originally taken. C. R. HARINGTON.

Structure of fructose, γ-fructose, and sucrose. W. N. HAWORTH and E. L. HIRST (J.C.S., 1926, 1858—1868).—Oxidation of normal tetramethylfructose with nitric acid (*d* 1·2) followed by isolation of the product as the methyl ester gives a compound, $C_{10}H_{18}O_7$, m. p. 119—120°, $[\alpha]_D$ −107° in water, derived from a monobasic *acid*, $C_9H_{16}O_7$. The ester contains one free hydroxyl group and is readily methylated to an *ester*, $C_{11}H_{20}O_7$, m. p. 102—103°, $[\alpha]_D$ −116° in methyl alcohol, $[\alpha]_D$ −129° in water. The conclusion of Irvine and Patterson (*ibid.*, 1922, **121**, 2696) that the acid, isolated by them as the ethyl ester, is dimethoxyhydroxyglutaric acid appears to require revision and the constitution (I) is suggested for it. More drastic oxidation of tetramethylfructose with nitric acid affords a mixture of *methyl* meso*dimethoxysuccinate*, m. p. 67—68° [meso*dimethoxysuccinamide*, m. p. 245—246° (decomp.) after darkening at 220°], and methyl *d*-arabotrimethoxyglutarate, thus indicating the amylene oxide structure for normal tetramethylfructose. For tetramethyl-γ-fructose, a butylene oxide structure is suggested. H. WREN.


(I)

Heterolævulosan. A. PICTET and J. CHAVAN (Helv. Chim. Acta, 1926, **9**, 809—814).—The action of hydrochloric acid (*d* 1·2) on lævulose at 0° for 72 hrs. yields a new anhydride of lævulose (cf. Pictet and

Reilly, A., 1921, i, 544), *heterolævulosan*, an amorphous, hygroscopic powder, $[\alpha]_D$ −66·23°, together with 30% of a *diheterolævulosan*, m. p. 266—267°, $[\alpha]_D$ −43·35°. Neither product reduces Fehling's solution or cold potassium permanganate, and neither is fermented by yeast. Either the mono- or the di-meride yields, by the action of benzoyl chloride, the same *hexabenzoate* of the dimeride, m. p. 118°, $[\alpha]_D$ −122°, whilst hydrochloric and nitric acids yield, respectively, the *hexahydrochloride* and the *hexanitrate*, m. p. 75°, $[\alpha]_D$ −41·50°. J. W. Baker.

Relation between rotatory power and structure in the sugar group. XVII. Structure of neolactose. A. Kunz and C. S. Hudson (J. Amer. Chem. Soc., 1926, **48**, 2435—2439; cf. this vol., 941).—Deacetylation of α-neolactose octa-acetate and subsequent treatment with phenylhydrazine affords *neolactosazone*, m. p. 195° (decomp.), whilst oxidation of the deacetylated product with bromine yields *neolactobionic acid*, amorphous. On hydrolysis, the latter yields *d*-galactose and *d*-altronic acid (cf. Levene and Jacobs, A., 1911, i, 14). Hydrolysis of neolactose yields *d*-galactose and *d*-altrose, so that neolactose is *d*-galactosido-*d*-altrose. The latter has $[\alpha]_D$ +35°, and *d*-altrose −98°, in water. F. G. Willson.

Reversion syntheses. II. Gentiobiose and *iso*maltose. H. Pringsheim, J. Bonde, and J. Leibowitz (Ber., 1926, **59**, [*B*], 1983—1986; cf. A., 1924, i, 1169).—The action of a dry preparation of brewer's yeast on 50% dextrose solution at p_H 6·6 leads to the isolation of a disaccharide identified by its phenylosazone and octa-acetate as gentiobiose. The maximal yield is 4% of the dextrose. The non-identity of gentiobiose and revertose is thus established.

The authors consider that the disaccharide obtained indirectly from starch by Ling and Nanji (A., 1925, i, 516) is not *iso*maltose, and suggest the possible identity of the *iso*maltose of Georg and Pictet (this vol. 823) with revertose. H. Wren.

Syntheses of polysaccharides. III. The galactosidoglucose of E. Fischer and E. F. Armstrong. II. H. H. Schlubach and W. Rauchenberger (Ber., 1926, **59**, [*B*], 2102—2106; cf. A., 1925, i, 888).—It is considered highly probable that Fischer and Armstrong's galactosidoglucose is identical with lactose. Fractionation of the glucose portion obtained by hydrolysis of permethylated galactosidoglucose reveals the presence of a dimethylglucose in addition to trimethylglucose. The latter substance has not been obtained crystalline, but its optical activity now approaches more nearly to that of βγζ-trimethylglucose, and similar evidence as to its identity is derived from determination of its reducing power (cf. Zemplén and Braun, this vol., 149).

During the reaction between acetochlorogalactose, dextrose, and sodium ethoxide, *trimethyl-β-glucosan*, m. p. 63—64°, $[\alpha]_D^{20}$ −59·8° in water, is formed. H. Wren.

Cellulose. XX. K. Hess (Koll.-Chem. Beih., 1926, **23**, 93—108; cf. this vol., 715).—Cellulose acetate crystallises in well-defined needles from dilute solutions of cellulose triacetate in tetrachloroethane concentrated gradually at the ordinary temperature; the needles are unstable, and change slowly into compact rhombs. If the crystallisation is very slow, only the rhombic form separates. Cellulose diacetate is obtained in fine needles by the repeated cooling of a warm 10% solution of cellulose diacetate in a 50% mixture of benzene and alcohol. The triacetate needles show positive double refraction in the direction of their long axis, whilst the diacetate needles show negative. By the isolation and examination of the optically active cellulose–copper compound formed from the hydrolytic product of cellulose acetate, it is shown that the carbohydrate in cellulose acetate is actually unchanged cellulose. The cryoscopic behaviour of crystalline cellulose acetate dissolved in glacial acetic acid leads to the conclusion that the structure of cellulose may be represented by that of a glucose anhydride, which, contrary to the behaviour of other known glucosans, is capable of swelling and is sparingly soluble in water. L. L. Bircumshaw.

Cellulose esters of higher fatty acids. G. Kita, T. Mazuma, J. Sakrada, and T. Nakashima. See B., 1926, 870.

Cello*iso*biose and cellotriose. H. Ost (Z. angew. Chem., 1926, **39**, 1117—1119).—The cello*iso*biose isolated from the product of the acetylation of cellulose by Ost and Prosiegel (A., 1920, i, 423) is obtained in better yield (6% of the cotton used) if the period of acetolysis is shortened and the syrup extracted with warm alcohol instead of with ether. The biose is then concentrated in the most soluble portion, full details of the procedure being given. The portion soluble with difficulty in the alcohol contains, in addition to dextrin, a new *cellotriose*, $C_{18}H_{32}O_{16}$. After removal of the dextrin from the aqueous solution by repeated precipitation with small quantities of alcohol, the triose is precipitated with a larger volume of alcohol as a crystalline powder having $[\alpha]_D$ +9·6° to +10·0°, reducing power 47·1 (dextrose 100), ash 0·27%. It is soluble in 10—15 parts of cold water, readily soluble in hot water, possesses scarcely any sweet taste, is not fermented by yeast, forms a slimy osazone, and is only very slowly hydrolysed by 8% hydrochloric acid at the temperature of the water-bath. J. W. Baker.

Constitution of melezitose and turanose. R. Kuhn and G. E. von Grundherr (Ber., 1926, **59**, [*B*], 1655—1664).—Melezitose, m. p. 153—154°, $[\alpha]_D^{20}$ +88·2° in water, is hydrolysed by cold, dilute acid to dextrose and turanose and by more drastic treatment to dextrose and lævulose. Since the mixture obtained by gentle hydrolysis has twice as great reducing power towards Fehling's solution as towards hypoiodite, the components of the trisaccharide must be arranged in the sequence dextrose, lævulose, dextrose. Its close relationship to sucrose is confirmed by their analogous velocities of hydrolysis. The point of attachment of the glucose residue to the lævulose portion in turanose is not yet definitely determinable, but the dissimilarity of turanosazone from the osazones of maltose, gentiobiose, and cellobiose shows that it is not structurally similar to these disaccharides.

Melezitose is completely stable towards invertase, probably on account of the absence of a free lævulose

residue. On the other hand, the mixture of enzymes from *Aspergillus oryzæ* readily hydrolyses melezitose, but it is not possible to decide whether the turanose or sucrose linking is first attacked, since either disaccharide is more readily hydrolysed than the trisaccharide. *Penicillium glaucum* or *A. niger* causes partial hydrolysis to turanose and dextrose. Purified preparations of emulsin do not attack melezitose or turanose. The autolysates of fresh Löwenbrau yeast appear to contain a specific enzyme, melezitase, which hydrolyses melezitose to dextrose and turanose. Hydrolysis is also readily effected by certain types of yeast, turanose being readily isolated from the products. H. WREN.

Starch. XVIII. Molecular size and association of polyamyloses. H. PRINGSHEIM and J. LEIBOWITZ (Ber., 1926, **59**, [*B*], 2058—2064).—Direct comparison of the mol. wts. of tri- and β-hexa-amylose by the Barger–Rast method confirms the values for the mol. wt. assigned to these substances by Pringsheim (contrast Karrer and Bürklin, A., 1922, i, 435). The observation that diamylose in highly concentrated aqueous solution at the atmospheric temperature undergoes partial transformation into α-hexa-amylose (cf. A., 1922, i, 632) is confirmed by the conversion of the product into α-hexa-amylose octadeca-acetate and determination of its mol. wt. in glacial acetic acid and camphor. The maximal yield of α-hexa-amylose is 5% of the theoretical, so that the change appears to proceed to an equilibrium dependent on concentration.

The acetyl and methyl derivatives of α-hexa-amylose (trimeric diamylose) and of β-hexa-amylose (dimeric triamylose) retain their molecular size in camphor, whereas the monomeric acetates exhibit association. H. WREN.

Constitution of spermine. III. Structure and synthesis. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING (Biochem. J., 1926, **20**, 1082—1094).—Destructive distillation of spermine hydrochloride yields pyrrolidine, whilst decamethylspermine sulphide obtained from the mercurichloride of the quaternary ammonium base (this vol., 194) on degradation yields *hexamethylspermine* and tetramethyltrimethylenediamine, $NMe_2{\cdot}[CH_2]_3{\cdot}NMe_2$. These degradation products suggest the presence of the chains N·C·C·C·N and N·C·C·C·C·N in the molecule. Spermine also contains two amino-groups and two imino-groups (this vol., 194). It was finally shown by synthesis that spermine is *αδ-bis-[γ'-aminopropylamino]butane*, $NH_2{\cdot}[CH_2]_3{\cdot}NH{\cdot}[CH_2]_4{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH_2$. *αδ-Bis-[γ'-phenoxypropylamino]butane hydrobromide* (m. p. 292°; picrate, m. p. 178—180°), was obtained by heating tetramethylenediamine with γ-bromo-α-phenoxypropane in absolute alcohol. From the phenoxy-compound *αδ-bis-[γ'-bromopropylamino]butane hydrobromide* [m. p. 274° (decomp.); picrate, m. p. 186—188°] was prepared by heating the former in a sealed tube with hydrobromic acid, and finally *αδ-bis-[γ'-aminopropylamino]butane phosphate* (synthetic spermine phosphate) was obtained by heating the bromo-compound with alcoholic ammonia in a sealed tube and converting the base thus obtained into the characteristic phosphate (A., 1925, i, 294). The picrate, picrolonate, chloroaurate, chloroplatinate, and the benzoyl derivative were prepared from the synthesised spermine, and all these derivatives were found to be identical with the corresponding compounds obtained from natural spermine isolated from animal organs.

On mild oxidation, spermine yields a base volatile in steam which forms a crystalline, readily oxidisable hydrochloride and a chloroaurate [m. p. 204—206° (decomp.)]. This base is also obtained together with a substance giving a nitroso-reaction by the action of nitrous acid on spermine, and consequently Van Slyke determinations give inconclusive results (cf. Wrede, this vol., 751). S. S. ZILVA.

Preparation of amino-acids by electro-reduction of oximino-esters. A. ANZIEGIN and W. GULEWITSCH [with K. NORDHEIM].—See this vol., 1111.

Disruption of the aliphatic six-carbon chain. J. VON BRAUN, W. LEISTNER, and W. MÜNCH (Ber., 1926, **59**, [*B*], 1950—1958).—The action of diethylamine on ethyl αα'-dibromoadipate affords a small proportion of ethyl αα'-bisdiethylaminoadipate, but leads mainly to fission of the six carbon chain with formation of ethyl α-diethylaminopropionate and ethyl pyruvate. The reaction is not shown by the dibromo-derivatives of pimelic, suberic, or glutaric acid, and is thus doubtless connected with the spatial proximity of the bromine atoms in the adipic molecule. Di-*n*-propylamine and di*iso*amylamine behave similarly to diethylamine, thus differing from piperidine and dimethylamine (this vol., 1122). The difference is attributed to the form of the basic molecule; this hypothesis is supported by the observation that 2-methyl-5-ethylpiperidine behaves in the main like diethylamine. Fission of the adipic molecule occurs at the moment of reaction, since ethyl bisdiethylaminoadipate is perfectly stable towards diethylamine.

The following compounds are described: *ethyl α-diethylaminopropionate*, b. p. 85—88°/13 mm. (*methiodide*, m. p. 79—80°), and thence *β-diethylamino-n-propyl alcohol*, b. p. 78°/12 mm.; *ethyl* meso-*αα'-bisdiethylaminoadipate*, b. p. 192—196°/13 mm. (*picrate*, m. p. 185—188° after darkening at 175°); meso-*αα'-bisdiethylaminoadipic acid*; *ethyl* r-*αα'-bisdiethylaminoadipate*; *ethyl α-di-n-propylaminopropionate*, b. p. 102—104°/12 mm. (*methiodide*, m. p. 76°; non-crystalline *picrate* and *hydrochloride*); *ethyl α-diisoamylaminopropionate*, b. p. 148—150°/15 mm.; *ethyl* α-2-*methyl-5-ethylpiperidinopropionate*, b. p. 130—132°/12 mm.; *ethyl αα'-di-2-methyl-5-ethylpiperidinoadipate*, b. p. 230—240°/12 mm. Ethyl αα'-dibromo-β-methyladipic acid reacts in a complex manner with diethylamine, yielding ethyl pyruvate, ethyl crotonate, probably ethyl β-methylmuconate, and the bromo-ester, $CO_2Et{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2Et$, the basic *ester*, $CO_2Et{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH(NEt_2){\cdot}CO_2Et$, b. p. 160°/16 mm., and *ethyl α-diethylamino-n-butyrate*, b. p. 204—208°. A mixture of ethyl *r*- and *meso*-αα'-dibromosuberates is transformed by diethylamine into *ethyl αα'-bisdiethylaminosuberate*, b. p. 212°/14 mm. (*picrate*, m. p. 157—161°), which doubtless consists of a mixture

of isomerides inseparable by distillation, since it is hydrolysed to a mixture of *αα'-bisdiethylaminosuberic acids*, m. p. 228—230° and 215—220°, respectively. Analogously, ethyl αα'-dibromopimelate affords *ethyl αα'-bisdiethylaminopimelate*, b. p. 200°/15 mm. (*picrate*, m. p. 107—113°), from which two *αα'-bisdiethylaminopimelic acids*, m. p. 231° and 208—212°, respectively, are derived. Homogeneous ethyl *meso*-αα'-dibromoglutarate gives in small yield *ethyl αα'-bisdiethylaminoglutarate*, b. p. 165°/16 mm., which, however, is a mixture of isomerides, since it is hydrolysed to a mixture of *αα'-bisdiethylaminoglutaric acids*, m. p. 222° and 213°, respectively. The main product of the action is free from nitrogen and contains ethyl pyromellitate and ethyl dihydropyromellitate. H. WREN.

Aminohydroxy-compounds which show the biuret reaction. M. TOMITA (Z. physiol. Chem., 1926, **158**, 42—57).—It is found that various compounds containing the grouping $\cdot CH(OH)\cdot CH_2\cdot NH_2$ show the biuret reaction, *e.g.*, *iso*serine, γ-chloro-β-hydroxy-*n*-propylamine (epichloroamine, m. p. 104°), βγ-dihydroxy-*n*-propylamine, δ-amino-γ-hydroxyvaleric acid, and δ-amino-αγ-dihydroxyvaleric acid.

γ-Iodo-β-hydroxypropylphthalimide (from the chloro-compound and sodium iodide) reacts with aqueous-alcoholic potassium cyanide to form β-hydroxy-γ-cyanopropylphthalimide, m. p. 132° (*benzoate*, m. p. 109°). *γ-Chloroacetamido-β-hydroxybutyric acid*, prepared from γ-amino-β-hydroxybutyric acid and chloroacetyl chloride, is converted by 25% aqueous ammonia at the ordinary temperature into *γ-glycylamino-β-hydroxybutyric acid*, which does not show the biuret reaction. γ-Chloro-β-hydroxypropylphthalimide condenses with ethyl sodiomalonate to give *ethyl γ-phthalimido-β-hydroxypropylmalonate*, together with two *substances*, m. p. 197° and 205°, respectively. C. HOLLINS.

Decomposition of creatinine with barium hydroxide. O. H. GAEBLER (J. Biol. Chem., 1926, **69**, 613—624).—Creatinine in aqueous solution was heated with slightly more than 1 equivalent of barium hydroxide at 100° for varying periods from 15 min. to 12 hrs. With increasing length of heating, the yield of methylcarbamidoacetic acid and of ammonia increased; that of carbamide reached a maximum at 1 hr., at which time only traces of unchanged creatinine were left and the yield of sarcosine was also greatest, and thereafter diminished. This indicates that the methylcarbamidoacetic acid is, partly, at any rate, a product of the interaction of sarcosine with carbamide. C. R. HARINGTON.

Reversible oxidation–reduction systems of cysteine–cystine and reduced and oxidised glutathione. E. C. KENDALL and F. F. NORD (J. Biol. Chem., 1926, **69**, 295—337).—The results of Dixon and Quastel (J.C.S., 1923, **123**, 2943) have been confirmed, and the hydrogen electrode has been employed for the further study of the above reversible systems. It is found that whereas cysteine, in absence of oxygen, cannot reduce indigo-carmine, the presence in the solution of small amounts of oxygen or hydrogen peroxide enables the reduction to take place; the necessity is therefore postulated of the formation of an active intermediate compound by interaction of hydrogen peroxide with the cysteine; similar results were obtained with reduced glutathione, and an effect of the same type was observed on addition to the solution of sodium disulphide in place of the hydrogen peroxide. C. R. HARINGTON.

Nitrocarbamide. R. WILLSTÄTTER and A. PFANNENSTIEL (Ber., 1926, **59**, [*B*], 1870—1871).—Contrary to the literature, nitrocarbamide has m. p. 159° (decomp.), is readily crystallised from alcohol, is relatively stable when dissolved in cold, concentrated nitric acid, but readily decomposed by sodium hydroxide. H. WREN.

Guanidine derivatives. M. SCHENCK and H. KIRCHHOF (Z. physiol. Chem., 1926, **158**, 90—110).—*NN*-Dimethyl-*N'*-ethylguanidine, prepared from *S*-methyl-*N*-ethyl-ψ-thiocarbamide hydriodide and dimethylamine, is identical with the product obtained earlier (this vol., 717) from *NNS*-trimethyl-ψ-thiocarbamide hydriodide and ethylamine. *iso*Amylguanidine (dihydrogalegine), from *S*-methyl-ψ-thiocarbamide hydriodide or sulphate and *iso*amylamine, gives salts identical with those from dihydrogalegine (Barger and White, A., 1924, i, 272). Allylguanidine (*picrolonate*, decomp. 262—263°) is prepared from *S*-methyl-*N*-allyl-ψ-thiocarbamide hydriodide and ammonia, or from *S*-methyl-ψ-thiocarbamide sulphate and allylamine. αβ-Diguanidinoethane (Schenck and Kirchhof, *loc. cit.*) is prepared in purer form from the sulphate of *S*-methyl-ψ-thiocarbamide and ethylenediamine hydrate. It gives a *sulphate* ($+2H_2O$), decomp. 289—290°. *dl*-αβ-Diguanidinopropane [*dipicrolonate*, m. p. 293° (decomp.); *dipicrate*, m. p. 239—240°; *dichloroaurate*, m. p. 214—215°; *chloroplatinate*, m. p. 244—245°], prepared from *S*-methyl-ψ-thiocarbamide hydriodide and propylenediamine, is accompanied by a little α- or β-guanidinopropane (*dipicrolonate*, decomp. 267°); it is not identical with vitiatine (Kutscher, A., 1907, ii, 569, 708). αγ-Diguanidinopropane (*dipicrolonate*, decomp. above 296°; *dipicrate*, m. p. 242°; *dichloroaurate*, m. p. 183—184°; *chloroplatinate*, decomp. 245—246°; *sulphate*, darkens at 285°, not much decomposed at 296°) is similarly prepared from trimethylenediamine. C. HOLLINS.

Constitution of dicyanodiamide; a mercury derivative. J. BELL (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 207—210).—Reduction of dicyanodiamide with zinc and hydrochloric acid is preceded even in cold solution by its conversion into dicyanodiamidine. This invalidates Bamberger's evidence for the cyanoguanidine formula for dicyanodiamide (cf. A., 1883, 1900). The original cyclic formula for the substance accounts for all its known reactions. A *mercury* derivative, $C_2N_4H_2Hg_2(OH)_2$, is described which loses 1 mol. of water at 150°. G. M. BENNETT.

Supposed water of crystallisation of mercury fulminate. H. KAST and H. SELLE (Ber., 1926, **59**, [*B*], 1958—1962).—Mercury fulminate, crystallised from an aqueous solution of potassium cyanide, gives analytical data agreeing with those required for the anhydrous compound. Technical and crystallised mercury fulminates when suitably exploded in a bomb in the presence of calcium carbide do not

generate acetylene. The heat evolved during the explosion of technical mercury fulminate is identical with that of the crystallised product. H. WREN.

Lecture experiments with the new halogenoid, azidocarbondisulphide. A. W. BROWNE and R. S. VON HAZMBURG (J. Amer. Chem. Soc., 1926, **48**, 2383—2385; cf. A., 1924, ii, 40).—Methods of demonstration of the halogenoid character of azidocarbondisulphide, its decomposition with production of thiocyanogen, and its instability are recorded. F. G. WILLSON.

Constitution of mixed magnesium organic compounds. A. P. TERENTJEV (Z. anorg. Chem., 1926, **156**, 73—84).—Various structural formulæ have been proposed for the magnesium organic complexes (cf. A., 1905, ii, 802; 1925, i, 542, 1252), none of which accounts for the general behaviour of these substances. Determinations of the mol. wt. of the carefully prepared pure substance using Rüber's modification of Landsberger's apparatus indicated $(MgMeI)_2$. From this, the co-ordination number of magnesium was taken to be 6 and the formula $Mg[Me_2MgI_2,2Et_2O]$ suggested. This formula explains most satisfactorily the behaviour of the compound, *e.g.*, the conduction of an electric current in ethereal solution with liberation of magnesium and of complex anions; inactivity towards metallic sodium; absence of iodine ions, etc. The mechanism of the formation of mixed magnesium organic compounds and the action of halogens, water, alcohols, amines, carbon dioxide, aldehydes, and ketones is discussed. M. CARLTON.

Organocalcium iodides. H. GILMAN and F. SCHULZE (J. Amer. Chem. Soc., 1926, **48**, 2463—2467).—Calcium reacts with certain primary alkyl iodides with formation of calcium alkyl iodides. The reaction is irregular, requires a higher concentration of ethereal iodine as catalyst than is necessary for the Grignard reaction, and often commences only after a considerable induction period. The yields of calcium alkyl iodide are low, on account of a side reaction leading to the coupling of two alkyl groups by elimination of the iodine as calcium iodide. The calcium alkyl iodides are soluble in ether (cf. Beckmann, A., 1905, i, 335), the solid compound deposited during their preparation being probably the dietherate of calcium iodide. Thus whilst calcium ethyl iodide could not be obtained, the reaction mixture deposited *calcium iodide dietherate*. Treatment of ethereal *n*-butyl iodide with calcium affords *calcium* n-*butyl iodide*, identified by its conversion, on addition of α-naphthylcarbimide, into *n*-valer-α-naphthalide, together with *n*-octane. *Calcium* n-*octyl iodide* was obtained analogously, together with hexadecane. *Calcium phenyl iodide* affords benzanilide when treated with phenylcarbimide, but reacts very slowly with benzoyl chloride. F. G. WILLSON.

Inactive 1 : 3-dimethyl*cyclo*pentane. G. CHAVANNE (Bull. Soc. chim. Belg., 1926, **35**, 283—297).—β-Methyladipic acid is converted at 300° in presence of manganese dioxide into 3-*methyl*cyclo*pentanone*, b. p. 143·6—143·9°/747 mm., *semicarbazone* (decomp. 188°±2°), which, with magnesium methyl iodide, affords 1 : 3-*dimethyl*cyclo*pentanol*, b. p. 144·2—144·6°/766 mm., $d_4^{14\cdot65}$ 0·8941, $n_D^{15\cdot3}$ 1·4444. Dehydration of the alcohol by *p*-toluenesulphonic acid yields dimethyl*cyclo*pentene, b. p. 92·8—93°/760 mm., which appears to be a mixture of the two possible isomerides; it is hydrogenated in acetic acid solution in the presence of platinum-black to 1 : 3-*dimethyl*cyclo*pentane*, b. p. 90·6—90·8°/760 mm., d_4^{15} 0·7498, n_D^{16} 1·4104, which appears homogeneous. It is spontaneously oxidisable in air at the atmospheric temperature. P. V. McKIE.

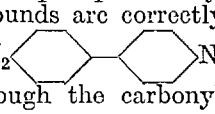
Nitration of xylene by dilute nitric acid (*d* 1·35—1·29) in presence of mercury. E. I. ORLOFF (Ber., 1926, **59**, [*B*], 2114—2116).—A nitrotrihydroxybenzenedicarboxylic acid is isolated from the products of the reaction. H. WREN.

Catalytic condensation of acetone at high temperatures and pressures. W. IPATIEV and A. D. PETROV (Ber., 1926, **59**, [*B*], 2035—2038).—Acetone at 300—500° and a maximal pressure of 200 atm. in the presence of aluminium oxide, zinc chloride, zinc dust, or calcium oxide affords mainly mesitylene in yield considerably greater than that obtained from acetone and sulphuric acid. Considerable amounts of other hydrocarbons of the aromatic and terpene series (C 88·36—88·60%; H 11·67—11·51%) are also produced. Mesityl oxide is formed in slight amount. The production of phorone or hexamethylbenzene could not be detected, but *iso*phorone is possibly formed. H. WREN.

Sulphonation of inorganic and organic compounds. P. BAUMGARTEN (Ber., 1926, **59**, [B], 1976—1983).—1-Pyridiniumsulphonic acid (this vol., 844) is applicable as a sulphonating agent to all inorganic and organic compounds from which sulphonic acids can be obtained by other methods. It may be used in aqueous medium, by simple mixture, or by fusion of the components at a suitable temperature. In the presence of water, the temperature cannot be raised much above that of the atmosphere. The yields are generally 70—80%, sometimes quantitative. Ammonia in aqueous solution at 10° is transformed into sulphamic acid; this conversion is also effected by anhydrotrimethylsulphamic and anhydrophenyldimethylsulphamic acids. Hydrazine affords the corresponding monosulphonic acid. Sodium hydrogen sulphide yields sodium thiosulphate, $2NaSH+C_5H_5NSO_3=Na_2S_2O_3+H_2S+C_5H_5N$, whilst ammonium fluoride gives ammonium fluorosulphonate, $NH_4F+C_5H_5NSO_3=(NH_4)O_3SF+C_5H_5N$. Primary and secondary amines afford the ammonium salts of the corresponding sulphamic acids. Aniline in aqueous suspension yields aniline phenylsulphamate, whereas at 170° aniline sulphanilate is produced. Tertiary aliphatic amines replace pyridine, $NR_3+C_5H_5NSO_3=R_3NSO_3+C_5H_5N$, with formation of anhydrotrialkylsulphamic acids (cf. A., 1924, i, 839). Alcohols and phenols react according to the scheme $R_3N{\cdot}O{\cdot}SO_2+R{\cdot}OH=R_3NH{\cdot}O{\cdot}SO_2{\cdot}OR$, whilst at more elevated temperatures nuclear substitution occurs in the case of phenols. Hydrocarbons are sulphonated when heated, naphthalene yielding mainly the α-sulphonic acid with a little β-acid.

Pyridinium ethyl sulphate, m. p. 107° after softening, is described. H. WREN.

Hydrolysis of salts of aromatic sulphonic acids at high temperatures and pressures. W. IPATIEV and A. PETROV (Ber., 1926, **59**, [*B*], 1737—1741).—The action of water in the presence of aluminium hydroxide on the salts of phenol-*o*- and -*p*-sulphonic acid, cresol-*o*- and -*p*-sulphonic acid, benzene-, toluene-, and xylene-sulphonic acids, benzene-*m*-disulphonic acid, naphthalene-β-sulphonic acid, α-naphthol-4-sulphonic acid, naphthionic acid, sulphanilic acid, chloro- and bromo-benzenesulphonic acids gives phenols or hydrocarbons. Reaction consists in primary hydrolysis of the salts (accelerated by aluminium hydroxide) to free sulphonic acid and alkali hydroxide followed by decomposition of the acid into phenol or hydrocarbon and sulphuric acid. The temperature of incipient hydrolysis of the salts is considerably higher than that of the corresponding free acids and varies greatly from case to case, thus affording a better opportunity for "fractional hydrolysis" than is given by the acids. H. WREN.

Space formula of diphenyl. R. J. W. LE FÈVRE and E. E. TURNER (J.C.S., 1926, 2476—2484).—The condensation of monophthalyl-, carbonyl-, and thiocarbonyl-benzidines with benzaldehyde and salicylaldehyde, yielding *benzylidene* and *salicylidene* derivatives, and the formation of *sulphates* of each of these substances, when they are dissolved in concentrated sulphuric acid and precipitated by water, indicates that these compounds are correctly represented by the structure  , although the carbonyl derivative may have the formula $(NH_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH)_2CO$. Further proof of an unsubstituted amino-group present in the molecule is afforded by the normal diazotisation of the monophthalyl- and thiocarbonyl-benzidines, and the condensation of the latter compound with phenol and aniline, giving *phenyl* 4′-*aminodiphenylylthiocarbamate* and 4′-*aminodiphenylylphenylthiocarbamide*, indicates the thiocarbimide structure. The space formula of diphenyl (Kaufler, A., 1907, i, 307, 794) is discussed in view of this and other recent work (cf. Christie and Kenner, J.C.S., 1922, **121**, 614). H. BURTON.

Alternating effect in carbon chains. IX. Directive influence of groups of form $-CRR'{\cdot}NO_2$ in aromatic substitution. J. W. BAKER and C. K. INGOLD (J.C.S., 1926, 2462—2475).—The nitration of (*a*) phenylnitromethane, (*b*) phenylbromocyanonitromethane, (*c*) β-phenyl-β-nitropropane, (*d*) α-phenyl-α-bromo-α-nitroethane, and (*e*) phenyldibromonitromethane gives the following percentages of mononitro-derivatives, determined by oxidation of the nitro-compounds to the nitrobenzoic acids, with subsequent separation of the isomerides or analysis of the mixture: (*a*) 48—50% *meta*, 14% *para*; (*b*) 47—52% *meta*, 14% *para*; (*c*) 27—29% *meta*, 37% *para*; (*d*) 38—40% *meta*, 25% *para*; (*e*) 79—84% *meta*, 6% *para*. The amounts of *meta*-substitution products formed are in agreement with the dipolar structures of phenylnitromethane derivatives, considered in the light of the theory previously proposed (Ingold and Ingold, this vol., 833). H. BURTON.

Reactivity of *meso*-substituted anthracenes. III. J. W. COOK (J.C.S., 1926, 2160—2171).—The diminution in the capacity of an anthracene derivative to enter into reactions of 9 : 10-addition, due to the introduction of an unsaturated *meso*-substituent (this vol., 838), is removed when this substituent is saturated. Reduction of benzylideneanthrone (prepared from anthrone and benzaldehyde) with zinc and acetic anhydride yields 9-*benzylanthranyl*-10-*acetate*, m. p. 210—211°, whilst with zinc and ammonia the product is 10-hydroxy-9-benzyl-9 : 10-dihydroanthracene, which is converted by acetic acid into 9-benzylanthracene, m. p. 133°. With 1 mol. of bromine, 9-benzylanthracene gives 10-*bromo*-9-*benzylanthracene*, m. p. 144°, but excess leads to 9 : 10-dibromoanthracene, whence it is concluded that bromination is preceded by addition. Bromobenzylanthracene and bromine give 10-*bromo*-9-*benzylanthracene tetrabromide*, m. p. 192° (decomp.) [also 127° (decomp.)], which is converted by alcoholic potassium hydroxide into 2 : 3 : 10-*tribromo*-9-*benzylanthracene*, m. p. 206—207° (oxidisable to 2 : 3-dibromoanthraquinone). Pyridine perbromide in pyridine solution converts benzylanthracene into 9-*benzyl*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide*, m. p. 138—140°, which with acid or alkaline reagents passes into 9-*benzylanthranyl*-10-*pyridinium bromide*, m. p. 226°. 9-Phenylanthracene and pyridine perbromide yield 10-*bromo*-9-*phenylanthracene*, m. p. 154—155°. The action of chlorine on 9-benzylanthracene results in 10-*chloro*-9-*benzylanthracene*, m. p. 127—128°, which is also formed, together with 9 : 10-dichloroanthracene, by the use of sulphuryl chloride. With nitric acid in the presence of acetic acid, benzylanthracene yields 10-*nitro*-9-*hydroxy*-9-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 160° (decomp.), which is changed by mineral acids into 10-*nitro*-9-*benzylanthracene*, m. p. 178—180°, also obtained by addition of nitrogen dioxide to benzylanthracene, followed by treatment with pyridine. Benzylanthracene is reduced by sodium and amyl alcohol to 9-benzyl-9 : 10-dihydroanthracene. 10-*Benzylanthraphenone*, m. p. 237° (prepared by interaction of benzylanthracene, benzoic anhydride, and aluminium chloride), and 10-phenylanthraquinone are with difficulty reduced to 10-*benzyl*-9 : 10-*dihydroanthraphenone*, m. p. 171—172°, and 10-*phenyl*-9 : 10-*dihydroanthraphenone*, m. p. 165°, respectively, but are both more readily hydrolysed than is benzoylanthraphenone. Benzylideneanthrone dibromide, when treated with silver oxide, gives a *compound*, $C_{21}H_{14}O_2$, m. p. 133—134° (*acetyl* derivative, m. p. 140—141°). F. M. HAMER.

Acetylation of aniline and the toluidines in anhydrous glycerol. I. GASOPOULOS (Ber., 1926 **59**, [*B*], 2187).—Acetanilide is obtained in 86·8% yield when a mixture of aniline (1 part), glacial acetic acid (2 parts), and anhydrous glycerol (½ part) is heated under a reflux condenser during 2½ hrs. Aceto-*o*-, -*m*-, and -*p*-toluidide are prepared similarly. H. WREN.

Acetoacetanilide. H. PFEIFFER (J. pr. Chem., 1926, [ii], **114**, 56).—Acetoacetanilide is prepared (yield 74—77% of theory) by heating ethyl acetoacetate (20 g.) and aniline (80 g.) as rapidly as possible to 158—160° and distilling off the alcohol formed at this temperature. R. W. WEST.

Reaction between thionylaniline and organomagnesium halides. H. GILMAN and H. L. MORRIS (J. Amer. Chem. Soc., 1926, **48**, 2399—2404).—Condensation of thionylaniline with magnesium phenyl bromide affords benzenesulphinanilide, m. p. 115° (cf. von Braun and Kaiser, A., 1923, i, 316; Sonn and Schmidt, *ibid.*, 1924, i, 1181). When kept in moist or anhydrous ether or benzene solution, or a mixture of the two, benzenesulphinanilide is oxidised to aniline benzenesulphonate. Thionylaniline and magnesium *p*-tolyl bromide react similarly; the *p*-toluenesulphinanilide was not isolated, but allowed to transform, as above, into aniline *p*-toluenesulphonate. Magnesium *n*-butyl bromide affords similarly *aniline* n-*butylsulphonate*, m. p. 159°, whilst magnesium benzyl chloride yields toluene-ω-sulphinanilide, which is similarly transformed into *aniline toluene-ω-sulphonate*, m. p. 230—235°. Magnesium *cyclo*hexyl bromide yields, in the same way, *aniline* cyclo*hexylsulphonate*, m. p. 214°. F. G. WILLSON.

Catalytic action of Japanese acid earth. I. Action on a mixture of aniline and methyl alcohol. H. INOUE (Bull. Chem. Soc. Japan, 1926, **1**, 157—162).—The formation of mono- and dimethylaniline when a mixture of aniline and methyl alcohol is passed at 400° over pure silica (cf. Brown and Reid, A., 1924, i, 1182) or alumina (Mailhe, *ibid.*, 1918, i, 217) is confirmed. The same products are obtained at 250° when an impure silica containing ferric oxide, or Japanese acid earth, is used as a catalyst. At 350°, the product consists mainly of *p*-toluidine, which is also formed under these conditions from methylaniline, whilst dimethylaniline is partly converted into methyl-*p*-toluidine. H. E. F. NOTTON.

Urethanes. Preparation of various substituted urethanes. S. BASTERFIELD, E. L. WOODS, and H. N. WRIGHT (J. Amer. Chem. Soc., 1926, **48**, 2371—2375; cf. this vol., 1138).—*Phenylacetylurethane*, $CH_2Ph\cdot CO\cdot NH\cdot CO_2Et$, m. p. 113°, is obtained by condensing urethane with phenylacetyl chloride in boiling benzene. The formation of *p*-acetylphenylurethane (*p*-carbethoxyaminoacetophenone) from *p*-aminoacetophenone and ethyl chloroformate in ether–alcohol solution in presence of potassium hydroxide (cf. Nijk, A., 1921, i, 23) is not confirmed, but this compound is obtained by the gradual addition of ethyl chloroformate to ethereal *p*-aminoacetophenone in presence of aqueous potassium hydroxide, or by heating together *p*-aminoacetophenone and ethyl chloroformate. *Benzylurethane*, m. p. 44°, p-*bromophenylurethane*, m. p. 85°, and p-*iodophenylurethane*, m. p. 116°, obtained from ethyl chloroformate and the appropriate amines, are described. *Malonyldiphenyldiurethane*, m. p. 123—124°, is obtained by heating malonyl chloride with phenylurethane at 50—60° for about a week. Benzylurethane affords similarly, but more readily, *malonyldibenzyldiurethane*, m. p. 75°. Treatment of ethereal diphenylguanidine with malonyl chloride in presence of aqueous potassium hydroxide affords 2-*imino*-1 : 3-*diphenylbarbituric acid*, m. p. 148°. Diphenylethylenediamine, ethyl chloroformate, and aqueous potassium hydroxide yield *diphenylethylenediurethane*, m. p. 88°. Condensation of ethyl*iso*carbamide with *n*-butyl chloroformate yields n-*butyl* O-*ethylallophanate*, $NH{:}C(OEt)\cdot NH\cdot CO_2C_4H_9$, m. p. 77°. Acetylphenylurethane has a narcotic action, but its above isomerides are practically inert. *n*-Butyl *O*-ethylallophanate is also practically inactive pharmacologically, in contrast to the corresponding ethyl ester. F. G. WILLSON.

Interaction of chloroacetyl chloride and aceto-*m*-toluidide. F. RICHTER (Arch. Pharm., 1926, **264**, 447—448).—Kunckell's conclusion (A., 1911, i, 990) that when aceto-*m*-toluidide is treated with chloroacetyl chloride in presence of aluminium chloride, 5-acetamido-*m*-tolyl chloromethyl ketone is formed is shown to be unsound. A direct comparison of the 5-amino-*o*-toluic acid (m. p. 165°) of Jacobsen (cf. Gabriel and Thieme, *ibid.*, 1919, i, 398) with that of the same m. p. obtained, on oxidising his product, by Kunckell, is desirable. W. A. SILVESTER.

Modification of the Gabriel synthesis of amines. H. R. ING and R. H. F. MANSKE (J.C.S., 1926, 2348—2351).—Alkylphthalimides are obtained by heating phthalimide with alkyl halides and potassium carbonate at 180—200°. The preparation of benzylphthalimide, m. p. 116°, from benzyl chloride, of γ-bromopropylphthalimide, m. p. 72° (together with αγ-diphthalimidopropane, m. p. 197°), from trimethylene dibromide, and of β-*phenylethylphthalimide*, m. p. 131—132°, from phenylethyl bromide is described. *cyclo*Hexyl bromide and potassium phthalimide, however, give *cyclo*hexene and phthalimide. The usual difficulty of hydrolysing alkylphthalimides is circumvented by condensing the alkylphthalimide with hydrazine hydrate, the product formed being readily and nearly quantitatively hydrolysed by acid to phthalylhydrazide and the primary alkylamine. In this manner were prepared: benzylamine, b. p. 185—187°, *o*-, *m*-, and *p*-nitrobenzylamine, β-phenylethylamine, b. p. 200—205°, ethylenediamine, trimethylenediamine, b. p. 134—136°. The hydrochlorides of *o*-, *m*-, and *p*-nitrobenzylamine melt at 248°, 220°, and 250°, respectively, whilst the nitrates of *m*- and *p*-nitrobenzylamine melt at 181—182° and 218°, respectively (cf. Holmes and Ingold, A., 1925, i, 1142). J. H. S. DAVIES.

Nature of the alternating effect in carbon chains. VIII. Nitration of some benzylamine derivatives with special reference to the respective rôles of the ions, salts, and bases. F. R. GOSS, C. K. INGOLD, and I. S. WILSON (J.C.S., 1926, 2440—2462).—A quantitative study of the nitration of the following benzylamine derivatives and a discussion from the point of view indicated in the title lead to the conclusion that benzylammonium ions substitute almost wholly in the *m*-position, that undissociated salts substitute largely in the *m*-position, whilst free bases yield *op*-products. The amounts of the isomerides produced are ascertained by fractional

separation of the mixture before or after oxidation to the corresponding nitrobenzoic acid, and the ratio of *m*- to *op*-derivatives by means of Francis and Hill's bromide–bromate method of bromination after the reduction of the nitro-groups (A., 1925, ii, 163). In the case of benzylamine, the proportions are: *ortho*, 8%; *meta*, 49%; *para*, 43%. The percentage of *m*-nitro-derivatives is appended to the name of the product nitrated: *benzyltriethylammonium picrate*, m. p. 124° (85%); dibenzylamine (76%); tribenzylamine (53%); dibenzylmethylamine (58%); benzyldimethylamine (58%); benzyldiethylamine (51%); acetobenzylamide (7%); acetobenzylmethylamide (8%); acetodibenzylamide (25%); succinbenzylimide (1%); diacetylbenzylamine (small); benzylmethylamine (69%). m-*Nitrobenzyltriethylammonium picrate*, m. p. 149°, p-*nitro*-isomeride, m. p. 155°; *m*- and *p*-nitrobenzylamine, *picrates*, m. p. 197° and 194°, hydrochlorides, m. p. 225° and 256° (decomp.), nitrates, m. p. 187° and 214° (decomp.); aceto-*m*- and -*p*-nitrobenzylamides, m. p. 107° and 133°, respectively; mm'm''-*trinitrotribenzylamine*, m. p. 163°; m-*nitrobenzyldimethylamine*, b. p. 195°/18 mm., *p*-nitro-isomeride, b. p. 146—148°/18 mm.; aceto-*p*-nitrobenzylmethylamide, m. p. 83°; aceto-*pp'*-dinitrodibenzylamide, m. p. 185°; succinbenzylimide, m. p. 103°, *p*-nitro-derivative, m. p. 153°, and *dibenzyldimethylammonium picrate*, m. p. 146°, are also prepared and characterised. J. S. H. DAVIES.

Hydrindene. III. W. BORSCHE and A. BODENSTEIN (Ber., 1926, **59**, [*B*], 1909—1915; cf. Borsche and John, A., 1924, i, 723).—4-Nitro-5-acetylhydrindene has m. p. 82°. 4-Nitro-5-acetylhydrindeneoxime, m. p. 171°, is converted by phosphorus pentachloride into 4-nitro-5-acetamidohydrindene, m. p. 108°, which is more conveniently prepared by direct nitration of 5-acetamidohydrindene. 4-*Nitro*-5-*aminohydrindene*, m. p. 128—129°, and its *benzoyl* derivative, m. p. 125—126°, are described; the former substance is converted by reduction and subsequent treatment with benzil into the *compound*, $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_2<\begin{matrix}N{:}CPh\\N{:}CPh\end{matrix}$, m. p. 162°. 4-Nitro-5-aminohydrindene is deaminated to 4-*nitrohydrindene*, b. p. 145—146°/16 mm., m. p. 40°, which is reduced to 4-*aminohydrindene*, b. p. 130—131°/16 mm., m. p. about 9° (*acetyl* derivative, m. p. 40—41°; *benzoyl* compound, m. p. 136°; 4'-*hydrindeneazo*-β-*naphthol*, m. p. 148°). 5-Acetamidohydrindene is smoothly brominated in glacial acetic acid solution to 6-*bromo*-5-*acetamidohydrindene*, m. p. 143°, which is hydrolysed to 6-*bromo*-5-*aminohydrindene*, m. p. 43° (*hydrochloride*, m. p. 214°). Deamination of the base affords 5-*bromohydrindene*, b. p. 113—114°/16 mm., m. p. —7°, also prepared from 5-aminohydrindene. 5-*Bromo*-4 : 6-*dinitrohydrindene*, m. p. 128°, and 4 : 6-*dinitro*-5-*methoxyhydrindene*, m. p. 72°, are described. 5-Bromohydrindene reacts with difficulty with magnesium and the product is converted by carbon dioxide into hydrindene-5-carboxylic acid. 4 : 6-*Dibromo*-5-*aminohydrindene*, m. p. 70°, prepared by bromination of the base in chloroform, yields the corresponding *acetyl* derivative, m. p. 168—169°, and 4 : 6-*dibromohydrindene*, b. p. 148°/15 mm. 5 : 7-*Dibromo*-4 : 6-*dinitrohydrindene*, m. p. 143°, is described.

6-Acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene is converted by cautious nitration into 5-*nitro*-6-*acetyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 145°; the corresponding *oxime*, m. p. 161°, is converted by the Beckmann transformation into 5-nitro-6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene.

6-Bromo-1 : 2 : 3 : 4-tetrahydronaphthalene could not be caused to react with magnesium. The corresponding 5-bromo-compound reacts readily, the product being converted by carbon dioxide into 1 : 2 : 3 : 4-tetrahydronaphthalene-5-carboxylic acid.

H. WREN.

Benzhydrylamine from benzophenoneoxime. C. D. HURD (J. Amer. Chem. Soc., 1926, **48**, 2484—2485; cf. Billon, this vol., 405).—Attention is directed to earlier accounts of this preparation (Noyes, A., 1894, i, 65; Konovalov, *ibid.*, 1901, i, 281; Jones and Hurd, *ibid.*, 1922, i, 248). F. G. WILLSON.

***s*-Diphenyldimethyl-*p*-phenylenediamine and the colour of mono-salts and di-salts of holoquinonic compounds.** J. PICCARD (J. Amer. Chem. Soc., 1926, **48**, 2355—2358; cf. this vol., 1079).—*s*-*Diphenyldimethyl*-p-*phenylenediamine*, m. p. 147—151°, is best prepared by treating *s*-diphenyl-*p*-phenylenediamine with methyl sulphate. It can also be obtained by heating together *p*-di-iodobenzene, methylaniline, potassium carbonate, nitrobenzene, and copper powder, or quinol, methylaniline, calcium chloride, and zinc chloride (cf. Calm, A., 1884, 591). *s*-Diphenyldimethylbenzidine (cf. Wieland, *ibid.*, 1919, i, 355) was synthesised by methylating *s*-diphenylbenzidine, and from *pp'*-di-iododiphenyl and methylaniline. The holoquinonic salts of these tetra-substituted derivatives (obtained on oxidation of the bases) can only be di-salts, and the paleness of their colours, as compared with those of the mono-salts of the corresponding disubstituted derivatives, is in accordance with previous observations (cf. Piccard, Helv. Chim. Acta, 1924, **7**, 790).

F. G. WILLSON.

Diphenyl series. II. Nitration of diphthalylbenzidine. H. H. HODGSON (J.C.S., 1926, 2384—2386).—The isolation of 4 : 4'-di-iodo-3 : 5'-dinitrodiphenyl, m. p. 252°, from the nitration products of diphthalylbenzidine after hydrolysis and application of the Sandmeyer reaction, shows that in addition to 2 : 3'- and 2 : 2'-dinitrobenzidine and a mononitrobenzidine, 3 : 5'-dinitrobenzidine is formed in the nitration of diphthalylbenzidine (cf. Cain and others, J.C.S., 1912, **101**, 2298; Brady and McHugh, *ibid.*, 1923, **123**, 2047; Le Fèvre and Turner, this vol., 946). The following compounds are described: 4 : 4'-*di-iodo*-2-*nitrodiphenyl*, m. p. 156°, from 2-nitrobenzidine; 4 : 4'-di-iodo-2 : 3'-dinitrodiphenyl, m. p. 156—157° (Cain, *loc. cit.*, gives m. p. 151—152°), by nitrating the 2-nitro-compound; 4 : 4'-*di-iodo*-2 : 2'-*dinitrodiphenyl*, m. p. 188°, from 2 : 2'-dinitrobenzidine. J. S. H. DAVIES.

Reaction between azobenzene hydrochloride and phenol. R. PUMMERER and M. DALLY (Ber., 1926, **59**, [*B*], 2175—2181).—*p*-Amino-*p'*-hydroxydiphenyl, m. p. 267°, is obtained in very poor yield

when a solution of azobenzene in an excess of phenol is saturated with hydrogen chloride in the presence of zinc chloride at a temperature not exceeding 40°. The compound is also prepared from benzidine. The *diacetyl* derivative, m. p. 219°, *triacetyl* compound, m. p. 139°, and *benzylidene* derivative, m. p. 203°, are described. At higher temperatures, azines of the induline type appear to be produced. These compounds are also obtained when a solution of azobenzene in phenol saturated with hydrogen chloride is heated in a sealed tube at 180—200°. Since oxygen-free induline bases are produced, the phenol appears to play the part of solvent or, possibly, catalyst. An induline soluble in dilute hydrochloric acid and a spirit-soluble induline have been isolated, but not completely identified. H. WREN.

Irreversible reduction of organic compounds. III. Reduction of azo-dyes. J. B. CONANT and M. F. PRATT (J. Amer. Chem. Soc., 1926, **48**, 2468—2484; cf. this vol., 616).—The normal reduction potentials of the system azobenzenedisulphonate–hydrazobenzenedisulphonate and of two analogous azo–hydrazo-systems have been measured in 0·2*N*-hydrochloric acid at 25°, and the reversibility of these systems has thereby been demonstrated. The rate of irreversible reduction of certain azo-dyes has been found to be essentially independent of the dilution, indicating that this rate appertains to a unimolecular reaction. It is suggested that the hydrazo-derivative first formed reversibly from a hydroxyazo-compound (R·N:N·R′·OH) is reduced slowly and irreversibly to a quinoneimine, which then undergoes further reduction, either reversibly or irreversibly, to the corresponding aminophenol, the second of these reductions, a unimolecular reaction, controlling the rate of the total reduction. The apparent reduction potentials of 27 hydroxyazo-dyes in 0·2*N*-hydrochloric acid at 23° are recorded. The structure of the nucleus bearing the hydroxyl group appears to have the chief influence on this value, and the compounds examined fall into four classes: (I), reduction potential 0·435—0·410, *p*-hydroxyazo-compounds with a substituent other than hydroxyl or sulphonic groups, *ortho* or *meta* to the azo-group, and *o*-hydroxyazo-compounds with a similar substituent *meta* to the azo-group (the substituent in all cases being in the same nucleus as the hydroxyl group); (II), potential 0·400—0·385, 2 : 4-dihydroxyazo-compounds, and 4-hydroxyazo-2-sulphonic acids; (III), potential 0·360—0·315, α- or β-azonaphthols, and their sulphonic acids; and (IV), potential 0·300—0·305, 2 : 4 : 6-trihydroxyazo-compounds. The reduction of *o*- and *p*-hydroxyazo-compounds involves complete fission of the molecule in all cases, and the rate of reduction is a function of the potential of the reducing agent, and not of its specific nature. Equations are derived by means of which certain relative rates of reduction with two reagents, in agreement with experimental values, are calculated.

F. G. WILLSON.

Optically active diazo-compounds. III. Crystalline, alicyclic diazo-ester. F. E. KENDALL and W. A. NOYES (J. Amer. Chem. Soc., 1926, **48**, 2404—2412; cf. A., 1922, i, 924).—When ethereal nitroso-*cis*-aminocamphonanic anhydride is treated with methyl-alcoholic sodium methoxide at −20°, it yields *methyl* cis-*diazocamphonanate*, rouge-red, m. p. 30° (rapidly heated), $[\alpha]_D$ +420° in ether. This decomposes at 10°, with evolution of nitrogen and formation of the bishydrazone of methyl camphonanate (90%) (cf. Noyes and Tavcau, A., 1904, i, 807) and unsaturated, nitrogen-free products (10%). When methyl *trans*-aminocamphonanate is treated with carbonyl chloride in toluene, it affords the corresponding disubstituted *carbamide*, m. p. 305°, which is also obtained by the action of nitrous acid on the corresponding monosubstituted derivative. Treatment of the disubstituted carbamide with nitrous anhydride in ether, followed by decomposition with sodium methoxide, affords *methyl* trans-*diazocamphonanate*, $[\alpha]_D$ +348° to 430° in ether. The rotatory dispersion of the diazo-compound agrees closely with that calculated from Drude's equation. The results do not establish conclusively the asymmetry of the carbon atom bearing the diazo-group.

F. G. WILLSON.

Alkaline hydrolysis of esters in aqueous-alcoholic solution. I Interaction of phenoxides and aliphatic esters in alcoholic solution. E. S. GYNGELL (J.C.S., 1926, 2484—2491).—The course of the interaction of potassium phenoxide and ethyl acetate, methyl and ethyl oxalates, and malonic, succinic, and dimethylmalonic esters in absolute alcohol has been examined by an acidimetric method. Normally the reaction does not proceed to completion, nor according to the equation $Ph{\cdot}OK+Me{\cdot}CO_2Et \rightarrow Ph{\cdot}O{\cdot}Et+Me{\cdot}CO_2K$, and the usual bimolecular law is not obeyed. Neither phenetole nor ether was formed from ethyl acetate, but anisole and phenetole were produced in quantity from methyl and ethyl oxalates. The equilibrium reaction proceeds not as the result of "alcoholysis" of the phenoxide, but as a result of the hydrolysis of the phenoxide by traces of water present in, or added to, the solution. A satisfactory mathematical expression for the reaction is developed. J. S. H. DAVIES.

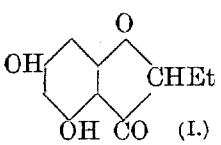
Compound of *o*- and *p*-cresols: correction. A. E. HILL and T. W. DAVIS (J. Amer. Chem. Soc., 1926, **48**, 2448—2449; cf. A., 1925, ii, 1161).—The compound between *o*- and *p*-cresol has the composition 2*p* : 1*o*, as reported by Dawson and Mountford (J.C.S., 1918, **113**, 932). F. G. WILLSON.

Reaction velocity and the influence of constitution in the benzoylation of monohydric phenols. A. L. BERNOULLI and A. S. GOAR.—See this vol., 1108.

1-Amino-4-anilino-β-naphthol. H. GOLDSTEIN and H. RADOVANOVITCH (Helv. Chim. Acta, 1926, **9**, 783—785).—The action of hydroxylamine on 2-hydroxy-β-naphthaquinone-4-anil yields the corresponding *oxime*, m. p. 220°, which on reduction with stannous chloride yields 1-*amino*-4-*anilino*-β-*naphthol* (*diacetyl* derivative, m. p. 212°), stable only in the form of its *hydrochloride*, the free base being readily oxidised by air to form 2-*hydroxy*-α-*naphthaquinone*-1-*imine*-4-*anil*, m. p. 212° (decomp.). J. W. BAKER.

Diphensuccindene series. XIII. 9-Chloro-12-alkoxy-$\Delta^{9:11}$-diphensuccindadiene. K. BRAND, K. O. MÜLLER, and H. KESSLER (Ber., 1926, **59**, [*B*], 1962—1964). — 9 : 12-Dichloro-$\Delta^{9:11}$-diphensuccindadiene (A., 1922, i, 444) is converted by sodium methoxide into *9-chloro-12-methoxy-$\Delta^{9:11}$-diphensuccindadiene*, m. p. 178·5°, which is reduced by zinc dust and glacial acetic acid to Δ^{10}-diphensuccindene, m. p. 210° (*loc. cit.*). The latter compound is also obtained by reduction of *9-chloro-12-ethoxy-$\Delta^{9:11}$-diphensuccindadiene*, m. p. 123°. H. WREN.

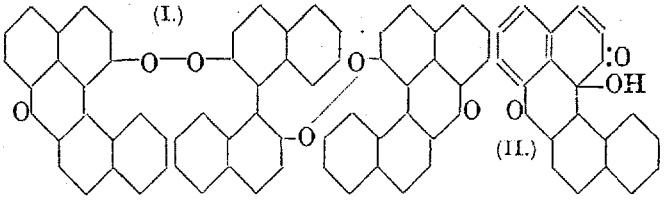
Introduction of alkyl and aryl groups into the nucleus of polyhydric phenols. E. KLARMANN (J. Amer. Chem. Soc., 1926, **48**, 2358—2367).—Condensation of β-phenylpropionitrile with resorcinol in ether in presence of zinc chloride and hydrogen chloride at 0°, followed by boiling with water, affords 2 : 4-*dihydroxyphenyl β-phenylethyl ketone* ($+1H_2O$), m. p. 84°, which, on reduction with zinc and hydrochloric acid, yields *αγ-2 : 4-dihydroxydiphenylpropane*, m. p. 70—71°. 2 : 4 : 6-*Trihydroxyphenyl β-phenylethyl ketone* ($1H_2O$), m. p. 140°, and *αγ-2 : 4 : 6-trihydroxydiphenylpropane*, m. p. 80—81°, were prepared analogously from phloroglucinol. m-*Phenylene dibutyrate*, b. p. 195—200°, and *dihexoate*, b. p. 210—220°, were obtained by heating resorcinol with the appropriate acid chloride at 70—75°, and the following acylresorcinols were prepared by rearrangement of the corresponding esters (cf. Doebner, A., 1882, 507; Eijkman, *ibid.*, 1905, i, 359): diacetyl-, m. p. 182° (cf. Eijkman, *loc. cit.*); dipropionyl- (cf. Wittig, this vol., 302); *dibutyryl-*, m. p. 64—65°; *dihexoyl-*, b. p. 215—220°; *lauroyl-*, m. p. 79—80°; and *α-bromobutyryl-resorcinol*, m. p. 114—115°. The following dialkylresorcinols were obtained by reducing the above acyl derivatives with zinc and hydrochloric acid: *diethyl-*, m. p. 71°; *dipropyl-*, m. p. 59°; *dibutyl-*, b. p. 194—196°; *dihexyl-*, b. p. 205°; and *dodecyl-resorcinol*, m. p. 65—66°. Phloroglucinol triacetate affords *triethylphloroglucinol*, m. p. 126°, on reduction. When phloroglucinol is condensed with bromobutyronitrile and the product boiled with water, 3 : 5-*dihydroxy-2-keto-1-ethylcoumaran* (I), m. p. 165—166°, is obtained. Dihydroxydiphenylethane (cf. Klarmann, this vol., 515) is the most powerful antiseptic of the monoarylresorcinols so far examined. Dialkylresorcinols are sometimes stronger and sometimes weaker antiseptics than the corresponding monoalkyl derivatives. Triethylphloroglucinol is a weaker antiseptic than hexylphloroglucinol (cf. Klarmann and Figdor, this vol., 516). It is suggested that the increase in germicidal power associated with the introduction of alkyl groups into phenols is connected with an accompanying reluctance of the substituted phenol to assume the tautomeric keto-form. F. G. WILLSON.


(I.)

Terpenes and related compounds. I. Rapid method of isomerising safrole. N. HIRAO (J. Soc. Chem. Ind. Japan, 1926, **29**, 241—247).—By using an absolute-alcoholic solution of potassium hydroxide, metallic sodium, or sodium hydroxide instead of aqueous solutions of alkali, safrole is easily isomerised in almost theoretical yield. The presence of water markedly disturbs the reaction. K. KASHIMA.

Preparation of dinaphthylene dioxide. R. PUMMERER, E. PRELL, and A. RIECHE (Ber., 1926, **59**, [*B*], 2159—2161; cf. Bünzly and Decker, A., 1905, i, 884; Pummerer and Frankfurter, *ibid.*, 1914, i, 714).—Dinaphthol is obtained in 90% yield by the oxidation of β-naphthol dissolved in much boiling water with ferric chloride. It is converted into dinaphthylene dioxide by heating its copper salt at 280—290° or by heating it with copper oxide in the presence of nitrobenzene or naphthalene. H. WREN.

Oxidation of phenols. IX. Aromatic peroxides with univalent oxygen. R. PUMMERER and A. RIECHE (Ber., 1926, **59**, [*B*], 2161—2175).—The colourless product of the oxidation of dinaphthol (cf. A., 1914, i, 714) is isolated when the phenol dissolved in sodium hydroxide (3 mols.) is oxidised by potassium ferricyanide at −5° in the presence of much ether, from which it separates ($+\frac{1}{2}Et_2O$). Contrary to the previous assumption (*loc. cit.*), it does not represent the ethane form of dehydrohydroxydinaphthylene oxide, since it has only two thirds of the reducing power required by this compound. That the remaining third is represented by dinaphthol is established by preparative isolation and by acetylation of the total product of reduction. The result is the same whether reduction is effected by zinc dust and acetic acid, hydriodic acid, or platinum sponge and hydrogen. Since hydroxydinaphthylene oxide is stable towards these reducing agents, the compound must contain a derivative of dinaphthol united with 2 mols. of hydroxydinaphthylene oxide by reversible dehydrogenation. This conception is confirmed by observations of its oxidising power, for which hydrazobenzene is more suitable than quinol. The peroxide structure is established by the absence of aliphatic double linkings, since the compound is stable towards permanganate in acetone or pyridine at −40° (at which temperature dissociation into radicals does not occur). Further evidence for the constitution (I) for "*dinaphthyldiperoxydinaphthylene oxide*" is derived from its hydrolysis with perchloric acid to a


(I.) (II.)

violet-black *perchlorate*, $C_{20}H_{11}O_6Cl$, which is converted by sodium hydroxide into *hydroxyketodinaphthylene oxide* (II), m. p. 240° after softening at 165—166°. The carbinol is smoothly reduced to hydroxydinaphthylene oxide, and when heated gives water and dinaphthylene dioxide. As a quinol, it contains an aliphatic double linking and reduces permanganate at −40°. The violet perchlorate is also obtained from dehydrohydroxydinaphthylene oxide.

The main difference between dehydrohydroxydinaphthylene oxide and the colourless peroxide lies in the production from the latter of an initially

colourless solution in cold benzene, which slowly becomes violet and then exhibits nearly all the properties of a solution of dehydrohydroxydinaphthylene oxide. Moreover, the coloured component can be removed by reducing agents, after which the phenomenon recurs until about 60% conversion has been effected. Apparently the middle portion of the colourless peroxide gives a radical with bivalent oxygen which rapidly undergoes internal disproportioning to hydroxydinaphthylene oxide, leaving a radical solution which, apart from the presence of hydroxydinaphthylene oxide, is identical with dehydrohydroxydinaphthylene oxide solution. The conversion of the colourless peroxide to dehydrohydroxynaphthylene oxide is thus readily effected, but the reverse change could not be accomplished.

Improvements have been effected in the preparation of dehydrohydroxydinaphthylene oxide, m. p. 144°, from hydroxydinaphthylene oxide (*loc. cit.*). Contrary to previous observations, the compound is stable towards permanganate in acetone or pyridine at −30°. It therefore does not contain a quinol nucleus and must be regarded as an aromatic peroxide.

H. WREN.

Cholesterol. E. MONTIGNE (Bull. Soc. chim., 1926, [iv], **39**, 1275—1279).—Cholesterol does not react with benzyl chloride in the presence of potassium hydroxide, with benzoquinone, with ethyl oxalate, amyl nitrite, or an aldehyde in the presence of sodium ethoxide, or with aniline. Since compounds containing the indene or *cyclo*pentene ring yield characteristic condensation products with these reagents, this negative behaviour is consistent with the presence of a naphthalene ring (Windaus, A., 1912, i, 449) and not a five-carbon ring.

With nitrous fumes in ether, or with nitric acid in ether in the presence of mercury, cholesterol affords (yield 80%) a green *ψ-nitrosite*, $C_{27}H_{45}O_4N_3O_7$, m. p. 75° (decomp.), which gradually turns yellow even in the dark. Cold nitric acid converts it into a yellow *nitro*-derivative, $C_{27}H_{41}O(NO_2)_2$, alcoholic potassium hydroxide into a non-crystalline unsaturated substance, aniline into a dark, reddish-brown *azo*-derivative, $C_{27}H_{45}O_3(N{:}NPh)\cdot N{:}N\cdot C_6H_4\cdot NO_2$, m. p. 95°. Sulphuric acid affords a maroon substance, $C_{27}H_{50}O_9N_2$, m. p. 150° (decomp.) with elimination of nitrous acid, whilst by reduction with zinc, ammonium chloride, and water at the boil, the *ψ*-nitrosite is converted into a brown *compound*, $C_{27}H_{45}O_3(NO_2)\cdot(NH\cdot NH_2)$, m. p. 72°.

R. BRIGHTMAN.

Dyes of the triphenylmethane series [containing chlorobenzyl groups]. CHEM. FABR. GRIESHEIM-ELEKTRON.—See B., 1926, 815.

Polyhydroxybenzyl alcohols. 3 : 4 : 5-Trihydroxybenzyl alcohol and a tannin derived therefrom. K. W. ROSENMUND and T. BOEHM (Arch. Pharm., 1926, **264**, 448—459).—The polyhydroxybenzaldehydes show surprising differences in their behaviour when treated with hydrogen and palladised barium sulphate. Thus, protocatechualdehyde is easily reduced to homopyrocatechol, whereas the dicarbomethoxy-derivative yields the corresponding alcohol, and the dicarbethoxy-derivative is unaffected. *Dicarbomethoxyprotocatechualdehyde* (m. p. 99—100°; p-*nitrophenylhydrazone*, m. p. 187—189°) is obtained by treating protocatechualdehyde with potassium hydroxide and an excess of methyl chloroformate. When reduced as described (cf. Rosenmund and Jordan, A., 1925, i, 257), it yields 3 : 4-*dicarbomethoxydihydroxybenzyl alcohol* (an oil; p-*nitrobenzoate*, m. p. 129—130°; *α-naphthylurethane*, m. p. 103—104°), which is hydrolysed by cold dilute sodium hydroxide (in an atmosphere of hydrogen) to *protocatechuyl alcohol* (3 : 4-*dihydroxybenzyl alcohol*), m. p. 137—138°.

Similarly, gallaldehyde (cf. Rosenmund and Pfankuch, A., 1922, i, 1030) and its carbomethoxy-derivative behave differently. *Tricarbomethoxygallaldehyde* (m. p. 81—82°; p-*nitrophenylhydrazone*, m. p. 206—207°) is obtained by treating gallaldehyde, in dilute potassium hydroxide solution, with an excess of methyl chloroformate. When no excess of methyl chloroformate is used, the 3 : 5(?)-*dicarbomethoxy*-derivative (m. p. 155°; p-*nitrophenylhydrazone*, m. p. 193°) is produced; this resists reduction by hydrogen and palladised barium sulphate. The tricarbomethoxy-compound, however, when so treated, yields 3 : 4 : 5-*tricarbomethoxytrihydroxybenzyl alcohol* (m. p. 67—68°; p-*nitrobenzoate*, m. p. 147—148°; *α-naphthylurethane*, m. p. 131—132°). Similarly, *tricarbethoxygallaldehyde* (m. p. 69—70°; p-*nitrophenylhydrazone*, m. p. 198—199°) affords, but less readily, 3 : 4 : 5 - *tricarbethoxytrihydroxybenzyl alcohol* (m. p. 58—59°; *α-naphthylurethane*, m. p. 87—88°). The tricarbomethoxy-alcohol is hydrolysed in ice-cold sodium hydroxide under hydrogen to a syrupy *compound* which has the properties of the expected trihydroxybenzyl alcohol, but changes in a desiccator to a brown, pulverulent mass having no sharp m. p. (blackens at 80°). This substance, unlike the syrup, has pronounced tanning properties. No urethane is formed. The *acetyl* derivative (sinters at 160—170°, decomposes above) resembles acetyl-tannin in properties. This production of a "tannin," presumably a mixture of condensation products, is of interest in connexion with the formation of tannins in nature.

W. A. SILVESTER.

ω-*cyclo*Hexyl derivatives of normal aliphatic acids. IV. G. S. HIERS and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2385—2393; cf. this vol., 597).—The following alcohols were obtained by condensation of formaldehyde or ethylene oxide with appropriate Grignard reagents: *cyclo*hexyl-methyl, b. p. 88—89°/22 mm., n_D^{25} 1·4640, d_4^{25} 0·9215 (cf. Noller and Adams, "Organic Syntheses," 1926, **6**, 22); -ethyl, b. p. 87—89°/6 mm., n_D^{25} 1·4636, d_4^{25} 0·9183 (cf. Zelinsky, A., 1908, i, 727); -propyl, b. p. 91—92°/5 mm., n_D^{25} 1·4624, d_4^{25} 0·9061 (cf. Skita, A., 1916, i, 41); -*butyl*, b. p. 103—104°/4 mm., n_D^{25} 1·4632, d_4^{25} 0·9015; -*amyl*, b. p. 118—119°/4 mm., n_D^{25} 1·4638, d_4^{25} 0·8959; and -*hexyl alcohol*, b. p. 123—124°/4 mm., n_D^{25} 1·4648, d_4^{25} 0·8963. These were converted into the corresponding halides: *cyclo*hexylmethyl iodide, b. p. 106—108°/26 mm., n_D^{25} 1·4922, d_4^{25} 1·3751 (cf. Freundler, A., 1906, i, 283, 733); *cyclo*hexylmethyl bromide, b. p. 76—77°/26 mm., n_D^{25} 1·4889, d_4^{25} 1·2690 (Freundler,

loc. cit.); cyclo*hexyl-ethyl bromide*, b. p. 70·5—71°/6 mm., n_D^{25} 1·4862, d_4^{25} 1·2096; *-propyl bromide*, b. p. 77—79°/4 mm., n_D^{25} 1·4848, d_4^{25} 1·1521; *-butyl bromide*, b. p. 91·6—92·2°/4 mm., n_D^{25} 1·4832, d_4^{25} 1·1350; *-amyl bromide*, b. p. 113—114°/5 mm., n_D^{25} 1·4814, d_4^{25} 1·1198; and *-hexyl bromide*, b. p. 124—125°/4 mm., n_D^{25} 1·4802, d_4^{25} 1·1073. Conversion of the above halides into the corresponding Grignard reagents, and subsequent condensation with ethyl malonate afforded the corresponding substituted ethyl malonates, from which the free acids were obtained on hydrolysis with aqueous potassium hydroxide. The following are described: *cyclo*hexylmalonic acid, m. p. 183—184° (cf. Hope and Perkin, J.C.S., 1909, **95**, 1363) (diethyl ester, b. p. 122—123°/4 mm., n_D^{25} 1·4478, d_4^{25} 1·0228, cf. Freundler, *loc. cit.*); *cyclo*hexylmethylmalonic acid, m. p. 114—115° (cf. Zelinsky, A., 1908, i, 864) (diethyl ester, b. p. 135—136°/3 mm., n_D^{25} 1·4469, d_4^{25} 1·0059, cf. Kamm and Marvel, "Organic Syntheses," 1921, **1**, 1); cyclo*hexylethylmalonic acid*, m. p. 129—130° (*diethyl* ester, b. p. 139·8—140·2°/3 mm., n_D^{25} 1·4476, d_4^{25} 0·9956); γ-cyclo*hexylpropylmalonic acid*, m. p. 88—89° (*diethyl* ester, b. p. 153·5—154°/4 mm., n_D^{25} 1·4489, d_4^{25} 0·9870); δ-cyclo*hexylbutylmalonic acid*, m. p. 118—119° (*diethyl* ester, b. p. 169—170°/5 mm., n_D^{25} 1·4500, d_4^{25} 0·9787); ε-cyclo*hexylamylmalonic acid*, m. p. 111—112° (*diethyl* ester, b. p. 186—187°/6 mm., n_D^{25} 1·4509, d_4^{25} 0·9717); and ζ-cyclo*hexylhexylmalonic acid*, m. p. 114—115° (*diethyl* ester, b. p. 192—193°/4 mm., n_D^{25} 1·4522, d_4^{25} 0·9647). When heated at 20—30° above their m. p., the above malonic acids yield the corresponding monobasic acids, further members of this series being obtained by condensation of Grignard reagents with aldehyde esters (cf. Hiers and Adams, *loc. cit.*). The following are described: hexahydrobenzoic acid, b. p. 105—106°/4 mm., m. p. 29—30°, n_D^{38} 1·4520, d_4^{38} 1·0251; *cyclo*hexylacetic acid, m. p. 29—30°, b. p. 116—117°/4 mm., n_D^{38} 1·4537, d_4^{38} 1·0020; β-*cyclo*hexylpropionic acid, m. p. 15—16°, b. p. 125—126°/4 mm., n_D^{38} 1·4553, d_4^{38} 0·9848 (cf. Sabatier and Murat, A., 1913, i, 468); γ-cyclo*hexylbutyric acid*, m. p. 29—30°, b. p. 132—134°/3 mm., n_D^{38} 1·4562, d_4^{38} 0·9693; δ-cyclo*hexylvaleric acid*, m. p. 6—8°, b. p. 151—153°/5 mm., n_D^{38} 1·4570, d_4^{38} 0·9589; ε-cyclo*hexylhexoic acid*, m. p. 33—34°, b. p. 157—158°/4 mm., n_D^{38} 1·4580, d_4^{38} 0·9506; ζ-cyclo*hexylheptoic acid*, m. p. 25—26°, b. p. 171—172°/4 mm., n_D^{38} 1·4588, d_4^{38} 0·9436; η-cyclo*hexyloctoic acid*, m. p. 37—38°, b. p. 182—183°/4 mm., n_D^{38} 1·4598, d_4^{38} 0·9359; θ-cyclo*hexylnonoic acid*, m. p. 45·5—46·5; ι-cyclo*hexyldecoic acid*, m. p. 52·5—53·5°; κ-cyclo*hexylundecoic acid*, m. p. 58—59°; λ-cyclo*hexyldodecoic acid*, m. p. 61·5—62°; and μ-cyclo*hexyltridecoic acid*, m. p. 63—64°. The following hydroxy-acids were obtained in the course of the above syntheses: θ-*hydroxy*-θ-cyclo*hexylnonoic acid*, m. p. 78—79° (*methyl* ester, b. p. 186—192°/5 mm.); ι-*hydroxy*-ι-cyclo*hexyldecoic acid*, m. p. 63—64° (*methyl* ester, b. p. 191—195°/4 mm.); and ι-*hydroxy*-λ-cyclo*hexyldodecoic acid*, m. p. 58—59° (*methyl* ester, b. p. 214—218°/4 mm.). Of the above acids, β-*cyclo*hexylpropionic acid has a slight action on *Bacillus leprœ*. This increases with increase in the length of the side-chain, reaching a maximum at 9 carbon atoms, and again diminishing until the effect is only slight with 13 carbon atoms. The hydroxy-acids containing chains of 12 and 13 carbon atoms are much more effective than those without the hydroxyl group. The substituted malonic acids are almost inert against the above bacillus. F. G. WILLSON.

Synthesis of chaulmoogrylacetic acid. V. R. H. VAN DYKE and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2393—2395; cf. preceding abstract).—Ethyl chaulmoograte was reduced to chaulmoogryl alcohol (cf. Power and Gornall, J.C.S., 1904, **85**, 838) by the method of Grün and Wirth (A., 1922, i, 804). Treatment of the alcohol with phosphorus tribromide in toluene afforded *chaulmoogryl bromide*, m. p. 18·6°, b. p. 230°/16 mm., n_D 1·8486, d_{25}^{25} 1·0461, $[\alpha]_D$ +42·1°, which, condensed with ethyl sodiomalonate, yielded the *ethyl* ester of *chaulmoogrylmalonic acid*, m. p. 94—95°, $[\alpha]_D$ +45·0° in chloroform, and this, when boiled with xylene, yielded *chaulmoogrylacetic acid*, m. p. 72—73°, $[\alpha]_D$ +43·34° in chloroform. F. G. WILLSON.

Synthesis of homochaulmoogric acid, homohydnocarpic acid, and chaulmoogrylamines. VI. J. SACKS and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2395—2399; cf. preceding abstract).—Condensation of chaulmoogryl bromide with alcoholic potassium cyanide affords *chaulmoogryl cyanide* (*homochaulmoogronitrile*), m. p. 24·5°, b. p. 230°/16 mm., n_D^{25} 1·4691, d_{25}^{25} 0·8928, $[\alpha]_D$ +49·5° in chloroform, from which, on hydrolysis with alkali, *homochaulmoogric acid*, $C_{19}H_{34}O_2$, m. p. 66—67°, $[\alpha]_D$ +54·0° in chloroform, was obtained. Condensation of the above bromide with potassium phthalimide, followed by hydrolysis, yields *chaulmoogrylamine*, b. p. 206°/16 mm. (hydrochloride, m. p. 114°, $[\alpha]_D$ +44·2° in chloroform), whilst diethylamine affords similarly *chaulmoogryldiethylamine* (*hydrochloride*, m. p. 99°, $[\alpha]_D$ +34·5° in chloroform). Ethyl hydnocarpate, b. p. 217°/23 mm., n_D^{25} 1·4577 (cf. Power and Barrowcliff, J.C.S., 1907, **91**, 557) was converted, by the method described in the preceding abstract, into *hydnocarpyl alcohol*, m. p. 23°, b. p. 199·5°/14 mm., n_D^{25} 1·4733, $[\alpha]_D$ +67·8° in chloroform, *hydnocarpyl bromide*, m. p. 1°, b. p. 206—210°/14 mm., n_D^{25} 1·4871, $[\alpha]_D$ +40·0°, and *homohydnocarpic acid*, m. p. 56—57°, $[\alpha]_D$ +56·7° in chloroform. Homochaulmoogric, homohydnocarpic, and chaulmoogrylacetic acids have little effect on *Bacillus leprœ*. Cinnamic and furylacrylic acids tend to inhibit the growth of this bacillus, but various derivatives of cinnamic acid are inert (cf. Schöbl, A., 1924, i, 1386). Phenylpropiolic, cinnamylideneacetic, and umbelliferone-β-acetic acids also possess inhibitory properties. F. G. WILLSON.

Synthesis of a homologue of chaulmoogric acid. Δ^2-*cyclo*Pentenylacetic acid. VII. C. R. NOLLER and R. ADAMS (J. Amer. Chem. Soc., 1926, **48**, 2444—2448; cf. preceding abstract).—The action of dry hydrogen chloride on *cyclo*pentadiene at −20° affords Δ^2-cyclo*pentenyl chloride*, b. p. 25—31°/30 mm., which rapidly decomposes at the ordinary temperature, but can be condensed with ethyl sodiomalonate, with formation of the *diethyl* ester, b. p. 120°/6 mm., n_D^{20} 1·4536, d_4^{20} 1·0507, of Δ^2-cyclo*pentenylmalonic acid*, m. p. 149—149·5°, at which temperature it decomposes into Δ^2-cyclo*pentenylacetic acid*, b. p. 94—95°/3 mm., n_D^{20} 1·4682, d_4^{20} 1·0519. The *ethyl* ester of the

latter, b. p. 85—86°/15 mm., n_D^{20} 1·4480, d_4^{20} 0·9659, is reduced by sodium and alcohol to β-Δ^2-cyclo*pentenyl-ethyl alcohol*, b. p. 86—87°/16 mm., n_D^{20} 1·4721, d_4^{20} 0·9446. F. G. WILLSON.

Reaction of benzoyl peroxide with iodine. H. ERLENMEYER (Helv. Chim. Acta, 1926, 9, 819—822; cf. this vol., 400).—When benzoyl peroxide is exploded in an atmosphere of iodine vapour, both carefully dried with phosphorus pentoxide, without contact between the substances before the explosion, only diphenyl and carbon dioxide result, no iodobenzene being formed. If, on the other hand, the two substances are carefully fused together, reaction occurs without explosion, a good yield of iodobenzene being obtained, and the author is of the opinion that the formation of iodobenzene occurs by this reaction between the iodine and the peroxide before the explosion, and constitutes no evidence for the production of free radicals (cf. Wieland and Fischer, this vol., 46). J. W. BAKER.

Hydrogenation of salts of aromatic acids under pressure. W. IPATIEV and G. RASUVAJEV (Ber., 1926, 59, [*B*], 2028—2031; cf. this vol., 400).—The reactions, $2R{\cdot}CO_2Na+4H_2=2RH+CH_4+Na_2CO_3+H_2O$ and $C_6H_5{\cdot}CO_2Na+3H_2=C_6H_{11}{\cdot}CO_2Na$, are more complete in the presence than in absence of water. In presence of water at 300° and 92 atm. in presence of nickel oxide, sodium benzoate affords *cyclo*hexane containing a little benzene and hexahydrobenzoic acid. Sodium mandelate gives mainly a mixture of methyl*cyclo*hexane, toluene, and probably *cyclo*hexane; *cyclo*hexylacetic acid is formed in very small amount. Sodium phenylacetate yields a similar mixture of hydrocarbons together with *cyclo*hexylacetic acid. Sodium cinnamate gives very little hydrocarbon, but β-*cyclo*hexyl- and β-phenylpropionic acids. Sodium acetate is decomposed to methane and sodium carbonate, whilst sodium heptoate gives methane and hexane. In absence of solvent, methyl salicylate gives phenol and resins; in methyl-alcoholic solution, *cyclo*hexanol, b. p. 160—161·5°, is produced in good yield. H. WREN.

Imino-aryl ethers. IV. Reversible migration of an aryl group. A. W. CHAPMAN (J.C.S., 1926, 2296—2300).—N-*Phenylbenziminophenyl thioether* (I), m. p. 58°, prepared from benzanilideiminochloride and thiophenol (*ibid.*, 1922, **121**, 1679), is hydrolysed by 50% sulphuric acid to aniline and phenyl thiolbenzoate. It is converted very slowly into thiobenzoyldiphenylamine (II) by heating at 280—290° (cf. A., 1925, i, 1400), whereas the latter compound is practically unchanged at this temperature. Diphenyl sulphide, benzonitrile, thiophenol, and 1-phenylbenzthiazole are obtained by decomposition of either the thioether or the thiobenzoyldiphenylamine at 320° or above. The formation from the amine of compounds containing the PhS· group is explained by assuming reversible isomeric change of the thioether into the amine, although the high temperature required renders impossible the attainment of an actual equilibrium:

$$Ph_2S,\ PhCN,\ PhSH,\ C_{13}H_9NS \xleftarrow{\text{decomp.}} PhS{\cdot}C{\cdot}Ph{:}NPh \rightleftharpoons S{:}CPh{\cdot}NPh_2.$$
(I.) (II.)

N-p-*Tolylbenzimino*-p-*tolyl thioether*, m. p. 50°, obtained from benz-*p*-toluidideiminochloride and *p*-thiocresol, is hydrolysed by 50% sulphuric acid to *p*-toluidine and *p*-tolyl thiolbenzoate. When heated at 320° for 6 hrs., it yields 1-phenyl-5-methylbenzthiazole, and not 1-phenyl-4-methylbenzthiazole. Thus formation of the thiazole from the thioether is effected either by elimination of the group attached to the sulphur atom or by previous migration of this group to the nitrogen atom. *Thiobenzoyl*-p-*tolylamine*, obtained by the action of phosphorus pentasulphide on benzoyldi-*p*-tolylamine, has m. p. 189—190°.

M. CLARK.

Derivatives of phenylanthranilic acid. I. H. GOLDSTEIN and W. RODEL (Helv. Chim. Acta, 1926, 9, 765—772).—*Methyl* m'-*nitrodiphenylamine*-o-*carboxylate*, m. p. 84—85°; *methyl* p-*aminodiphenylamine*-o-*carboxylate* (*acetyl* derivative, m. p. 148°), and *methyl* p'-*aminodiphenylamine*-o-*carboxylate*, m. p. 106° (*acetyl* derivative, m. p. 157°), are readily obtained by direct esterification of the corresponding acids, but *methyl* p-*nitrodiphenylamino*-o-*carboxylate*, m. p. 111°, can be prepared only from its silver salt. 2-Chloro-5-nitrobenzoic acid condenses with *p*-phenylenediamine in the presence of copper powder to yield *p*-nitro-*p'*-aminodiphenylamine-*o*-carboxylic acid, m. p. 226—227° (decomp.), together with (?) di-(2'-chloro-5'-nitrobenzoyl)-*p*-phenylenediamine, m. p. 176—177°. On reduction with stannous chloride in alcohol, the former compound yields p:p'-*diaminodiphenylamine*-o-*carboxylic acid*, m. p. 200° (*dihydrochloride*, *methyl* ester, m. p. 147°, *diacetyl* derivative of ester, m. p. 230°). Similarly, 2-chloro-5-nitrobenzoic acid condenses with *o*-nitroaniline to yield o'p-*dinitrodiphenylamine*-o-*carboxylic acid*, m. p. 265—266° (together with a little 5-nitrosalicylic acid, and an *acid*, m. p. 140—141°), which on reduction yields o'p-*diaminodiphenylamine*-o-*carboxylic acid*, m. p. 223—224° (decomp.) (*dihydrochloride*, *methyl* ester, m. p. 116—117°). 3-Aminoacridone on acetylation yields 3-*acetamidoacridone*, m. p. above 340°.

J. W. BAKER.

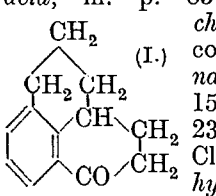
Urethanes. II. Isomeric urethane derivatives of phenylacetic acid, and related compounds. S. BASTERFIELD and H. N. WRIGHT (J. Amer. Chem. Soc., 1926, 48, 2367—2370; cf. this vol., 1132).—p-*Carbethoxyaminophenylacetic acid*, m. p. 125° (sodium salt, sinters 168—170°; *ethyl* ester, m. p. 80°), is obtained by condensation of *p*-aminophenylacetic acid with ethyl chloroformate in presence of alkali. On treatment with ethyl sulphate in ethyl alcohol, it yields p-*carbethoxyethylaminophenylacetic acid* (*ammonium* salt, m. p. 99—100°). α-Aminophenylacetic acid and ethyl chloroformate afford similarly dl-α-*carbethoxyaminophenylacetic acid*, m. p. 121—122° (*sodium* salt, decomp. 220—225° after sintering at 210°). The *sodium* salt, m. p. 227°, of *N*-carbethoxyphenylglycine (cf. Leuchs and Mannasse, A., 1907, i, 770) was prepared. p-*Carbethoxyaminobenzoic acid*, m. p. 201° (*ethyl* ester, m. p. 130°), was obtained as above. These compounds are apparently non-toxic and pharmacologically inert.

F. G. WILLSON.

Synthesis of ψ-cholestan from cholanic acid. H. WIELAND and R. JACOBI (Ber., 1926, 59, [*B*], 2064—2067; cf. Windaus and Neukirchen, A., 1920, i, 41).—Ethyl cholanate is converted by magnesium *iso*propyl iodide into *diisopropylnorcholylcarbinol*, $C_{30}H_{54}O$, m. p. 95°, which is oxidised by chromic acid in glacial acetic acid solution to the *ketone*, $C_{22}H_{37}\cdot CH_2\cdot COPr^s$, m. p. 58—59° (*semicarbazone*, m. p. 180—181°). Reduction of the latter compound by Clemmensen's method affords ψ-cholestan, m. p. 70—71°. H. WREN.

Benzopolymethylene compounds. XII. J. VON BRAUN and J. REUTTER (Ber., 1926, 59, [*B*], 1922—1927).—Whereas 1-hydrindyl chloride does not undergo internal condensation in the presence of aluminium chloride (cf. A., 1917, i, 260), this type of reaction is readily effected with the β-propionic acid derivatives of hydrindene and tetrahydronaphthalene, thus lending support to the view that the carbon atoms of the six-membered ring do not all lie in the same plane. β-1-Hydrindylethyl alcohol is converted successively into β-1-*hydrindylethyl bromide*, b. p. 145—147°/16 mm.; β-1-*hydrindylpropionitrile*, b. p. 160—162°/16 mm.; β-1-*hydrindylpropionic acid*, m. p. 50°, and β-1-*hydrindylpropionyl chloride*, b. p. 155°/16 mm. (corresponding *amide*, m. p. 90°). The chloride is converted by aluminium chloride in presence of carbon disulphide or light petroleum into 3-*ketotetrahydroacenaphthene*, m. p. 85—86° (*semicarbazone*, m. p. 228—230°). The corresponding *oxime*, m. p. 199°, is reduced by sodium and alcohol to 3-*aminotetrahydroacenaphthene*, b. p. 170°/14 mm. (*hydrochloride*, m. p. 230° after darkening; *picrate*, m. p. 246° after darkening at 230°; *acetyl* derivative, m. p. 168°; *phenylthiocarbamate* compound, m. p. 166°). 3-*Hydroxytetrahydroacenaphthene* has b. p. 158—160°/18 mm.

1 : 2 : 3 : 4-Tetrahydronaphthyl-1-acetic acid, b. p. 195—197°/16 mm., is converted into the corresponding *chloride*, b. p. 160—162°/15 mm., and thence into *tetrahydroacenaphthenone*, m. p. 102° (oxime, m. p. 176°; *semicarbazone*, m. p. 196°). 1 : 2 : 3 : 4-Tetrahydronaphthyl-1-acetic ester is reduced by sodium and alcohol to β-1-*tetrahydronaphthylethyl alcohol*, b. p. 175—176°/14 mm., which yields successively β-1-*tetrahydronaphthylethyl bromide*, b. p. 165—167°/13 mm., β-1-*tetrahydronaphthylpropionitrile*, b. p. 182—184°/12 mm., and β-1-*tetrahydronaphthylpropionic acid*, m. p. 83°. β-1-*Tetrahydronaphthylpropionyl chloride*, b. p. 172—174°/14 mm., is converted into "α-*ketohexahydrobenznaphthene*" (I), m. p. 72° (*oxime*, m. p. 159—160°; *semicarbazone*, m. p. 235°). Reduction of the ketone by Clemmensen's method affords *hexahydrobenznaphthene*, b. p. 132—135°/14 mm., d_4^{23} 1·027, n_D^{23} 1·5636. H. WREN.


(I.)

Additive reactions of unsaturated α-ketonic acids. M. REIMER (J. Amer. Chem. Soc., 1926, 48, 2454—2462).—Benzylidenepyruvic acid (styrylglyoxylic acid) crystallises with 1 mol. of benzene (m. p. 70—76°) and with 1 mol. of water (m. p. 55—57°), the anhydrous acid having m. p. 60—62°. The m. p. of the dibromide (cf. Erlenmeyer, A., 1903, i, 698; Ciusa, *ibid.*, 1919, i, 402) is indefinite on account of the ease with which this derivative loses hydrobromic acid when heated, either alone or in aqueous suspension, with formation of β-*bromostyrylglyoxylic acid*, m. p. 100° ($1H_2O$) or m. p. 131—132° (anhydrous). The *methyl* ester, liquid, of the latter is not formed by treating the acid with methyl-alcoholic hydrogen chloride, but is obtained by treating *methyl* αβ-*dibromo*-β-*phenylethylglyoxylate*, m. p. 117°, with methyl-alcoholic potassium acetate. Styrylglyoxylic acid does not add hydrogen bromide or methyl hypobromite. *p*-Methoxystyrylglyoxylic acid, m. p. 131° (solvent-free; cf. Ciusa, *loc. cit.*) (*methyl* ester, m. p. 106°; *ethyl* ester, m. p. 48°), reacts with bromine in chloroform with formation of αβ-*dibromo*-β-p-*anisylethylglyoxylic acid*, m. p. 98—100°; the *methyl* ester, m. p. 93°, and *ethyl* ester, m. p. 100—108°, are obtained similarly from the corresponding unsaturated esters. β-*Bromo*-p-*methoxystyrylglyoxylic acid*, m. p. 100—125° ($1H_2O$), m. p. 136° (anhydrous), obtained by boiling the above dibromide with water, yields α-*bromo*-p-*methoxycinnamic acid*, m. p. 188° (*methyl* ester, m. p. 55°), on oxidation with hydrogen peroxide. The latter acid can be obtained by treating methyl αβ-dibromo-*p*-anisylpropionate with cold 10% alcoholic potassium hydroxide, whilst treatment of the free acid with potassium acetate affords an *isomeride*, m. p. 155°. The *methyl* ester, liquid, of the latter yields the acid of m. p. 188° on hydrolysis. *p*-Methoxystyrylglyoxylic acid does not react with hydrogen bromide. Treatment with bromine in methyl-alcoholic solution yields either β-bromo-*p*-methoxystyrylglyoxylic acid alone, or this acid in admixture with β-3-*dibromo*-p-*methoxystyrylglyoxylic acid*, m. p. 135°, as the *methyl* ester, m. p. 145°, oxidation of which with permanganate in acetone yields 3-bromoanisic acid, whilst hydrogen peroxide affords α-3-*dibromo*-p-*methoxycinnamic acid*, m. p. 181°. The *methyl* ester of the last, m. p. 91°, is obtained by treating αβ-3-tribromo-β-anisylpropionic acid with methyl-alcoholic hydrogen chloride (cf. Eigel, A., 1887, 1109), whilst the action of water on this compound affords 3-*bromo*-p-*methoxystyrene*, m. p. 76°. The above results indicate that no connexion is apparent between ease of addition and tendency to polymerisation under the influence of light among these styryl derivatives (cf. Rice, A., 1924, i, 287).

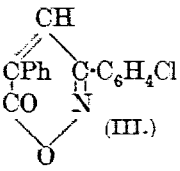
F. G. WILLSON.

Hexahydrophenylglycine-*o*-carboxylic acid. D. VORLÄNDER and H. KLAGE (Ber., 1926, 59, [*B*], 2075—2078).—*Hexahydrophenylglycine-o-carboxylic acid*, m. p. 233—235° (decomp.), is prepared by hydrogenation of phenylglycine-*o*-carboxylic acid dissolved in glacial acetic acid in the presence of spongy platinum, but not with sodium and amyl alcohol or from hexahydroanthranilic acid and chloroacetic acid; its *sodium* salt, decomp. about 264°, *mercury* salt, m. p. about 175° (decomp.), and *lead* salt, decomp. 246—254°, are described. Its behaviour as a monobasic acid suggests the structure $CO<^{O\text{——}}_{C_6H_{10}}>NH_2\cdot CH_2\cdot CO_2H$. Catalytic hydrogenation of phenylglycine-*o*-carboxylic esters gives the corresponding hexahydro-esters in good yield. *Methyl hexahydrophenylglycine-o-carboxylate*, m. p. 60° [*hydro-*

chloride, m. p. 162° (decomp.); *benzyl* derivative, m. p. 66—68° (decomp.); *nitroso*-compound, b. p. 215—220°/17 mm., m. p. 54°], and *ethyl hexahydrophenylglycine-o-carboxylate* (*hydrochloride*, m. p. about 90°) are described. The esters are converted by sodium alkoxide in the presence of ether into *methyl* and *ethyl hexahydroindoxylate*, m. p. 148° and 95°, respectively, in very poor yield. H. WREN.

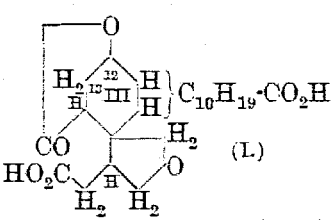
Salts and derivatives of phenolphthalin. C. FINZI and D. ACCARINI (Annali Chim. Appl., 1926, **16**, 314—323).—Phenolphthalin (4 : 4'-dihydroxytriphenylmethane-2''-carboxylic acid), m. p. 229—232° (lit., 225°), gives *magnesium*, *calcium*, and *strontium* salts crystallising with 14, 8½, and 8½ H_2O, respectively, and the following derivatives: 3 : 3'-*dinitro*-4 : 4'-*dihydroxytriphenylmethane*-2''-*carboxylic acid*, m. p. 132—134°; 3 : 5 : 3' : 5'-*tetranitro*-4 : 4'-*dihydroxytriphenylmethane*-2''-*carboxylic acid*, m. p. 172°; 3 : 3'-*dibromo*-4 : 4'-*dihydroxytriphenylmethane*-2''-*carboxylic acid*, m. p. 173—175°; 3 : 3'-*dibromo*-5 : 5'-*dinitro*-4 : 4'-*dihydroxytriphenylmethane*-2''-*carboxylic acid*, m.p. 168—170°; *methyl* 4 : 4'-*dihydroxytriphenylmethane*-2''-*carboxylate*, m. p. 153—154° (*diacetyl* derivative, m. p. 112—114°). E. W. WIGNALL.

***iso*Oxazoline oxides.** E. P. KOHLER and J. B. SHOHAN (J. Amer. Chem. Soc., 1926, **48**, 2425—2434; cf. A., 1924, i, 998).—Treatment of the brominated condensation product of nitromethane and *p*-chlorophenyl styryl ketone [$CH_2(NO_2)$·CHPh·CHBr·CO·C_6H_4Cl] (cf. Smith, Diss., Harvard, 1920) with methyl-alcoholic potassium acetate affords *methyl* β-*hydroxy*-γ-*oximino*-α-*phenyl*-γ-p-*chlorophenylbutyrate* (I), m. p. 165° [N-*acetyl*-derivative, m. p. 105°, N-*benzoyl*-, m. p. 134—135°; *copper* derivatives, dark green, amorphous, m. p. 222° (decomp.), and light bluish-green, crystalline, m. p. 168—170° (decomp.)]. This decomposes above the m. p., with formation of *p*-chlorobenzonitrile, and on hydrolysis with alkali yields the corresponding *acid*, m. p. 174°, and subsequently β-*hydroxy*-γ-*keto*-α-*phenyl*-γ-p-*chlorophenylbutyric acid* (II), m. p. 139—140° (*methyl* ester, m. p. 105°), decomposing in alkaline solution with formation of *p*-chlorophenyl styryl ketone. Treatment of this ketone with potassium cyanide in aqueous alcohol affords β-p-*chlorobenzoyl*-α-*phenylpropionitrile*, m. p. 121°, which, on treatment with methyl-alcoholic hydrogen chloride, yields the *methyl* ester, m. p. 111·5°, of β-p-*chlorobenzoyl*-α-*phenylpropionic acid*, m. p. 152°. This, on bromination, affords the β-*bromo*-derivative, m. p. 216°, which, on treatment with alkali, is converted into (II), from which the oximino-acid is obtained by the action of hydroxylamine. Treatment of the *N*-acetyl derivative of (I) in ether with aqueous ammonia affords β-*hydroxy*-γ-*oximino*-α-*phenyl*-γ-p-*chlorophenylbutyramide*, m. p. 171°, whilst hydrolysis with methyl-alcoholic hydrochloric acid yields the above methyl ester, m. p. 105°, which also affords an *acetyl* derivative, m. p. 84—85°. Treatment of the above *N*-acetyl derivative with acetyl chloride yields the *diacetate*, m. p. 122°, which is hydrolysed by ammonia to the isomeric O-*acetyl* derivative, m. p. 151°, and this in turn affords the O-*acetyl*-N-*benzoyl* derivative, m. p. 128°. The ON-*dibenzoyl* derivative, m. p. 135°, was also prepared. 6-*Keto*-5-*phenyl*-3-p-*chlorophenyl*-1 : 2-*oxazine* (III), m. p. 164° (*sodium* salt), is obtained as a by-product in the reaction with potassium acetate first described. Treatment of (I) with methyl sulphate and alkali affords 4-*hydroxy*-6-*methoxy*-5-*phenyl*-3-p-*chlorophenyl*-1 : 2-*oxazine*, m. p. 184° (benzoyl derivative, m. p. 215—216°).


(III.)

F. G. WILLSON.

Constitution of the bile acids. IX. Catalytic reduction of ketonic acids of the bile acid group. W. BORSCHE and R. FRANK (Ber., 1926, **59**, [*B*], 1748—1754).—Under more energetic conditions than those adopted by Borsche and Hallwass (A., 1922, i, 1159), dehydrocholic acid is reduced by hydrogen in glacial acetic acid in the presence of platinum-black to 3 : 7 : 12-*trihydroxycholanic acid*, m. p. 196°, $[\alpha]_D^{20}$ +59° 35' in alcohol (*triacetyl* derivative, m. p. 257°; *methyl* ester, m. p. 152°; p-*nitrobenzoyl* derivative of methyl ester, m. p. 217—218°), which is differentiated from natural cholic acid only by its specific rotation. Similarly, *methyl dehydrodeoxycholate*, m. p. 238° (or +MeOH, m. p. 92—93° after softening at 82°), affords *methyl deoxycholate*, m. p. 92—93°, $[\alpha]_D^{15}$ +9° 37' in alcohol. 7 : 12-Diketocholanic acid gives 7 : 12-*dihydroxycholanic acid*, m. p. 207—208° (*methyl* ester, m. p. 154°). Bilianic acid is reduced somewhat uncertainly to biliobanic acid, m. p. 304°. Methyl bilianate, m. p. 131°, is converted by aluminium amalgam into methyl biliobanate, m. p. 186° (monoxime, m. p. 187°; cf. Hallwass, Diss., Göttingen, 1922). Biliobanic acid is transformed by zinc and boiling glacial acetic acid into chenodeoxybiliobanic acid, m. p. 255—256° (dimethyl ester, m. p. 106°; trimethyl ester, m. p. 94°). Since the constitution of chenodeoxybiliobanic acid is firmly established (cf. Windaus and van Schoor, this vol., 169), the constitution (I) must be assigned to biliobanic acid, and it must be assumed that the hydroxy-group in ring III of the cholic acid molecule is attached to the carbon atom 12 instead of 13. *iso*Bilianic acid is catalytically reduced to *reductoisobiliobanic acid*, $C_{24}H_{36}O_7$, m. p. 276° (*methyl* ester, m. p. 162—163°). H. WREN.


(I.)

Anhydro-compounds of o-aminobenzaldehyde. F. SEIDEL (Ber., 1926, **59**, [*B*], 1894—1908).—Attempts to prepare Posner's anhydromono-*o*-aminobenzaldehyde by the action of zinc chloride on *o*-aminobenzaldehyde in anhydrous ether were unsuccessful, the products being the compound $C_7H_5N,0{\cdot}5ZnCl_2$, m. p. 348—350°, and *anhydrotris*-*o*-*aminobenzaldehyde*, NH_2-C_6H_4-CH:N-C_6H_4-CH:N-C_6H_4-CHO, m. p. 235° (*dihydrochloride*). The latter compound is also obtained from *o*-aminobenzaldehyde by the action of phosphoric oxide in ether, glacial acetic acid, or aqueous hydrochloric acid under certain conditions;

it is formed when *o*-aminobenzaldehyde is preserved over calcium chloride and is present in the technical aldehyde. *o*-Aminobenzaldehyde is converted by boiling acetic anhydride into *o*-acetamidobenzaldehyde, whereas the cold reagent in the presence of light petroleum affords *acetylanhydrotris-o-aminobenzaldehyde*, m. p. 235 (*monohydrochloride*), also obtained from anhydrotris-*o*-aminobenzaldehyde under similar conditions. The presence of a reactive aldehydic group in anhydrotris-*o*-aminobenzaldehyde is shown by its reaction with *p*-nitroaniline, whereby a substance is produced which gives remarkably stable *compounds*, $C_{30}H_{27}O_3N_5$ and $C_{32}H_{26}O_2N_6$, m. p. 315° and 290°, respectively, with acetone and pyridine. *Acetylanhydrotris-o-aminobenzaldehyde* is converted by phenylhydrazine in boiling acetic acid solution into unimolecular *o-acetamidobenzaldehydephenylhydrazone*, m. p. 182°, also prepared from *o*-acetamidobenzaldehyde and phenylhydrazine in boiling alcohol. In cold acetic acid solution, acetylanhydrotris-*o*-aminobenzaldehyde affords the *phenylhydrazone*, $C_{31}H_{25}ON_5$, m. p. 280—281°. *o-Aminobenzaldehydephenylhydrazone* has m. p. 227—229°. The colour of a solution of anhydrotris-*o*-aminobenzaldehyde in concentrated hydrochloric acid indicates that it is present in the termolecular form; nevertheless, when diazotised and coupled with acetoacetanilide, it affords unimolecular *o-aldehydobenzeneazoacetoacetanilide*, m. p. 183°.

o-Aminobenzaldehyde is converted by hydrochloric and sulphuric acids, respectively, into the red *salts*, $C_{35}H_{24}O_3N_5Cl_3$ and $C_{28}H_{22}ON_4,2H_2SO_4$, from which pyridine liberates *anhydrotetrakis-o-aminobenzaldehyde*, $NH_2\cdot[C_6H_4\cdot CH{:}N]_3\cdot C_6H_4\cdot CHO$, m. p. 235—237° (*acetyl* derivative, m. p. 263—265°). Attempts to establish the presence of the aldehydo-group by the action of amines are rendered uncertain, since *p*-nitroaniline yields a stable additive *compound*, $C_{34}H_{28}O_3N_6$, m. p. 295°, and 2 : 4-dinitroaniline gives an ill-defined *substance*, $C_{62}H_{45}O_4N_{11}$, m. p. 220—240°. On the other hand, benzoylhydrazine in pyridine gives a well-defined *benzoylhydrazone*, m. p. 243—245°. With hydrazine hydrate, *oo'*-diaminobenzaldazine is produced. Anhydrotetrakis-*o*-aminobenzaldehyde is converted by gaseous hydrogen chloride into the *dihydrochloride*, whereas the acetylated base affords a *monohydrochloride*. *o-Aminobenzaldehyde-2 : 4-dinitrophenylhydrazone hydrochloride*, m. p. 245° after darkening at 200°, is converted by 80% alcohol into *o-aminobenzaldehyde-2 : 4-dinitrophenylhydrazone*, m.p. 250°, which is also prepared from anhydrotetrakis-*o*-aminobenzaldehyde. H. WREN.

Action of hydrazines on semicarbazones. II. W. BAIRD and F. J. WILSON (J.C.S., 1926, 2367—2376).—Ketonic semicarbazones react with phenylhydrazine in two ways, yielding either (1) a δ-anilinosemicarbazone, or (2) a phenylhydrazone and semicarbazide (or its decomposition product, hydrazodicarbonamide) (cf. A., 1925, i, 42). It is now found that the semicarbazones of acetaldehyde, furfuraldehyde, benzaldehyde, anisaldehyde, cinnamaldehyde, and piperonal react almost exclusively according to (2), whereas *n*-heptaldehydesemicarbazone reacts in both ways, the yield of *n-heptaldehyde-δ-anilinosemicarbazone*, m. p. 176°, being 8%. The behaviour of the ketonic semicarbazones studied varied with the mol. wt. and position of the substituting groups of both the ketonic semicarbazone and of the reacting hydrazine, the effects of which are discussed. The approximate percentage yields of δ-anilinosemicarbazone, indicating the extent to which reaction (1) takes place, and the m. p. of the *δ-anilinosemicarbazone*, are appended after the name of the ketone concerned. With phenylhydrazine: acetone (5), methyl ethyl ketone (0), methyl *n*-propyl ketone (0), diethyl ketone (2), m. p. 141°; methyl *tert.*-butyl ketone (60), m. p. 179°; di-*n*-propyl ketone (13), m. p. 152°; di*iso*propyl ketone (90), m. p. 181°; *cyclo*hexanone (12), m. p. 192°; 1-methyl*cyclo*hexan-2-one (10), m. p. 182—183°; benzophenone (95); acetophenone (95); methyl benzyl ketone (13), m. p. 181—182°; benzylacetone (8), m. p. 162°; dibenzyl ketone (90), m. p. 205°; with α-methyl-α-phenylhydrazine: acetophenone [(85), *δ-methylanilinosemicarbazone*, m. p. 196°], acetone [(52), *δ-methylanilinosemicarbazone*, m. p. 194°], benzylacetone [(65), *δ-methylanilinosemicarbazone*, m. p. 113°], *n*-heptaldehyde (0); with *p*-tolylhydrazine: acetone [(9), *δ-p-toluidinosemicarbazone*, m. p. 175—176°], benzylacetone (0); with αα-diphenylhydrazine: acetone [(80), *δ-diphenylaminosemicarbazone*, m. p. 186—187°], acetophenone [(90), *δ-diphenylaminosemicarbazone*, m. p. 236—237° (decomp.)]; with α-carbethoxy-α-phenylhydrazine: acetophenone [*δ-carbethoxyanilinosemicarbazone*, m. p. 192°]. Acetophenone-δ-carbethoxyanilinosemicarbazone is hydrolysed by hydrochloric acid to *δ-carbethoxyanilinosemicarbazide hydrochloride*, m. p. 190° [*benzylidene* derivative, m. p. 158° (decomp.)], which is further hydrolysed by 50% sulphuric acid to hydrazine and phenylhydrazine. Acetophenone-δ-diphenylaminosemicarbazone is hydrolysed by hydrochloric acid to *δ-diphenylaminosemicarbazide hydrochloride* [*benzylidene* derivative, m. p. 235—236° (decomp.)]. 1-Methyl*cyclo*hexan-2-onephenylhydrazone, contrary to the statement of Plancher (A., 1900, i, 562), is a solid, m. p. 45—46°; *benzylacetone-p-tolylhydrazone* has m. p. 74—78°. Acetophenone-δ-anilinosemicarbazone, when thermally decomposed, yields acetophenonephenylhydrazone, phenyl methyl ketazine, and 1-aminourazole, m. p. 273—274°, whilst benzophenone-δ-anilinosemicarbazone gives, according to the conditions, benzophenonephenylhydrazone and a *compound*, m. p. 213°, or benzophenonecarbohydrazone, m. p. 223—225°, with perhaps some diphenylcarbohydrazide. When an equimolecular mixture of diphenylcarbohydrazide and benzophenonecarbohydrazone is heated at 185°, benzophenonephenylhydrazone and, apparently, 1-aminourazole are formed. J. H. S. DAVIES.

Isomerism of oximes. XXVI. Methyl ethers of aldoximes. O. L. BRADY, F. P. DUNN, and R. F. GOLDSTEIN (J.C.S., 1926, 2386—2403).—*N*-Methyl ethers are the sole products of the action of β-methylhydroxylamine on aldehydes, and of methyl sulphate (giving the corresponding methosulphates) and methyl iodide (giving the corresponding hydriodides) alone on α-aldoximes; they are the main products, together with β-*O*-methyl ethers, of

the action of methyl sulphate on β-aldoximes in sodium hydroxide solution, and are the lesser products, together with α-*O*-ethers, of the action of methyl sulphate on α-aldoximes in sodium hydroxide solution, and of methyl iodide on α-aldoximes in the presence of sodium methoxide and a hydrolytic solvent, and of methyl iodide and silver oxide on aldoximes. In no case was there any evidence of the formation of the second *N*-ether demanded by theory from unsymmetrical oximes. The formation of *N*-ethers in considerable quantities during the methylation of α-oximes in alkaline solution precludes the possibility that the α-oximes are equilibrium mixtures of the two isomerides (cf. Cameron, A., 1899, ii, 411), and it appears that the quantity formed bears an inverse ratio to the degree of dissociation of the sodium salt of the oxime (see following abstract). The β-*O*-methyl ethers are best prepared by boiling the β-oxime with methyl iodide, ether, and dry silver oxide. The preparation of β-*O*-methyl-*m*-nitro-*p*-methoxybenzaldoxime by this method is the third case of the definite characterisation of both *O*-methyl ethers of an aldoxime. The preparation of the following compounds by the various methods is described: N-*methyl*-3 : 4-*methylenedioxybenzaldoxime*, m. p. 108° [*hydrochloride*, m. p. 176—180° (decomp.); *monohydrate*, m. p. 77°; methosulphate, m. p. 97—100°]; *N*-methylbenzaldoxime, m. p. 82° [*hydrochloride*, m. p. 131—136° (decomp. 171°); *methosulphate*, m. p. 60—63°]; *N*-methyl-*p*-nitrobenzaldoxime, m. p. 208° [*hydrochloride*, m. p. 133—135° (decomp.); *methosulphate*, m. p. 85—91°]; N-*methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime*, m. p. 210° (decomp.) [*hydrochloride*, m. p. 173—175° (decomp.)]; N-*methyl*-3 : 4-*dimethoxybenzaldoxime*, m. p. 127°; N-*methyl*-o-*methoxybenzaldoxime*, m. p. 85° [*hydrochloride*, m. p. 70—100° (decomp. 151°); *polyhydrate*, m. p. 27—28°; *hydriodide*, m. p. 142° (decomp.)]; N-*methyl*-p-*chlorobenzaldoxime*, m. p. 128°; *N*-methyl-*o*-nitrobenzaldoxime, m. p. 92° (*hydrochloride*, m. p. 125—134°; *methosulphate*, m. p. 99—107°); *N*-methyl-*m*-nitrobenzaldoxime, m. p. 118—119° [*hydrochloride*, m. p. 172—177° (decomp.); *methosulphate*, m. p. 58—60°]; *N*-methylanisaldoxime, m. p. 76° [*hydrochloride*, m. p. 175—179° (decomp.); monohydrate, m. p. 45°; *methosulphate*, m. p. 89—90°; *hydriodide*, m. p. 145°; $(OMe\cdot C_6H_4\cdot CH{:}NMeO)_2,HI$, m. p. 160°]; N-*methylcinnamaldoxime*, m. p. 87° (*hydriodide*, m. p. 71—79°); N-*methyl*-2 : 4-*dinitrobenzaldoxime*, m. p. 136°. No appreciable reaction occurs between methyl iodide and α-*m*-nitro-, -*p*-nitro-, and -3 : 4-methylenedioxy-benzaldoximes in 3 months. α-O-*Methyl*-o-*methoxybenzaldoxime*, b. p. 241°/761 mm., 138—139°/25 mm.; α-O-*methyl*-p-*chlorobenzaldoxime*, m. p. 28°; α-O-*methyl*-3 : 4-*methylenedioxybenzaldoxime*, m. p. 37°; α-O-*methyl*-6-*nitro*-3 : 4-*methylenedioxybenzaldoxime*, m. p. 147°; β-O-*methyl*-3-*nitroanisaldoxime*, m. p. 135°, were also prepared. The last compound, on treatment with hydrogen chloride in ether, is completely converted into the α-*O*-methyl ether. Boiling 2*N*-sodium hydroxide has no appreciable action on the *O*-methyl ethers, whilst the *N*-ethers of benzaldoxime and anisaldoxime are decomposed into the aldehyde and β-methylhydroxylamine. J. S. H. Davies.

Isomerism of oximes. XXVII. Mechanism of methylation of aldoximes. O. L. Brady and R. F. Goldstein (J.C.S., 1926, 2403—2411; see preceding abstract).—The relative amounts of *O*- and *N*-ethers formed by methylating a number of α-aldoximes under a variety of conditions have been determined by treating the mixture with hydrochloric acid. The *O*-ethers remain unchanged, whilst the *N*-ethers are hydrolysed to the aldehyde and β-methylhydroxylamine hydrochloride, which is determined by a specially devised iodometric method. The relative amount of *O*-ether formed is proportional to the degree of ionisation of the sodium salt of the oxime. Three simultaneous bimolecular reactions take place, viz., a reaction between the ion from the sodium salt and the alkyl iodide or sulphate giving the *O*-ether, metathesis between the sodium salt and the alkyl compound to give again the *O*-ether, and a molecular reaction between the undissociated sodium salt and the alkyl compound, involving addition of the latter, giving the *N*-ether.

J. S. H. Davies.

Isomerism of oximes. XXVIII. Beckmann rearrangement of *N*-methyl ethers of aldoximes. O. L. Brady and F. P. Dunn (J.C.S., 1926, 2411—2416).—*N*-Methyl ethers of the aldoximes yield the corresponding methylamides on warming with acetic anhydride; *N*-methylanisaldoxime gives the acetomethylamide at once, whilst if the solution is boiled for some time the acetomethylamides are formed in other cases. These results are not explained by the theories of the Beckmann rearrangement involving the elimination of water and the formation of a univalent nitrogen compound, but they afford an indication of the configuration of the *N*-ethers, which appear to be similar in constitution to the β-aldoximes. The following compounds have been prepared in the manner indicated: *p*-nitrobenzomethylamide, m. p. 217° (*acetyl* derivative, m. p. 125°); o-*nitro*-isomeride, m. p. 107° (also from *o*-nitrobenzoyl chloride and methylamine); *m*-nitro-isomeride; benzomethylamide, m. p. 78°; 3 : 4-*methylenedioxybenzomethylamide*, m. p. 136° (also from ethyl 3 : 4-methylenedioxybenzoate and methylamine); cinnamomethylamide, m. p. 111° (similarly from ethyl cimamate); *anisomethylamide*, m. p. 116° (from anisoyl chloride and methylamine; *acetyl* derivative, m. p. 50°). *N*-Methyl-*o*-methoxybenzaldoxime gave an oil which was decomposed by boiling alcoholic potassium hydroxide into methylamine and *o*-methoxybenzoic acid. *O*-Methyl-*m*-nitrobenzaldoxime is unaffected by boiling with acetic anhydride for 2 hrs. The hydrochloride of *N*-methyl-*m*-nitrobenzaldoxime is converted into *m*-nitrobenzomethylamide when heated at 168—170°. J. S. H. Davies.

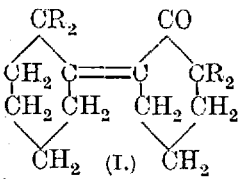
Odour and molecular asymmetry. III. J. von Braun and W. Haensel (Ber., 1926, 59, [*B*], 1999—2011; cf. A., 1924, i, 3; this vol., 65).—An instance of difference in odour between two inactive compounds containing two similar asymmetric carbon atoms and belonging, respectively, to the racemic and meso series is recorded; both compounds are derived from the same source. Technical *s*-*m*-xylenol is purified sufficiently to permit hydrogenation through

its acetate, b. p. 115—117°/14 mm. It is converted by aluminium into the corresponding *di*-m-5-*xylyl ether*, b. p. 181°/14 mm., m. p. 60—61° (*tetranitro*-derivative, m. p. 206°). Catalytic hydrogenation of *s*-*m*-xylenol in the presence of nickel leads to a mixture of unchanged material, *cis*- and *trans*-3 : 5-dimethyl*cyclo*hexanol, and *cis*- and *trans*-3 : 5-dimethyl*cyclo*hexanone. 3 : 5-*Dimethyl*cyclo*hexyl chloride*, b. p. 60°/14 mm., d_4^{15} 0·9499, 3 : 5-*dimethyl*cyclo*hexyl bromide*, b. p. 82°/14 mm., d_4^{15} 1·2155, and 3 : 5-*dimethyl*cyclo*hexyl hydrogen phthalate*, m. p. 94—97°, are prepared from the mixture of alcohols. The product, m. p. 38°, which crystallises from the mixed alcohols is identified as 3^c : 5^c-dimethyl*cyclo*hexanol. Oxidation of the mixture of alcohols with Beckmann's mixtures gives the corresponding ketones, converted by phenylhydrazine into *dimethyltetrahydrocarbazole*, m. p. 96—99°, which is dehydrogenated by lead oxide at 350° to *dimethylcarbazole*, m. p. 124—126° (*nitroso*-derivative, m. p. about 135°). Oxidation of 3 : 5-dimethyl*cyclo*hexanone with nitric acid yields methylsuccinic acid and a non-crystalline mixture of (presumably) the four stereoisomeric forms of αβ′-dimethyladipic acid (thence an *ethyl* ester, b. p. 131—132°/14 mm., d_4^{15} 0·9900; *chloride*, b. p. 127—131°/14 mm., d_4^{15} 1·1730; *amide*, m. p. 153—159°, and *dihydrazide*, m. p. 139—142°, from which *αε-diamino-β-methylpentane dihydrochloride*, m. p. 155—172°, is derived). Chlorination of the ketone in the presence of calcium carbonate and water affords 2-*chloro*-3 : 5-*dimethyl*cyclo*hexanone*, b. p. 123—124°/14 mm., d^{15} 1·1472. The mixture of ketones is converted by hydroxylamine hydrochloride and alkali in cold, aqueous-alcoholic solution into the readily separable 3^c : 5^c-dimethyl*cyclo*hexanoneoxime, m. p. 72° (*benzoyl* derivative, m. p. 79°), and non-crystalline 3^c : 5^t-*dimethyl*cyclo*hexanoneoxime*, an oil (non-crystalline *benzoyl* derivative). trans-3 : 5-*Dimethyl*cyclo*hexanone* has b. p. 180—181°, d_4^{15} 0·9032, n_D^{21} 1·4475 (*semicarbazone*, m. p. 193—194°; *tetrahydrocarbazole* derivative, m. p. 85—86°); the αβ′-dimethyladipic acid derived from it has b. p. 208—212°/14 mm. Reduction of the *trans*-oxime with sodium and alcohol gives 3 : 5-*dimethyl*cyclo*hexylamine*, b. p. 167—168° (*hydrochloride*, m. p. 198—200°; *picrate*, m. p. 195—197°; non-crystalline *acetyl* derivative; *benzoyl* derivative, m. p. 140—142°), the *trans* nature of which is established by its fission into optical antipodes by means of *d*-tartaric acid. cis-3 : 5-*Dimethyl*cyclo*hexanone* has b. p. 182—183°, d_4^{15} 0·8942, n_D^{15} 1·4407 (*semicarbazone*, m. p. 202—203°; *tetrahydrocarbazole* derivative, m. p. 105—106°). Oxidation of the ketone yields methylsuccinic acid and *αβ′-dimethyladipic acid*, m. p. 63—64°. Reduction of the oxime affords cis-3 : 5-*dimethyl*cyclo*hexylamine*, b. p. 168° (*hydrochloride*, m. p. 230°; *picrate*, m. p. 195—197°; *acetyl* derivative, m. p. 132°; *benzoyl* compound, m. p. 154°). The base could not be resolved into its antipodes by *d*-tartaric acid. The *cis*- and *trans*-3 : 5-dimethyl*cyclo*hexanones have distinctly different odours. H. WREN.

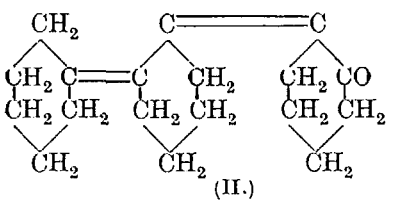
Carbon rings. VII. Constitution of muscone. L. RUZICKA (Helv. Chim. Acta, 1926, **9**, 715—729).—Muscone isolated from musk by the method of Walbaum (A., 1906, i, 595) contains 10% of similarly boiling substances with physical constants approximating to those of muscone, and in order to obtain the pure ketone, d_4^{15} 0·9237, n_D^{15} 1·4811, α_D −12·0°, it must be regenerated from its purified semicarbazone, m. p. 134°. The pure ketone has the composition $C_{16}H_{30}O$ and is identical in odour with *cyclo*pentadecanone and its methyl derivatives (cf. Ruzicka, Stoll, and Schinz, this vol., 615). The optical activity of muscone persists after treatment with hydrochloric acid in a sealed tube, on regeneration of the ketone from its sodium derivative prepared by the action of sodamide, on reduction with sodium and boiling alcohol to *muscol*, m. p. 35°, b. p. 140°/1 mm., α_D +14·9°, and dehydration of this to the hydrocarbon, *muscene*, b. p. 120°/1 mm., α_D −8·8°, and hence the asymmetric carbon atom cannot be adjacent to the carbonyl group. Oxidation of muscone with chromic acid yields a mixture of (?) two dicarboxylic acids, $C_{16}H_{30}O_4$, which could not be separated, together with succinic, adipic, suberic, sebacic, and decane-ακ-dicarboxylic acid. Since the m. p. of muscone-semicarbazone is depressed by mixing with 3-methyl-*cyclo*pentadecanonesemicarbazone (m. p. 164—165°), muscone must be either 2- or 4-methyl*cyclo*pentadecanone. J. W. BAKER.

Condensation of mesityl oxide with aliphatic ketones. J. B. EKELEY and M. S. CARPENTER (J. Amer. Chem. Soc., 1926, **48**, 2375—2378).—Mesityl oxide was condensed with a series of aliphatic ketones in presence of sodium ethoxide, sodium methoxide, sodamide, barium hydroxide, diethylamine, and piperidine under varying conditions of time, temperature, illumination, and solution. In each case, only one and the same of the possible isomeric condensation products was obtained. Unsaturated *ketones* were obtained from mesityl oxide and the following ketones: from methyl ethyl ketone, $C_{10}H_{16}O$, b. p. 99·5—100°/4·5 mm., d_4^{20} 0·92811, n_D^{20} 1·5048 (*semicarbazone*, m. p. 176°); from methyl propyl ketone, $C_{11}H_{18}O$, b. p. 122—126°/13 mm., d_4^{20} 0·92372, n_D^{20} 1·5112 (*semicarbazone*, m. p. 172°); from diethyl ketone, $C_{11}H_{18}O$, b. p. 102—105°/4 mm., d_4^{20} 0·93062, n_D^{20} 1·5218 (*semicarbazone*, m. p. 170°); from methyl butyl ketone, $C_{12}H_{20}O$, b. p. 119—121°/11 mm., d_4^{20} 0·92004, n_D^{20} 1·5130 (*semicarbazone*, m. p. 172°); and from methyl *iso*butyl ketone, $C_{12}H_{20}O$, b. p. 101—104°/3 mm., d_4^{20} 0·92616, n_D^{20} 1·5222 (*semicarbazone*, m. p. 170°). F. G. WILLSON.

***cyclo*Hexylidene*cyclo*hexanone.** K. KUNZE (Ber., 1926, **59**, [*B*], 2085—2088).—The probability that *cyclo*hexylidene*cyclo*hexanone has the constitution (I) (R=H) is strengthened by the observation that it condenses with aldehydes in aqueous-alcoholic solution in the presence of sodium hydroxide, giving *dibenzylidene*cyclo*hexylidene*cyclo*hexanone* (R_2=:CHPh), m. p. 173—174° (corr. decomp.), and *dianisylidene*cyclo*hexylidene*cyclo*hexanone* (R_2=:CH·C_6H_4·OMe), m. p. 152—153° (corr.). *cyclo*Hexylidene*cyclo*hexanone hydrochloride,


(I.)

m. p. 42—43°, and the corresponding *hydrobromide*, m. p. 40—41°, are described. *cyclo*Hexylidene-*cyclo*hexanone and ethyl alcohol in the presence of alkali give the *compound*, $C_{12}H_{18}O$,EtOH, m. p. 160° The observation that bis*cyclo*hexylidene*cyclo*-hexanone is converted by alcoholic alkali hydroxide into dodecahydrotriphenylene is most readily explained by assigning to it the constitution (II), which also accounts for the production of dodecahydrotriphenylene from *cyclo*hexylidene*cyclo*-hexanone and *cyclo*hexanone. H. WREN.



(II.)

Compounds of *cyclo*hexanone with benzaldehyde. D. VORLÄNDER and K. KUNZE (Ber., 1926, 59, [*B*], 2078—2085).—Benzaldehyde (1 mol.) and *cyclo*hexanone (2 mols. or excess) give benzylidene-*cyclo*hexanone (Wallach, A., 1907, i, 220) in presence of 0·36% aqueous alkali hydroxide, 2-α-*hydroxybenzyl*cyclo*hexanone*, m. p. 101—102° [*acetate*, m. p. 70·4—71·1° (corr.)], in presence of 0·1% aqueous alkali hydroxide, and dibenzylidene*cyclo*hexanone (cf. Wallach, *loc. cit.*) in alcoholic or aqueous-alcoholic alkali hydroxide. The latter substance is also obtained under similar conditions from equimolecular proportions of the components. Benzaldehyde (2 mols.) and *cyclo*hexanone (1 mol.) afford 2 : 6-*bis*-α-*hydroxybenzyl*cyclo*hexanone* or dibenzylidene*cyclo*-hexanone, respectively, in presence of 0·38% aqueous or alcoholic alkali hydroxide. Equimolecular proportions of benzaldehyde and benzylidene*cyclo*-hexanone, in presence of 1% aqueous or alcoholic alkali hydroxide, give 2-α-*hydroxybenzyl*-6-*benzylidene*cyclo*hexanone*, m. p. 102—103° (corr.), or dibenzylidene*cyclo*hexanone. 2 : 6-Bis-α-hydroxybenzyl*cyclo*hexanone and dibenzylidene*cyclo*hexanone are derived from 2-α-hydroxybenzyl*cyclo*hexanone in aqueous (0·35%) or alcoholic alkali hydroxide. 2 : 2-Hydroxybenzyl*cyclo*hexanone (1 mol.) and *cyclo*-hexanone (1 mol.), in presence of 0·38% aqueous alkali hydroxide, give benzylidene*cyclo*hexanone. 2-α-Hydroxybenzyl-6-benzylidene*cyclo*hexanone is not affected by 0·38% aqueous alkali hydroxide, but is transformed by alcoholic alkali hydroxide or acetic anhydride into dibenzylidene*cyclo*hexanone. 2 : 6-Bis-α-hydroxybenzyl*cyclo*hexanone is unchanged by aqueous alkali hydroxide, but converted into dibenzylidene*cyclo*hexanone by alcoholic alkali hydroxide. The detection of cyclic ketones or aldehydes as their dibenzylidene compounds must be effected, therefore, by condensation in methyl- or ethyl-alcoholic solution.

2-Benzylidene*cyclo*hexanone and ethyl sodiomalonate give the normal adduct, from which the *diamide*, $C_{16}H_{20}O_3N_2$, m. p. 169—170°, is obtained by means of ammonia. Hydrolysis of the ester gives the dibasic *acid*, $C_{16}H_{18}O_5$, m. p. 137—139° (corr.; decomp.), which by loss of carbon dioxide, passes into β-*phenyl*-β-2-*keto*cyclo*hexylpropionic acid*, m. p. 127—128° (corr.) [*anhydride*, m. p. 124—125°; *methyl* ester, m. p. 96—97° (corr.); *ethyl* ester, m. p. 74—75° (corr.)]. H. WREN.

Fission of methoxylated benzophenones. T. R. LEA and R. ROBINSON (J.C.S., 1926, 2351—2355).—The prediction by the electronic theory previously propounded (this vol., 397) that in the fission of methoxybenzophenones, the linking between *p*-methoxyphenyl and carbonyl would be less readily disrupted than that between phenyl and carbonyl, and that this in its turn would be more stable than the linking between *m*-methoxyphenyl and carbonyl has been found to be true in the main, although the behaviour of benzoyl*cyclo*propane (A., 1922, i, 350) is unexpected. Thus, by fission with sodamide, followed by hydrolysis of the resulting mixture of amides to the corresponding carboxylic acids, the following percentage fissions of the linkings connecting the respective groups to carbonyl have been found: Ph—$^{67\cdot1}$—CO—$^{32\cdot9}$—C_6H_4·OMe (*p*); Ph—$^{13\cdot6}$—CO—$^{82\cdot0}$—C_6H_4·OMe (*m*); (*m*) MeO·C_6H_4—$^{86\cdot4}$—CO—$^{13\cdot6}$—C_6H_4·OMe (*p*); Ph—$^{35\cdot6}$—CO—$^{64\cdot4}$—$C_6H_3(OMe)_2$ (*m*, *p*); (*m*) MeO·C_6H_4—$^{54\cdot1}$—CO—$^{45\cdot9}$—$C_6H_4(OMe)_2$ (*m*, *p*); (*p*) MeO·C_6H_4—$^{23\cdot1}$—CO—$^{76\cdot9}$—$C_6H_3(OMe)_2$ (*m*, *p*). 2-Methoxy-, 2 : 4- and 2 : 5-dimethoxy-benzophenone gave in each case almost pure benzoic acid, 4-cyanobenzophenone gave only 4-benzoylbenzoic acid. 3-Methoxybenzophenone is best obtained by oxidising *m*-methoxydiphenylcarbinol with sodium dichromate and sulphuric acid; 3 : 4′-*dimethoxybenzophenone*, m. p. 55°, is obtained by the action of aluminium chloride on a mixture of *m*-methoxybenzoyl chloride and anisole in carbon disulphide; 3 : 4 : 3′-*trimethoxybenzophenone*, m. p. 83—84° (*oxime*, m. p. 128°), is prepared similarly from veratrole.

J. S. H. DAVIES.

Condensation of benzyl methyl ketone with salicylaldehyde. R. DICKINSON (J.C.S., 1926, 2234—2241).—In the presence of piperidine or diethylamine the condensation furnishes *o-hydroxystyryl benzyl ketone*, m. p. 181° (*semicarbazone*, m. p. 205—206°; *carbomethoxy*-derivative, m. p. 64—65°; *methyl ether*, m. p. 79°). When, however, benzyl methyl ketone and salicylaldehyde are converted in the presence of aqueous-alcoholic alkali under stated conditions, a mixture of five isomerides, *A*, m. p. 185° (decomp.), *B*, m. p. 228° (decomp.), *C*, m. p. 186°, *D* (+1 mol. of benzene), m. p. 209° (decomp.), and *E*, m. p. 239° (decomp.), each having the empirical formula $C_{41}H_{36}O_4$, is produced. *E*, which probably contains two phenolic hydroxyl groups, differs from the rest in being soluble in cold aqueous alkali, and is reprecipitated unchanged on acidification. The interrelationships are shown by the scheme: $A \xrightarrow{\text{alkali}} B \xrightarrow{\text{acid}} D \xrightarrow{\text{alkali}} C$. These are probably stereoisomerides derived from the unisolated αγε-triphenylacetyl-βδ-di-*o*-hydroxyphenylpentane, $CH_2Ph{\cdot}CO{\cdot}CH[CH(C_6H_4{\cdot}OH){\cdot}CH_2{\cdot}CO{\cdot}CH_2Ph]_2$ by loss of 1 mol. of water, giving rise probably to pyran derivatives, for *A* readily yields a *disemicarbazone*, m. p. 230° (decomp., impure). The possible structural formulæ are discussed. The *dimethyl ethers* of *A* and *B* are identical, and melt at 135°; that of *D* melts at 138°. α-*Phenyl*-*o*-*methoxystyryl methyl ketone*, m. p. 145°, is obtained from *o*-methoxybenzaldehyde and benzyl methyl ketone in presence of hydrogen chloride.

J. S. H. DAVIES.

Pungent principles of ginger. III. Constitution of shogaol. H. NOMURA and S. TSURUMI (Proc. Imp. Acad. Tokyo, 1926, 2, 229—232; cf. J.C.S., 1917, **111**, 769, 777, 790; A., 1918, i, 446).—Three homologues of zingerone have been prepared, and that containing a *n*-heptyl radical is found to be identical with dihydroshogaol. 4-*Hydroxy*-3-*methoxystyryl* n-*hexyl ketone*, m. p. 49°, is reduced to 4-*hydroxy*-3-*methoxyphenylethyl* n-*hexyl ketone*, an oil (*benzoyl* derivative, m. p. 75°, *methyl ether* yielding an *oxime*, m. p. 89°, and a *semicarbazone*, m. p. 97·5—99°). 4-*Hydroxy*-3-*methoxystyryl* n-*heptyl ketone*, m. p. 43° (the *benzoyl* derivative, m. p. 72·5°, is not identical with that of shogaol), is reduced to 4-*hydroxy*-3-*methoxyphenylethyl* n-*heptyl ketone*, m. p. 31° (the *benzoyl* derivative, m. p. 64°, being identical with that of dihydroshogaol: *methyl ether* with *oxime*, m. p. 80·5°, and *semicarbazone*, m. p. 83·5°, described). 4-*Hydroxy*-3-*methoxystyryl* n-*octyl ketone*, m. p. 46° (*benzoyl* derivative, m. p. 78·5°), is reduced to 4-*hydroxy*-3-*methoxyphenylethyl* n-*octyl ketone*, m. p. 36·5° (*benzoyl* derivative, m. p. 46°; *methyl ether* yielding an *oxime*, m. p. 80°, and *semicarbazone*, m. p. 87·5°). Zingerone and *n*-heptaldehyde condense to yield α-(4-*hydroxy*-3-*methoxyphenyl*)-Δ^{δ}-*undecen*-γ-*one*, b. p. 227—229°/7·5 mm., d_4^{25} 1·0299, n_D^{25} 1·52317. From these observations, shogaol should be the corresponding α-(4-hydroxy-3-methoxyphenyl)-Δ^{δ}-decen-γ-one.

G. M. BENNETT.

Hydrolytic fission of substituted dibenzoylmethanes. W. BRADLEY and R. ROBINSON (J.C.S., 1926, 2356—2367).—Although the determination of the number of mols. of $R{\cdot}CO_2H$ and $R'{\cdot}CO_2H$, respectively, derived from 100 mols. of various diketones, $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R'$, by hydrolysis with 1% aqueous sodium hydroxide indicates that there is a definite tendency to produce in relatively greater amounts the stronger of the two acids which may be formed, the effect of substituents cannot be so simply accounted for. The effect of various factors on the probable mechanism of the reaction is discussed.

ω-*p*-Anisoylacetophenone, m. p. 132° [hydrolytic fission: (*p*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 50·2 : 49·8], is obtained by condensation of ethyl anisate with acetophenone or of ethyl benzoate with *p*-acetylanisole in presence of sodamide. The copper derivative has m. p. 241° (Pond and Maxwell, A., 1900, i, 102, give m. p. 247—249°); *phenylanisyldiveratrocopyrine* (*hydrochloride* and *acetate* described), formed by condensing the diketone with diaminoveratrone, has m. p. 352° (decomp.). The following compounds are prepared by the same general methods: ω-*o*-*anisoylacetophenone*, m. p. 65° [hydrolytic fission: (*o*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 82·1 : 17·9], from ethyl *o*-anisate and acetophenone, *copper* derivative, m. p. 196—197°; *phenyl*-o-*anisyldiveratrocopyrine*, m. p. 308° (*hydrochloride* and *acetate* described); ω-*m*-*anisoylacetophenone*, m. p. 59·5°, b. p. 157—159°/18 mm. [hydrolytic fission: (*m*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 61·9 : 38·1], *copper* derivative, m. p. 215°; *phenyl*-m-*anisyldiveratrocopyrine*, m. p. 315°; α-p-*anisoylpropiophenone*, m. p. 56·5° [hydrolytic fission: (*p*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 61·1 : 38·9], from ethyl benzoate and *p*-methoxypropiophenone, b. p. 178—180°/46 mm., but not from ethyl anisate and propiophenone, *copper* derivative, m. p. 218°; no copyrine derivative; ω-p-iso*propoxybenzoylacetophenone*, m. p. 73° (hydrolytic fission: (*p*) $Pr^{\beta}O{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 33·0 : 67·0), best from *p*-*iso*propoxyacetophenone (below) and ethyl benzoate, *copper* derivative, m. p. 228°; p-iso*propoxydiphenyldiveratrocopyrine*, m. p. >355° (*hydrochloride* described); ω-m-*chlorobenzoylacetophenone*, m. p. 70° [hydrolytic fission: (*m*) $Cl{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 66·4 : 33·6], from ethyl *m*-chlorobenzoate and acetophenone, *copper* derivative, m. p. 254°; m-*chlorodiphenyldiveratrocopyrine*, m. p. >355° (*hydrochloride* described); ω-*p*-chlorobenzoylacetophenone, m. p. 89° [hydrolytic fission: (*p*) $Cl{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 63·7 : 36·3], similarly from ethyl *p*-chlorobenzoate, b. p. 236—238°, *copper* derivative, m. p. 271°; *p*-chlorodiphenyldiveratrocopyrine, m. p. >370°; ω-*m*-nitrobenzoylacetophenone [hydrolytic fission: (*m*) $NO_2{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 82·3 : 17·7], *copper* derivative, m. p. 298°; m-*nitrodiphenyldiveratrocopyrine*, m. p. 324° (*hydrochloride* described); ω-*p*-nitrobenzoylacetophenone [hydrolytic fission: (*p*) $NO_2{\cdot}C_6H_4{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 80·7 : 19·3] in poor yield from ethyl *p*-nitrobenzoate and acetophenone, better by using Wieland's method (A., 1904, i, 432), *copper* derivative, m. p. 305°; p-*nitrodiphenyldiveratrocopyrine*, m. p. >355° (*hydrochloride* described); ω-2 : 4-dimethoxybenzoylacetophenone [hydrolytic fission: (*o*, *p*) $(MeO)_2{\cdot}C_6H_3{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 74·7 : 25·3], *copper* derivative, m. p. 193°; 2 : 4-*dimethoxydiphenyldiveratrocopyrine*, m. p. 296°; ω-veratroylacetophenone [hydrolytic fission: (*m*, *p*) $(MeO)_2{\cdot}C_6H_3{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 50·8 : 49·2]; *phenylveratryldiveratrocopyrine*, m. p. 289° (*hydrochloride* described); ω-m-*methoxybenzoyl*-p-*methoxyacetophenone*, m. p. 91° [hydrolytic fission: (*m*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: (*p*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$ = 79·0 : 21·0], from ethyl *m*-methoxybenzoate and *p*-acetylanisole, *copper* derivative, m. p. 218°; m-*anisyl*-p-*anisyldiveratrocopyrine*, m. p. 290—293° (*acetate* described); 3 : 4 : 5-*trimethoxybenzoylacetophenone*, m. p. 97° [hydrolytic fission: (*m*, *m*, *p*) $(MeO)_3{\cdot}C_6H_2{\cdot}CO_2H$: $Ph{\cdot}CO_2H$ = 68·8 : 31·2], from ethyl 3 : 4 : 5-trimethoxybenzoate and acetophenone, *copper* derivative, m. p. 254°; 3 : 4 : 5-*trimethoxydiphenyldiveratrocopyrine*, m. p. 323° (*hydrochloride* and *acetate* described); ω-m-*methoxybenzoyl*-3 : 4-*dimethoxyacetophenone*, m. p. 78·5° [hydrolytic fission: (*m*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: (*m*, *p*) $(MeO)_2C_6H_3{\cdot}CO_2H$ = 40·1 : 59·9], from ethyl *m*-methoxybenzoate and acetoveratrone, *copper* derivative, m. p. 223°; m-*anisylveratryldiveratrocopyrine*, m. p. 301·5° (*hydrochloride* described); ω-*anisoyl*-3 : 4-*dimethoxyacetophenone*, m. p. 97° [hydrolytic fission: (*p*) $MeO{\cdot}C_6H_4{\cdot}CO_2H$: (*m*, *p*) $(MeO)_2{\cdot}C_6H_3CO_2H$ = 34·2 : 65·8], best from ethyl veratrate and *p*-acetylanisole, *copper* derivative, m. p. 238°; p-*anisylveratryldiveratrocopyrine*, m. p. 300° (*acetate* described).

p-iso*Propoxybenzoic acid*, m. p. 161° (*ethyl* ester, b. p. 279—280°), is obtained from *p*-bromophenyl *iso*propyl ether by the Grignard reaction, whilst p-iso*propoxyacetophenone*, m. p. 38—39°, b. p. 153°/26 mm., is obtained in small yield from phenyl *iso*propyl ether by condensation with acetyl chloride in presence of aluminium chloride, and, better, by the interaction of *iso*propyl bromide and the sodium

salt of *p*-hydroxyacetophenone. ω-p-*Ethoxybenzoylacetophenone*, from ethyl *p*-ethoxybenzoate and acetophenone, has m. p. 68°, whilst ω-*piperonoylacetophenone*, prepared similarly from ethyl piperonylate, melts at 85·5°, and yields a *copper* derivative, m. p. 179°, and *phenylpiperonyldiveratrocopyrine*, m. p. 328°. J. S. H. DAVIES.

Oximes of amino- and hydroxy-benzoquinones. F. KEHRMANN and M. STERCHI (Helv. Chim. Acta, 1926, **9**, 859—866).—2 : 5-Dihydroxy-*p*-benzoquinone yields a *diacetyl* derivative, m. p. 150—152°, which, in alcoholic solution with powdered hydroxylamine hydrochloride, yields the *monoacetyl* derivative of 2 : 5-dihydroxy-*p*-benzoquinonemonoxime, m. p. 115—120° (decomp.); this on hydrolysis yields 2 : 5-*dihydroxy*-p-*benzoquinonemonoxime*, decomp. 170—180° (*diacetyl* derivative, m. p. 121°), which is also obtained by the action of hydroxylamine on 5-amino-2-hydroxy-*p*-benzoquinone. 4 : 5-Diamino-*o*-benzoquinone (cf. Hoehn, A., 1925, i, 938) reacts in its *p*-quinonoid (imine) form with hydroxylamine to yield 5-*amino*-2-*hydroxy*-p-*benzoquinone*-4-*oxime*, decomp. 220° [*monoacetyl* derivative, m. p. 135° (decomp.)]. The product obtained by the oxidation of triaminoresorcinol (Schreder, A., 1871, 227), which is considered to be 2 : 6-diamino-3-hydroxy-*p*-benzoquinone-4-imine, yields, with hydroxylamine, 2 : 6-diamino-3-hydroxy-*p*-benzoquinone-4-oxime, and forms a *diacetyl* derivative, which, when kept for 12 hrs. in alkaline solution at the ordinary temperature, is converted into 2 : 6-diacetamido-3-hydroxy-*p*-benzoquinone. This, with excess of hydroxylamine, yields the corresponding *dioxime* (?), decomp. 180°. J. W. BAKER.

Catalytic rôle of mercury in sulphonation of anthraquinone. A. MEYER (Compt. rend., 1926, **183**, 519—521).—Anthraquinone-α-sulphonic acid and its salts are not converted into the β-sulphonic acid by heating with sulphuric acid except in the presence of mercury. It is suggested that the α- is transformed into the β-acid by desulphonation in the presence of the catalyst and resulphonation in the β-position. The suggestion is thus discredited that in the absence of a catalyst the α-sulphonate is first formed and this is then converted into the β-sulphonate, whilst in the presence of mercury the formation of α-sulphonate is accelerated to such an extent that the conversion of α- into β-sulphonate does not proceed in any considerable degree (cf. Martinet, A., 1921, i, 732). L. F. HEWITT.

Manufacture of condensation products and dyes of the benzanthrone series [dibenzanthronyls and *iso*dibenzanthrones]. BADISCHE ANILIN- UND SODA-FABRIK.—See B., 1926, 780.

Saponins and their relation to other plant products. A. WINDAUS (Nachr. K. Ges. Wiss. Göttingen, 1925, 45; from Chem. Zentr., 1926, I, 1814).—Gitonin, $C_{49}H_{80}O_{28}$, yields, on hydrolysis, gitogenin, $C_{26}H_{42}O_4$, 3 mols. of hexose, and 1 mol. of pentose. Digitonin, probably $C_{55}H_{90}O_{29}$, yields digitogenin, $C_{26}H_{42}O_5$, 4 mols. of hexose, and 1 mol. of pentose. The structure of gitogenin and digitogenin is discussed (cf. A., 1925, i, 1438). Digitogenin, like cholesterol, contains a side-chain broken down by energetic oxidation to α-methylglutaric acid. Oxidation of gitogenin with nitric acid yields a lactonedicarboxylic acid, $C_{22}H_{32}O_6$ (*loc. cit.*), which can be converted through the compound $C_{21}H_{30}O_3$ into a saturated hydroxylactone, $C_{21}H_{32}O_3$. This substance belongs to the same homologous series as those similarly derived from the genins of the heart-poisons. The relationship of these and of gitogenin to cholesterol is discussed. Quillaic acid yields the sapogenin, $C_{29}H_{46}O_5$, a saturated ketonic dihydroxymonocarboxylic acid, containing a saturated 5-ring system in the molecule. Relationship with the bile acids is, therefore, improbable. The compound is probably related to the stigmasterol group. M. CLARK.

Oleandrin. A. WINDAUS and K. WESTPHAL (Nachr. K. Ges. Wiss. Göttingen, 1925, 78; from Chem. Zentr., 1926, I, 1814).—Oleandrin, probably $C_{31}H_{48}O_9$, m. p. 249°, has a methoxyl content of 5·61—6·17%. It is decomposed by warm acids into digitaligenin and a non-crystallising sugar, probably digitalose. The breakdown is formulated thus: $C_{31}H_{48}O_9+H_2O \rightarrow C_{24}H_{36}O_5+C_7H_{14}O_5$; $C_{24}H_{36}O_5 \rightarrow C_{24}H_{32}O_3+2H_2O$. The glucoside is destroyed by warm alkali hydroxide. M. CLARK.

Cyclamin. O. DAFERT [with F. GUND, O. MÜLLER, and A. J. NITSCHE] (Arch. Pharm., 1926, **264**, 409—439).—In investigating cyclamin, the saponin present in cyclamen tubers, Masson (A., 1912, ii, 674) obtained results radically different from those of earlier workers (cf. *e.g.* Plzak, A., 1903, i, 643). The earlier work, however, is generally trustworthy; lack of agreement in detail is doubtless due to differences in the method of extracting the cyclamin. This operation is best carried out on peeled, air-dry or even fresh tubers; as solvent, 90% alcohol is superior to 70%, in that less colouring matter and other impurities are present in the cyclamin obtained. The extraction is controlled by hæmolytic tests (cf. Kofler and Dafert, A., 1924, ii, 74; Windaus, *ibid.*, 1909, i, 172). The dried tubers contain about 15·9% of cyclamin, and 15·5% can be extracted by treating the crushed material with fifteen times its weight of alcohol in three successive portions. The crude product, which separates on cooling and concentration (at temperatures below 60°), is crystallised from 70% alcohol, and then repeatedly from 80 to 90% alcohol. The crystalline compound, $C_{63}H_{110}O_{32}$ (*M* in phenol, about 1000), is sparingly soluble or insoluble in organic solvents with the exception of alcohol, pyridine, and acetic acid. The hæmolytic index is 1 : 640,000, m. p. 251—253°, $[\alpha]_D^{20}$ −22° (in pyridine); ash, 0·02—0·1% (this is an important criterion). The substance is not hygroscopic, as has hitherto been supposed, but it retains about 5% of moisture at the ordinary temperature. Neither is it an acid, although it dissolves in dilute potassium hydroxide; the crystals that separate from this solution are apparently unaltered cyclamin, in spite of the change in appearance. Cyclamin cannot be methylated. Some earlier observations on hydrolytic scission are not substantiated: the compound is unattacked by yeast or bacterial enzymes. When treated with hot

dilute acid, *e.g.*, 3—5% sulphuric acid, it is decomposed into cyclamiretin (cf. Plzak, *loc. cit.*, etc.), $C_{35}H_{56}O_5$ (*M* in camphor, 557·5), pentoses, chiefly *l*-arabinose (identified as such by decomposition of the diphenylhydrazone, and as the *p*-bromophenylosazone), and hexoses, chiefly or entirely dextrose. Lævulose is absent; glycuronic acid groups are likewise absent. Quantitative determinations give the following results: dextrose, 33·1%; *l*-arabinose, 21·7%; methylpentoses (probably derived from impurities), 3·1%; total reducing sugars by Allihn's method, about 52%. In isolating the cyclamiretin, it is necessary to repeat the hydrolysis several times until the solution no longer reduces Fehling's solution. The product then obtained is crystalline (from alcohol) and has m. p. 231°. It is not an acid nor, apparently, a lactone. With methyl sulphate, it yields a *dimethyl* derivative, m. p. 126°. The *dibenzoyl* derivative (m. p. 216°) and *diacetyl* derivative (m. p. 213—214°) are readily obtained in pyridine solution. The formation of these compounds indicates that two hydroxyl groups are present, whilst that of an *oxime* suggests that the molecule contains also a carbonyl group, but, although *compounds* that appear to be the semicarbazone and thiosemicarbazone, respectively, are formed, they yield on analysis anomalous results. These, however, are the only discrepancies, all other analyses agreeing with the formulæ given above, and so with the following equation for the hydrolysis: $C_{63}H_{110}O_{32}+H_2O=C_{35}H_{56}O_5+3C_6H_{12}O_6+2C_5H_{10}O_5$.

W. A. Silvester.

Menthone series. II. Optically active menthones and menthylamines. J. Read and G. J. Robertson (J.C.S., 1926, 2209—2223).—The definite, although unequal effect of 90% sulphuric acid, formic acid, hydrogen chloride, hydrochloric acid, oxalic acid, chromic acid, sodium hydroxide, sodium ethoxide, and heat on *d*- and *l*-*iso*menthone indicates the existence of the equilibrium *d*-(or *l*-)*iso*menthone $\rightleftharpoons$ *l*-(or *d*-)menthone, whilst the hydrogenation of *d*-pulegone, b. p. 96·6—97·6°/12·5 mm., n_D^{15} 1·4852, $[\alpha]_D^{15}$ +23·60°, and of *l*-Δ^4-*p*-menthen-3-one, b. p. 85—88°/11 mm., n_D^{14} 1·4765, $[\alpha]_D^{15}$ −78·36° (preparation given), gives mixtures of *d*-*iso*menthone and *l*-menthone. *d*-*iso*Menthone, possibly not quite pure, obtained by hydrogenating *l*-piperitone, $[\alpha]_D^{15}$ −53·90°, has $[\alpha]_D^{15}$+69·10°; *l*-*iso*menthone, b. p. 79—80°/7 mm., n_D^{13} 1·4580, $[\alpha]_D^{15}$ −71·41°, is obtained similarly from *d*-piperitone, b. p. 95—97°/7·5 mm., $n_D^{16·5}$ 1·4860, $[\alpha]_D^{15}$ +62·50°; *l*-menthone has $[\alpha]_D^{20}$ −29·60°.

Formyl-d-neo*menthylamine*, m. p. 117—118°, $[\alpha]_D^{15}$ +53·8° (crystallographic data given) (*hydrochloride*, m. p. 75—80°), obtained from *l*-menthone, or preferably from "inverted *l*-menthone" by heating with ammonium formate, yields on hydrolysis *d*-neomenthylamine, $[\alpha]_D^{20}$ +15·73° (the *r*-menthylamine of Wallach, cf. A., 1893, i, 724), of which the following derivatives are described: hydrochloride, m. p. 189°, $[\alpha]_D^{15}$ +21·5° (crystallographic data given); acetyl derivative, m. p. 169—170°, $[\alpha]_D^{15}$ +53·0°; benzoyl derivative, m. p. 121·5°, $[\alpha]_D^{15}$ +22·7°; benzylidene derivative, m. p. 45—46°, $[\alpha]_D^{15}$ +61·7°, salicylidene derivative, m. p. 99—100°, $[\alpha]_D^{15}$ +30·0°; β-*naphthalenesulphonyl* derivative, m. p. 208°, $[\alpha]_D^{15}$ +43·7°. The hydrochloride furnishes partly racemised *d*-Δ^3-menthene with sodium nitrite. *Formyl*-l-neo*menthylamine*, m. p. 116—117°, $[\alpha]_D^{15}$ −53·6°, is obtained from *l*-*iso*menthone, and the properties of formyl-*dl*-*neo*menthylamine are described.

d-*iso*Menthylamine is best prepared by reducing *d*-*iso*menthoneoxime, a viscid oil, $[\alpha]_D^{15}$ +46·0°, n_D^{15} 1·4845, obtained by oximating *d*-*iso*menthone, the crude menthylamine hydrochloride obtained from *l*-menthone or "inverted *l*-menthone" being a mixture. With nitrous acid, it yields *d*-*iso*menthol. The following derivatives of *d*-*iso*menthylamine are described: *hydrochloride*, $[\alpha]_D^{15}$ +23·60°, m. p. >250°; *formyl* derivative, m. p. 45—46°, $[\alpha]_D^{15}$ +31·3°; *acetyl* derivative, m. p. 77—79°, $[\alpha]_D^{15}$ +30·7°; *benzoyl* derivative, m. p. 97—98°, $[\alpha]_D^{15}$ +18·3°; β-*naphthalenesulphonyl* derivative, m. p. 80—81°, $[\alpha]_D^{15}$ −2·8°; *benzylidene*, m. p. 67—68°, $[\alpha]_D^{15}$ +90·7°, and *salicylidene* derivative, m. p. 122°, $[\alpha]_D^{15}$ +77·6°; *carbamide*, m. p. 141·5—142·5°, $[\alpha]_D^{15}$ +29·0; *phenylcarbamide*, m. p. 142°, $[\alpha]_D^{15}$ +21·8°; *phenylthiocarbamide*, m. p. 114·5—115·5°, $[\alpha]_D^{15}$ +46·7°. *l*-*iso*Menthone yields similarly l-iso*menthoneoxime*, a viscid oil, n_D^{15} 1·4870, $[\alpha]_D^{15}$ −45·2°, which reduces to l-iso*menthylamine hydrochloride*, $[\alpha]_D^{15}$ −21·88°. *Salicylidene*-l-iso*menthylamine* has m. p. 122°, $[\alpha]_D^{15}$ −76·8, and an equimolecular mixture of the *d*- and *l*-forms melts at 95°. The relative molecular configurations of the various menthylamines are discussed.

J. S. H. Davies.

Menthone series. III. Optically inactive menthylamines. J. Read, (Miss) A. M. R. Cook, and (in part) (Miss) M. I. Shannon (J.C.S., 1926, 2223—2234).—dl-*Menthylamine*, a liquid resembling *l*-menthylamine, is obtained by reducing *dl*-menthoneoxime with sodium and ethyl alcohol, and yields the following derivatives: *hydrochloride*, m. p. above 250°; *chloroplatinate*, m. p. 201—202° (decomp.); *picrate*, m. p. 196—198°; *formyl* derivative, m. p. 77—78°; *acetyl* derivative, m. p. 123—124°; *benzoyl* derivative, m. p. 145—146°; β-*naphthalenesulphonyl* derivative, m. p. 145—146°; *benzylidene* derivative, an oil; *salicylidene* derivative, an oil; *carbamide*, m. p. 157°; *phenylcarbamide*, m. p. 162°; *phenylthiocarbamide*, m. p. 151°. The hydrochloride with sodium nitrite yields a mixture of *dl*-menthol and *dl*-Δ^3-menthene. *dl*-*neo*Menthylamine, liquid, is obtained as the *hydrochloride*, m. p. 184—185° (crystallographic data given), by heating *dl*-menthone or *dl*-*iso*menthone with ammonium formate, and hydrolysing the resulting *formyl*-dl-neo*menthylamine*, m. p. 86° (crystallographic data given), with hydrochloric acid. The following derivatives are described: *chloroplatinate*, m. p. 206—207° (decomp.); *hydrobromide*, m. p. above 220°; *picrate*, m. p. 183—184°; *acetyl* derivative, m. p. 160—161°; *benzoyl* derivative, m. p. 101—102°; β-*naphthalenesulphonyl* derivative, m. p. 209—210°; *benzylidene* derivative; *salicylidene* derivative, m. p. 69·5°; *carbamide*, m. p. 162—163°; *phenylcarbamide*, m. p. 183—184°; *phenylthiocarbamide*, m. p. 169—170°. The hydrochloride with sodium nitrite yields chiefly *dl*-Δ^3-menthene.

For the preparation of *dl*-*iso*menthylamine (the "*i*-menthylamine" of Wallach, A., 1913, i, 482), *dl*-piperitone is converted into *dl*-*iso*menthone by

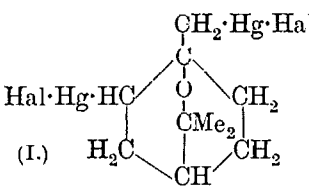
treatment with sodium and ethyl alcohol followed by oxidation with chromic acid. The derived *dl-iso*menthoneoxime is then reduced with sodium and ethyl alcohol to the amine; *hydrochloride*, m. p. above 250°; *chloroplatinate*, m. p. 212—213° (decomp.); *picrate*, m. p. 171—173°; *formyl* derivative, m. p. 45—47°; *acetyl* derivative, an oil crystallising on cooling; *benzoyl* derivative, m. p. 127—128°; β-*naphthalenesulphonyl* derivative, m. p. 141—142; *benzylidene* derivative, m. p. 41—44°; *salicylidene* derivative, m. p. 95°; *carbamide*, m. p. 203—204°; *phenylcarbamide*, m. p. 142—143°; *phenylthiocarbamide*, m. p. 137°. *dl-iso*Menthylamine with nitrous acid yields *dl-iso*menthol, m. p. 51—53°. The reduction of *dl*-piperitoneoxime under the conditions stated leads to the formation of a mixture of bases, including *dl-iso*menthylamine, and possibly *dl*-piperitylamine through incomplete reduction. The following derivatives of *l*-menthylamine are described: *benzoyl*, m. p. 157°, $[\alpha]_D$ −62·8°; β-*naphthalenesulphonyl*, m. p. 135°, $[\alpha]_D$ −53·3°; *benzylidene*, m. p. 69—70°, $[\alpha]_D$ −132·5°; *salicylidene*, m. p. 57—58°, $[\alpha]_D$ −119·2°.

J. S. H. DAVIES.

Catalytic isomerisation of pinene. F. RICHTER and W. WOLFF (Ber., 1926, **59**, [*B*], 1733—1736).—Treatment of α-pinene with hydrogen in the presence of palladium-black from palladium chloride affords mainly a mixture of α-pinene and pinane instead of *iso*pinene recorded by Zelinsky (A., 1911, i, 997). On the other hand, β-pinene is quantitatively isomerised to α-pinene by palladium saturated with hydrogen and subsequently reduced to pinane. Palladium alone does not effect the transformation.

H. WREN.

Reactions which differentiate between pinene and nopinene. I. GASOPOULOS (Ber., 1926, **59**, [*B*], 2184—2186).—In cold alcoholic solution pinene is rapidly oxidised by mercuric acetate with precipitation of mercurous acetate. Nopinene, under like conditions, gives an additive product which could not be obtained homogeneous, but readily yields stable halogeno-compounds (I); the *chloro-*, *bromo-*, and *iodo*-compounds are described.

(I.) 

H. WREN.

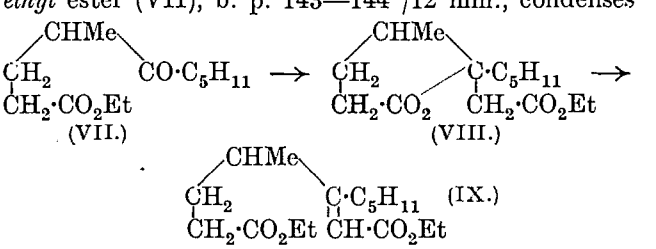
Higher terpenes. XXVIII. Elemol. L. RUZICKA and M. PFEIFFER (Helv. Chim. Acta, 1926, **9**, 841—859).—Elemol from Manila elemi oil, when purified by distilling the benzoate (Semmler and Liao, A., 1916, i, 492; Semmler, *ibid.*, 1918, i, 25) at 0·25 mm., gives a product, b. p. 141—142°/12 mm., m. p. 47°, d^{20} 0·9345, n_D^{20} 1·4980, R_D 69·72, $[\alpha]_D$ −2·33° in 20% alcoholic solution, identical with the α-elemol of Jansch and Fantl (A., 1923, i, 814), who state that such purification breaks down a labile dicyclic alcohol to a monocyclic "β-elemol."

Elemol when heated for a long period with formic acid yields elemene, b. p. 105—125°/12 mm., d_4^{15} 0·880—0·892, n_D^{15} 1·50—1·513 (cf. Semmler, *loc. cit.*), which must be considered as a mixture. Treatment of elemol or elemene with sulphur does not yield an aromatic derivative, but a *compound*, $C_{14}H_{18}S$, b. p. 150°/12 mm. (*picrate*, m. p. 111—112°; *styphnate*, m. p. 110—111°).

The ozonisation of tetrahydroelemene (cf. Semmler, *loc. cit.*) gives in the neutral portion of the final product, together with small quantities of a *ketone*, $C_{11}H_{20}O$ (*semicarbazone*, m. p. 205—206°), and other substances, the *ketone*, $C_{12}H_{22}O$, b. p. 127—128°/12 mm. (*semicarbazone*, m. p. 169°), the three carbon atoms which have been lost appearing as acetone. It is thus considered that this ketone, $[C_{10}H_{20}][\cdot CH_2\cdot CO\cdot]$ (I), is derived from the tetrahydroelemene $[C_{10}H_{20}][\cdot CH_2\cdot C(:CMe_2]$ (II), of which the isomeride with which it is mixed, $[C_{10}H_{20}][\cdot CH{:}C\cdot CHMe_2]$ (III), gives rise to the ketonic acid $[C_{10}H_{20}][\cdot CO_2H][\cdot CO\cdot CHMe_2]$ (IV), found in the acid portion of the final product; the latter oxidises to the dibasic acid, $C_{12}H_{22}O_4$ (*dimethyl* ester, b. p. 170—175°/12 mm.). The formula of the tetrahydroelemol corresponding to (II) and (III) is $[C_{10}H_{20}][\cdot CH_2\cdot C(OH)\cdot CHMe_2]$ (V), or $[C_{10}H_{20}][\cdot CH{:}CH\cdot CMe_2\cdot OH]$ (VI).

Ozonisation of elemol itself at 0° in light petroleum gives a *mono-* and a *di-ozonide*; from the neutral decomposition products of these an unsaturated *ketonic alcohol*, $C_{14}H_{24}O_2$, b. p. about 135°/1 mm., is obtained, which when heated with formic acid gives mainly the doubly unsaturated *ketone*, $C_{14}H_{22}O$, b. p. 125—127°/12 mm. Writing now $[(C_8H_{14}){:}CH_2]$ for the unidentified group in elemol, this last ketone is $[(C_8H_{14})CO]{:}C_5H_8$. The second double linking cannot be conjugated, from the behaviour of the ketone on reduction. Zinc causes no reduction in alkaline solution; sodium and alcohol yield the *alcohol*, $[C_8H_{14}(CH\cdot OH)][\cdot CH{:}C\cdot CHMe_2]$, or $[C_8H_{14}(CH\cdot OH)][\cdot CH_2\cdot C(:CMe_2]$, b. p. 119—122°/12 mm. (*phthalate* prepared), which is reduced catalytically to the *alcohol*, $[C_8H_{14}(CH\cdot OH)][\cdot CH_2\cdot CH\cdot CHMe_2]$, b. p. about 120°/12 mm.

If tetrahydroelemene had the structure proposed by Semmler, viz., $\begin{matrix}CH_2\text{—}CHMe\text{—}C\cdot C_5H_{11}\\ CH{:}C(CHMe_2)\cdot CH_2\end{matrix}$, the ketone (I) above would be identical with 3-methyl-4-*iso*amyl*cyclo*hexanone. This substance has therefore been prepared synthetically as follows. Ethyl β-keto-αε-dimethylheptoate is converted by ethyl β-iodopropionate and sodium ethoxide into ethyl α-(γ-methylpentanoyl)-α-methylglutarate, b. p. 170—180°/11 mm. This hydrolyses to δ-*keto*-γη-*dimethylnonoic acid*, b. p. 183—184°/12 mm., of which the *ethyl* ester (VII), b. p. 143—144°/12 mm., condenses



with bromoacetic acid in the presence of zinc to give the δ-*lactone* (VIII) of the *methyl hydrogen* ester of δ-*hydroxy*-γ-*methyl*-δ-iso*amylpimelic acid*, b. p. 155—160°/1 mm. This, treated with hydrobromic acid and then with alkali and esterified, gives *ethyl* γ-*methyl*-β-iso-

amyl-Δ$^{\alpha}$-pentene-αε-dicarboxylate (IX), b. p. 134—135°/0·25 mm., which reduces to *ethyl γ-methyl*-β-iso*amylpimelate*, b. p. 165°/12 mm. This, lastly, is condensed by sodium to give 4-*methyl*-5-iso*amyl*cyclo*hexanone*, b. p. about 120°/12 mm., of which the *semicarbazone*, m. p. 171°, shows considerable depression when mixed with that of the ketone (I). Hence the structure for tetrahydroelemene proposed by Semmler cannot be accepted, and the constitution of elemol is still uncertain. E. W. WIGNALL.

Derivatives of furfuraldehyde. II. Spectrographic study of furyl ketones. I. KASIWAGI (Bull. Chem. Soc. Japan, 1926, **1**, 145—151).—The ultra-violet absorption band at about 268 μμ which is shown by furfuraldehyde and very faintly by furylcarbinol, is also shown, in intermediate strength, by the saturated ketones, $C_4H_3O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}R$, previously described (this vol., 842). It must therefore be due to the furyl, and not to the furfurylidene group. Lengthening of the conjugated chain causes a marked increase in the intensity of absorption and shifts the band towards the red. The unsaturated ketones, $C_4H_3O{\cdot}CH{:}CH{\cdot}CO{\cdot}R$, give a band at about 314 μμ. In the case of difurylpentadienone the bathochromic effect is still greater. Comparison of these compounds with the corresponding phenyl derivatives shows that the furyl group is more bathochromic and produces more intense absorption than the phenyl group. H. E. F. NOTTON.

Condensation of o-hydroxy-aromatic aldehydes with ω-cyanoacetophenone. S. C. GHOSAL (J. Indian Chem. Soc., 1926, **3**, 105—109).—Salicylaldehyde and ω-cyanoacetophenone condense in presence of hydrogen chloride in glacial acetic acid solution to give 3-benzoylcoumarin (Knoevenagel and Arnot, A., 1905, i, 65), of which the *phenylhydrazone*, m. p. 95—100° (decomp.), is described. Nitration of 3-benzoylcoumarin yields 6-*nitro*-3-*benzoylcoumarin*, m. p. 200°, which may also be prepared by using 5-nitrosalicylaldehyde in the original condensation. By using appropriate aldehydes, the following substances are produced: 3-*benzoyl*-8-*methylcoumarin*, m. p. 126° (*phenylhydrazone*, m. p. 106—110°); 3-*benzoyl*-6-*methylcoumarin*, m. p. 174°; 3-*benzoyl*-7-*methylcoumarin*, m. p. 142° (*phenylhydrazone*, m. p. 115—120°); 7-*hydroxy*-3-*benzoylcoumarin*, m. p. 241° (*acetyl* derivative, m. p. 172°). With 1-naphthol-2-aldehyde the product is 3-benzoyl-β-naphthapyrone (Bartsch, A., 1903, i, 648). G. M. BENNETT.

Phthaleins direct from naphthalene. E. GEORGE (J. S. Afr. Chem. Inst., 1926, **9**, 3—5).—Resorcinol condenses with naphthalene, β-naphthaquinone, and tetrachloronaphthalene in presence of sulphuric acid, giving a 10—15% yield of fluorescein after 12—14 hrs.' heating. With naphthalene, the presence of small quantities of mercuric sulphate, ferric sulphate, or manganese dioxide causes an increase in the rate of reaction. Quinoline and phthalazine give resorcinolquinolinein and resorcinolphthalazinein. Negative results were obtained using phenol. Naphthalene retards the condensation of phenol and phthalic anhydride. H. BURTON.

Synthesis of fisetin and quercetin. J. ALLAN and R. ROBINSON (J.C.S., 1926, 2334—2336).—*Veratric anhydride*, m. p. 124—125°, is obtained by the action of pyridine on an ethereal solution of veratroyl chloride or by the action of a benzene solution of carbonyl chloride on a mixture of veratric acid, pyridine, and benzene. Interaction with ω-methoxyresacetophenone in presence of potassium veratrate at 180°, followed by hydrolysis of the product, gives *fisetin trimethyl ether*, m. p. 220°, which yields the tetramethyl ether on treatment with methyl sulphate. The *acetyl* derivative of the trimethyl ether, m. p. 229°, is converted by boiling hydriodic acid into fisetin. Similar veratroylation of ω-methoxyphloroacetophenone gives *quercetin trimethyl ether*, m. p. 240—245° (*diacetyl* derivative, m. p. 159—160°). Methylation of this compound gives the pentamethyl ether. Demethylation of the trimethyl ether gives quercetin. M. CLARK.

Synthesis of kaempferide and *iso*rhamnetin. T. HEAP and R. ROBINSON (J.C.S., 1926, 2336—2344).—Interaction of ω-*benzoxyresacetophenone*, m. p. 202—203° (*diacetyl* derivative, m. p. 112—113°), obtained by a Hoesch reaction from benzoxyacetonitrile and resorcinol, with benzoic anhydride and sodium benzoate at 180°, followed by hydrolysis of the product, yields resogalangin (3 : 7-dihydroxyflavone). Similar anisoylation gives resokaempferide (3 : 7-*dihydroxy*-4′-*methoxyflavone*), m. p. 283—284° (*diacetyl* derivative, m. p. 197°; *lead* and *potassium* salts). Benzoylation at 165—170° of ω-*benzoxyphloracetophenone*, m. p. 234—235° (*triacetyl* derivative, m. p. 115—116°), yields galangin (+H_2O), m. p. 214—215°. Anisoylation at 165—170° gives kaempferide (+MeOH), m. p. 225° (triacetyl derivative, m. p. 225°; lit. 193—195°). The product of interaction at 180° with benzoylvanillic anhydride yields on hydrolysis *iso*rhamnetin, m. p. 305° (decomp.) (lit. m. p. 295°) [tetra-acetyl derivative, m. p. 205—207°; lit. 195—196° and 198—200°]. p-*Ethylcarbonato*-m-*methoxybenzoic acid*, obtained by carbethoxylation of vanillic acid, has m. p. 147—148° (*anhydride*, m. p. 87—88·5°). M. CLARK.

Synthesis of acacetin and other flavone derivatives. R. ROBINSON and K. VENKATARAMAN (J.C.S., 1926, 2344—2348).—Interaction of resacetophenone, benzoic anhydride, and sodium benzoate at 180°, followed by hydrolysis of the product, yields 7-hydroxyflavone. Similar benzoylation of phloracetophenone yields chrysin (diacetyl derivative, m. p. 192°; lit. 185°). Corresponding anisoylation of resacetophenone yields, as main product, 7-*hydroxy*-4′-*methoxyflavone*, m. p. 262° (*acetyl* derivative, m. p. 167—168°). Acetylation of the crude flavone yields, besides the acetyl derivative, a *compound*, m. p. 171—172°, and a *compound*, m. p. 208°. The latter is apparently isomeric with 7-acetoxy-4′-methoxyflavone and yields, on hydrolysis, a *compound*, m. p. 290—291°, and 7-hydroxy-4′-methoxyflavone. The last-named substance is very probably identical with pratol (*ibid.*, 1910, **97**, 231). Corresponding anisoylation of phloracetophenone yields acacetin. M. CLARK.

Anthocyanin pigments of "morning glory." I. T. KATAOKA (Proc. Imp. Acad. Tokyo, 1926, 2, 274—276).—The flowers of the purple "morning glory" (*Pharbitis Nil*, Chois.) contain an amorphous diglucoside *cyanilin*, from which, by hydrolysis with hydrochloric acid, *cyanilidin chloride*, $C_{16}H_{13}O_6Cl,2H_2O$, is obtained (purified by means of the brownish-red *picrate*, $+7\frac{1}{3}H_2O$) and has been identified by the following reactions as 3 : 5 : 7 : 4′-*tetrahydroxy*-3′-*methoxyflavylium chloride*. The Zeisel reaction shows the presence of one methoxyl group and leaves a residue of cyanidin iodide. The chloride is more slowly converted into its colour base than cyanidin chloride, and it gives no reaction with ferric chloride. Alkaline decomposition of cyanilidin chloride yields phloroglucinol, whilst 50% potassium hydroxide acting on the picrate at 100° for 2 min. produces vanillic acid. Cyanilin appears to be an isomeride of peonidin (A., 1915, i, 288).

The red flowers of "morning glory" contain an anthocyanidin *pharbitidin*, which seems to be related to pelargonidin. G. M. BENNETT.

Violet vat dyes of the 2-thionaphthen-2-indole-indigo series. R. HERZ and W. BRUNNER.—See B., 1926, 816.

2 : 2′-Bis-1 : 3-benzdithiolene. W. R. H. HURTLEY and S. SMILES (J.C.S., 1926, 2263—2270).—Reaction of dithioalcohols with diketones involves in general only one ketonic oxygen atom. The condensation of *o*-dithiolbenzene with diacetyl, benzil, and acetylacetone yields, respectively, 2-*acetyl*-2-*methyl*-1 : 3-*benzdithiole*, m. p. 156°; 2-*benzoyl*-2-*phenyl*-1 : 3-*benzdithiole*, m. p. 175°, and 2-*acetonyl*-2-*methyl*-1 : 3-*benzdithiole*, m. p. 119°. Benzil and αβ-dithiolethane give 2-*benzoyl*-2-*phenyl*-1 : 3-*dithiolan*, m. p. 94—95°. Condensation of *o*-dithiolbenzene and ethyl orthoformate in the presence of hydrochloric acid gives 1 : 3-*benzdithiylium chloride* (cf. this vol., 948), isolated as the *chloroplatinate*, darkening at 220°, and the *zinc chloride double salt*, $2C_7H_5ClS_2,ZnCl_2$. Addition of this double salt to boiling acetic anhydride causes the formation of 2 : 2′-*bis*-1 : 3-*benzdithiolene* (I),

$C_6H_4<\begin{matrix}S\\S\end{matrix}>C{:}C<\begin{matrix}S\\S\end{matrix}>C_6H_4$, m. p. 234° (*tetraiodo*-derivative), also formed by interaction of *o*-dithiolbenzene and tetrachlorethylene in the presence of sodium. The action of oxalyl chloride on *o*-dithiolbenzene varies according to the conditions. Addition of the chloride to the mercaptan in dry acetone solution gives the unstable 1 : 4-*benzdithian*-2 : 3-*dione* (II),

$C_6H_4<\begin{matrix}S\cdot CO\\S\cdot CO\end{matrix}$, m. p. 160° (decomp.), whilst with excess of the dithiol in the absence of solvent, the very unstable 2 : 2′-*dihydroxybis*-1 : 3-*benzdithiole* (III), $C_6H_4<\begin{matrix}S\\S\end{matrix}>\overset{OH}{C}—\overset{OH}{C}<\begin{matrix}S\\S\end{matrix}>C_6H_4$, is produced. This substance yields the compound (I) on evaporation of its solution in benzene, and gives, with sulphuric acid, 2 : 2′-*bis*-1 : 3-*benzdithiylium sulphate*, $2C_{14}H_8S_4{\cdot}SO_4,H_2SO_4,2H_2O$, m. p. 268—270° (decomp.). The sulphate gives (I) on reduction in concentrated acid solution or on hydrolysis with ammonia, whilst hydrolysis by boiling in aqueous solution gives a mixture of (I) and 3-*keto*-1 : 4-*benzdithian*-2 : 2′-spiro-1′ : 3′-*benzdithiole* (IV),

$C_6H_4<\begin{matrix}S—\\S\cdot CO\end{matrix}>C<\begin{matrix}S\\S\end{matrix}>C_6H_4$, m. p. 168°, the constitution of which is established by its synthesis by condensation of *o*-dithiolbenzene with (II). *Ethylene trithioformate*, m. p. 104—105°, is formed by condensation of αβ-dithiolethane and ethyl orthoformate. M. CLARK.

Exhaustive chromic acid oxidation of hydrogenated cyclic bases. P. KARRER and A. WIDMER (Helv. Chim. Acta, 1926, 9, 886—891).—The exhaustive oxidation of various hydrogenated cyclic bases yields aliphatic amino-acids. Piperidine yields only β-aminopropionic acid, 2-methylpiperidine yields this acid and (?) β-aminobutyric acid, whilst coniine gives γ-aminobutyric acid. Pyrrolidine yields γ-aminobutyric acid, and 2-methylpyrrolidine β-aminobutyric acid together with either β-aminopropionic acid or γ-aminobutyric acid. Sparteine and methylsparteine both yield γ-aminobutyric acid, and hence probably contain the grouping $>CH{\cdot}CH_2{\cdot}CH_2{\cdot}N<$. δ-Aminovaleric acid on oxidation yielded an oil from which no crystalline product could be isolated, whilst ε-aminohexoic acid gave only a very small quantity of β-aminopropionic acid. J. W. BAKER.

Relative stability of cyclic bases. J. VON BRAUN and F. ZOBEL (Ber., 1926, 59, [*B*], 1786—1791).—The stability of the piperidine ring appears invariably to be greatly enhanced by the introduction of an alkyl group (cf. A., 1925, i, 1455). 2-Methylpiperidine is converted by αε-dibromopentane into *piperidinium*-2-*methylpiperidinium bromide*, m. p. 257°, which with ammonia at 180—190° gives unchanged bromide, piperidine, 2-methylpiperidine, and 2-*methyl*-1-ε-*aminoamylpiperidine*, b. p. 120—122°/12 mm., d_4^{18} 0·895 (non-crystalline *hydrochloride*, *picrate*, *chloroplatinate*, *acetyl* derivative, p-*nitrobenzoyl* compound, and *phenylthiocarbamide* derivative; *dimethiodide*, m. p. 278°, and corresponding *chloroplatinate*, m. p. 271—272°). The base is also prepared by hydrolysis of 2-*methyl*-1-ε-*benzamidoamylpiperidine*, b. p. 260°/13 mm. *Piperidinium*-2-*methyl*-5-*ethylpiperidinium bromide*, m. p. 253°, is somewhat sluggishly decomposed by ammonia into piperidine, 2-methyl-5-ethylpiperidine, and 2-*methyl*-5-*ethyl*-1-ε-*aminoamylpiperidine*, b. p. 145—147°/13 mm., d_4^{18} 0·888 [*dimethiodide*, m. p. 238—239°, and corresponding *chloroplatinate*, m. p. 250° (decomp.) after darkening at 140°]; the base is also derived from 2-*methyl*-5-*ethyl*-1-ε-*benzamidoamylpiperidine*. *Decahydroquinoliniumpiperidinium bromide*, m. p. 225°, appears to be decomposed by ammonia with formation of 1-ε-*aminoamyldecahydroquinoline*; the base, d_4^{17} 0·956, is obtained by hydrolysis of 1-ε-*benzamidoamyldecahydroquinoline*, but its derivatives, among which the *chloroplatinate*, decomp. 235—268°, of the methylated base is best defined, are not very characteristic. H. WREN.

New decahydro*iso*quinoline. L. HELFER (Helv. Chim. Acta, 1926, 9, 814—819).—A new form of decahydro*iso*quinoline, claimed to be the *trans*-iso-

meride, has been prepared as follows: ethyl *cyclo*hexan-1-ol-1-carboxylate (prepared by the method of Auwers and Krollpfeiffer, A., 1915, i, 1059) is converted by phosphorus pentachloride into *ethyl* Δ^1-*cyclohexene*-1-*carboxylate*, b. p. 91—93°/13 mm., which with ethyl malonate yields *ethyl* cyclo*hexane*-1-*carboxylate*-1-*malonate*, b. p. 181—183°/12 mm.; this hydrolyses to give the corresponding *acid*, m. p. 143—144° (decomp.), which readily loses carbon dioxide to form *trans-o*-carboxy*cyclo*hexaneacetic acid (hexahydrohomophthalic acid) identical with that obtained by Windaus, Hückel, and Reverey (A., 1923, i, 220). The anhydride of this acid heated with carbamide, or the ammonium salt on heating, yields the *imide*, m. p. 187°, which on energetic reduction with sodium and boiling amyl alcohol yields trans-*decahydroisoquinoline*, b. p. 81—83°/12 mm. (*hydrochloride*, m. p. 216°; *picrate*, m. p. 159—160°; *chloroplatinate*, m. p. 188—189°; cf. *cis*-isomeride, A., 1923, i, 1228). J. W. BAKER.

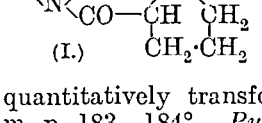
Derivatives of tetrahydrocarbazole. VI. Derivatives of 6-methyltetrahydrocarbazole. B. L. MANJUNATH and S. G. P. PLANT (J.C.S., 1926, 2260—2263; cf. *ibid.*, 1923, **123**, 676).—Acetylation of 6-methyltetrahydrocarbazole (Borsche and others, A., 1908, i, 365) gives 9-*acetyl*-6-*methyltetrahydrocarbazole*, m. p. 145°, yielding, on treatment with nitric acid in glacial acetic acid solution, a compound taken to be 5-*nitro*-9-*acetyl*-6-*methyltetrahydrocarbazole* (I), m. p. 165°, 10 : 11-*dihydroxy*-9-*acetyl*-6-*methylhexahydrocarbazole* (II), m. p. 220°, and compound (III), $C_{17}H_{21}O_4N$, m. p. 210°, presumed to be 11-hydroxy-10-acetoxy-9-acetyl-6-methylhexahydrocarbazole. Treatment of (I) with boiling aqueous-alcoholic potassium hydroxide gives 5-*nitro*-6-*methyltetrahydrocarbazole*, m. p. 181—182°. The products (II) and (III), under similar treatment, yield a *compound*, $C_{13}H_{15}ON$, m. p. 130°, apparently 11-hydroxy-6-methyltetrahydrocarbazolenine (*acetyl* derivative, m. p. 116—117°). Treatment of (III) with sodium hydroxide under slightly different conditions gives a *compound*, $C_{15}H_{17}O_2N$, m. p. 79°, supposed, on account of its colour, to be 10-acetoxy-6-methyltetrahydrocarbazolenine. The substance (III), when heated at 240°, yields acetic acid and a *compound*, $C_{15}H_{17}O_2N$, m. p. 174°, which is apparently 6-acetyl-9-methyl-ψ-indoxyl*spirocyclo*pentane.

6-Methyltetrahydrocarbazole was converted through 6-*methyltetrahydrocarbazyl*-9-*magnesium iodide* into 9-*benzoyl*-6-*methyltetrahydrocarbazole*, m. p. 118°. Crystalline derivatives could not be obtained by interaction with nitric acid. M. CLARK.

Carbazine syntheses. I. H. GOLDSTEIN and W. RODEL (Helv. Chim. Acta, 1926, **9**, 772—776).—By application of the method of Baeyer, Villiger, and Bassett (A., 1904, i, 898), the following aminocarbazines have been obtained by the action of magnesium phenyl bromide on the appropriate methyl aminophenylanthranilate, and the constitutions previously assigned to them by Kehrmann confirmed: 7-amino-5-diphenyldihydroacridine (*ibid.*, 1919, i, 552); 3 : 7- and 1 : 7-diamino-5-diphenyldihydroacridine (*loc. cit.*). Similar syntheses from methyl nitrophenylanthranilate (cf. Baeyer and others, A., 1904, i, 898) could not be effected. J. W. BAKER.

Compounds of the pyrrole and indole series and isomerisations in these series. N. PUTOCHIN (Ber., 1926, **59**, [*B*], 1987—1998).—The production of *N*- or *C*-derivatives of indole from magnesium indolyl iodide has been associated by Majima (A., 1923, i, 150, 482; 1925, i, 1451) with the particular solvent employed. It appears, however, that the direction of the reaction is primarily influenced by the temperature and the nature of the substances employed. Increasing mobility of the radicals of the compound reacting with magnesium indolyl iodide facilitates the wandering of the group from nitrogen to the 2- or 3-carbon atom of the hetero-ring.

Magnesium indolyl iodide is converted by ethyl formate in the presence of cold benzene, ether, or anisole into 1-*formylindole*, b. p. 125—126°/8 mm., 136—137°/15 mm., whereas when cooling is omitted the product is indole-3-aldehyde. Under precisely similar conditions, magnesium 2-methylindolyl iodide and ethyl formate yield 1-formyl-2-methylindole, b. p. about 155°/15 mm., d_4^{16} 1·1353, n_D^{16} 1·6170, which is so readily hydrolysed that it could not be obtained quite homogeneous, and 2-methylindole-3-aldehyde, m. p. 198°, obtained in poor yield owing to the hindrance to migration caused by the presence of a substituent in position 2. Magnesium pyrryl iodide and ethyl formate in ethereal solution without particular cooling afford pyrrole-2-aldehyde, b. p. 114°/15 mm., n_D^{15} 1·5939. Ethyl acetate and magnesium indolyl iodide at 85° yield much 1-acetylindole and little 3-acetylindole; the formation of the latter substance could not be detected when the reaction mixture was cooled thoroughly. 1-Formylindole is decomposed when heated in a sealed tube at 300° into carbon monoxide and indole, whereas at 350° 1-acetylindole gives carbon monoxide and quinoline. The preparation of pyrrole-2-aldoxime, m. p. 163—164°, *indole*-3-*aldoxime*, m. p. 197—198°, and 2-*methylindole*-3-*aldoxime*, m. p. 156—157°, is described in detail. Pyrrole-2-aldoxime is reduced by sodium and alcohol to 2-*aminomethylpyrrole*, b. p. 96°/8 mm., d_4^{18} 1·064, n_D^{18} 1·5533 (*picrate*). 3-*Aminomethylindole*, obtained similarly, has m. p. 84° (*picrate*). Reduction of 2-methylindole-3-aldoxime affords αβ-*di*-2-*methylindolylethane*, m. p. about 228° (*chloroplatinate*; *picrate*).



(I.)

Ethyl pyrrolidine-2-carboxylate slowly loses alcohol when preserved and becomes quantitatively transformed into the *anhydride* (I), m. p. 183—184°. *Pyrrolidine*-2-*carboxylamide*, m. p. 93°, is described. H. WREN.

Preparation of indole-3-propionic acid. L. KALB, F. SCHWEIZER, and G. SCHIMPF (Ber., 1926, **59**, [*B*], 1858—1860).—Ethyl *cyclo*pentan-2-one-1-carboxylate is converted by diazotised aniline into the corresponding azo-compound, which slowly solidifies owing to conversion into the *phenylhydrazone* of *ethyl* α-*ketoadipate*, m. p. 120°. Isomerisation, accompanied by hydrolysis, is more rapidly effected by sodium hydroxide, whereby the phenylhydrazone of α-ketoadipic acid, m. p. 140—141°, is produced. The latter substance is transformed by alcoholic

sulphuric acid into *ethyl indole-2-carboxylate-3-propionate*, m. p. 95°, which affords *indole-2-carboxylic-3-propionic acid*, m. p. 194—195°, and thence by loss of carbon dioxide at 225—230°, indole-3-propionic acid, m. p. 134°. H. WREN.

Substituted indole-2-carboxylic-3-propionic acids and some iodo-derivatives of benzene. L. KALB, F. SCHWEIZER, H. ZELLNER, and E. BERTHOLD (Ber., 1926, **59**, [*B*], 1860—1870; cf. preceding abstract). —*Ethyl* 1 : 4′-*nitrobenzeneazocyclopentan-2-one-1-carboxylate*, m. p. 50°, prepared from ethyl *cyclo*pentan-2-one-1-carboxylate and diazotised *p*-nitroaniline, is converted by boiling alcoholic sulphuric acid (30%) into the p-*nitrophenylhydrazone* of *ethyl α-ketoadipate*, m. p. 163°, and by the 50% acid into *ethyl 5-nitroindole-2-carboxylate-3-propionate*, m. p. 163°; *5-nitroindole-2-carboxylic-3-propionic acid* has m. p. 268—270° (decomp.). The p-*iodophenylhydrazone* of *α-ketoadipic acid*, m. p. 169°, is converted by alcoholic sulphuric acid and subsequent hydrolysis of the product into *5-iodoindole-2-carboxylic-3-propionic acid*, m. p. 252°, prepared also from indole-2-carboxylic-3-propionic acid and iodine chloride in glacial acetic acid. *Ethyl* 1 : 3′ : 4′ : 5′-*tri-iodobenzeneazocyclopentan-2-one-1-carboxylate*, m. p. 191° (decomp.), the 3 : 4 : 5-*tri-iodophenylhydrazone* of *α-ketoadipic acid*, m. p. 197° (decomp.), and 4 : 5 : 6-*tri-iodoindole-2-carboxylic-3-propionic acid*, m. p. 248° (decomp.), are described. *Ethyl* 1 : 3′ : 5′-*di-iodo-4′-methoxybenzeneazocyclopentan-2-one-1-carboxylate*, m. p. 173°, the 3 : 5-*di-iodo-4-methoxyphenylhydrazone* of *α-ketoadipic acid*, m. p. 192° (decomp.), 4 : 6-*di-iodomethoxyindole-2-carboxylic-3-propionic acid*, m. p. 236—238° (decomp.), and its *diethyl* ester, m. p. 163°, are analogously prepared. Conversion of the carboxylic-propionic into the propionic acids could not be effected by heat owing to the total decomposition induced thereby.

p-Nitroaniline is converted by excess of iodine monochloride in glacial acetic acid into 2 : 6-di-iodo-*p*-nitroaniline, which is diazotised in concentrated sulphuric acid solution and converted into 3 : 4 : 5-tri-iodonitrobenzene. The latter substance is reduced by stannous chloride in boiling acetone to 3 : 4 : 5-tri-iodoaniline, m. p. 174·5° (decomp.), which is diazotised in concentrated nitric acid solution to 3 : 4 : 5-*tri-iodobenzenediazonium nitrate* and in concentrated hydrochloric acid suspension to the *diazoamino*-compound, $C_{12}H_5N_3I_6$, m. p. 250° (decomp.). Iodination of 2-nitro-*m*-toluidine by iodine monochloride in chloroform affords 4-*iodo-2-nitro*-m-*toluidine*, m. p. 177—178° (*hydrochloride*), and 4 : 6-*di-iodo-2-nitro*-m-*toluidine*, m. p. 145—146°. The latter compound is converted into 4 : 5 : 6-*tri-iodo-2-nitrotoluene*, m. p. 139·5°, which is reduced by stannous chloride and hydrochloric acid in acetic acid solution to 4 : 5 : 6-*tri-iodo*-o-*toluidine*, m. p. 132—133° (*acetyl* derivative, m. p. 269·5°). 2-Nitro-5-acetamidotoluene is oxidised by potassium permanganate in the presence of magnesium sulphate to 2-nitro-5-acetamidobenzoic acid, which is deacetylated and iodinated to 4 : 6-*di-iodo-2-nitro-5-aminobenzoic acid*, m. p. 276° after darkening. 4 : 5 : 6-*Tri-iodo-2-nitrobenzoic acid* has m. p. 235°. *p*-Nitrophenol is converted by iodine and ammonia into 2 : 6-di-iodo-*p*-nitrophenol (*ammonium* salt), which is transformed successively into 2 : 6-*di-iodo-4-nitroanisole*, m. p. 134—135°, and 2 : 6-*di-iodo-4-aminoanisole*, m. p. 100° [*hydrochloride*, m. p. 214° (decomp.); *sulphate*, m. p. 186—187° (decomp.) after darkening at 176°; *acetyl* derivative, m. p. 200°]. 2 : 6-Di-iodo-*p*-nitrophenol is reduced by stannous chloride and hydrochloric acid in boiling alcoholic solution to 2 : 6-di-iodo-*p*-aminophenol [*hydrochloride*, m. p. 218—220° (decomp.); *sulphate*, m. p. 192—193° (decomp.)], which, when treated with nitrous acid, affords 2 : 6-*di-iodobenzoquinone-4-azide*. H. WREN.

Preparation of 5 : 7-di-iodoindole-3-acetic acid and its homologues. CHEM. FABR. AUF AKTIEN (VORM. E. SCHERING).—See B., 1926, 852.

Action of carbazide and of azoimide under pressure on aromatic hydrocarbons. Conversion of benzene derivatives into pyridine derivatives. I and II. T. CURTIUS and A. BERTHO (Sitzungsber. Heidelberg. Akad. Wiss., **A**, 1924, 3; 1925, 3; from Chem. Zentr., 1926, I, 1995—1997).—Carbazide (or azoimide) dissolved in benzene or *p*-xylene and heated in a sealed tube at 150°, gives pyridine and 2 : 5-lutidine, respectively. When heating is carried out on a larger scale in an iron autoclave with an enamel lining under a pressure of 6—7 atm., the corresponding aromatic amine is also obtained by the action of carbazide. The intermediate formation of a *s*-carbamide is assumed. Benzene yields pyridine and aniline; toluene yields *γ*-picoline and *o*-toluidine; *p*-xylene yields 2 : 5-lutidine and *p*-xylidine; *p*-cymene yields carvacrylamine and 2-*methyl*-5-*isopropylpyridine* (*picrate*, m. p. 167·5°; *chloroplatinate*, $+2H_2O$, m. p. 131°). Interaction of the hydrocarbons with azoimide yields the amines. The intermediate formation of N_4H_4, which gives identical products, is assumed. M. CLARK.

Pyridine-, quinoline-, and *iso*quinoline-*N*-oxide. J. MEISENHEIMER (Ber., 1926, **59**, [*B*], 1848—1853; cf. this vol., 77).—Quinoline, dissolved in benzene, is oxidised by perbenzoic acid to *quinoline-N-oxide* ($+2H_2O$), m. p. 62°; the *picrate*, m. p. 143°, and *hydrochloride*, m. p. 131—132°, are described. iso*Quinoline-N-oxide* ($+2H_2O$), m. p. 98° (*picrate*, m. p. 165°; *hydrochloride*, m. p. 151—152°), and *pyridine-N-oxide*, m. p. 66—68° (*picrate*, m. p. 179·5°; *hydrochloride*, m. p. 180—181°), are analogously prepared. 2 : 4 : 6-Triphenylpyridine is oxidised with greater difficulty to 2 : 4 : 6-*triphenylpyridine-N-oxide* (*picrate*, m. p. 189°; *hydrochloride*, m. p. 171—172°). The oxides are readily reduced by nascent hydrogen to the corresponding tertiary amines. Quinoline-*N*-oxide reacts unsatisfactorily with the chlorides of phosphorus, whereas it is transformed very smoothly by sulphuryl chloride into 4-chloroquinoline, m. p. 31° [picrate, m. p. 212—213° (decomp.)]. H. WREN.

Derivatives of 2- and 4-benzylpyridine. E. KOENIGS, H. MENSCHING, and P. KIRSCH (Ber., 1926, **59**, [*B*], 1717—1724; cf. Tschitschibabin and others, A., 1925, i, 1316; Koenigs and others, *ibid.*, 833).—2-*p*-Nitrobenzylpyridine, m. p. 81°, is readily isolated from the product of the action of nitric

acid (d 1·51) on a mixture of 2- and 4-benzylpyridines (the *nitrate*, m. p. 125° after softening, *hydrochloride*, m. p. 188° after softening, and picrate, m. p. 192° after softening at 180° and darkening at 186°, are described). It is converted by sodium ethoxide into a *substance*, $C_{14}H_{14}O_2N_2$, m. p. 221°. Oxidation of 2-*p*-nitrobenzylpyridine with potassium permanganate affords 2-*p*-nitrobenzoylpyridine, m. p. 99—100° (*hydrochloride*, m. p. 173°; *phenylhydrazone*, m. p. 171°). 2-*p*-Aminobenzylpyridine, m. p. 58°, yields a *dihydrochloride*, decomp. about 240°, *monopicrate*, m. p. 141°, and *dipicrate*, m. p. 182—184°; it is oxidised by permanganate to pyridine-2-carboxylic acid. 2-*p*-Nitrobenzoylpyridine is reduced by stannous chloride and hydrochloric acid to 2-p-*aminobenzoylpyridine*, m. p. 138° (*dihydrochloride*, m. p. above 190° after softening; *monohydrochloride*; *dipicrate*, m. p. 181°). 4-*p*-Aminobenzylpyridine, m. p. 158—159°, is isolated from the product obtained by reducing the mixture of 2- and 4-nitrobenzylpyridines by means of the sparingly soluble *chlorostannate*; the *dihydrochloride*, m. p. 265—268° (decomp.) after darkening, *monopicrate*, m. p. 153°, and *dipicrate*, m. p. 194° after softening at 160°, are described. 4-*p*-Nitrobenzoylpyridine, m. p. 121—122°, is isolated from the mixture of 2- and 4-*p*-nitrobenzoylpyridines by means of somewhat moist ether; it yields a *hydrochloride*, m. p. 202° after softening, *phenylhydrazone*, m. p. 226°, and *oxime*, m. p. 209°. 4-p-*Aminobenzoylpyridine*, m. p. 154—155°, its *monopicrate*, m. p. 186°, and *monohydrochloride*, m. p. 226°, are described. H. WREN.

Antiseptic properties of amino-derivatives of styryl- and anil-quinoline. C. H. BROWNING, J. B. COHEN, S. ELLINGWORTH, and R. GULBRANSEN (Proc. Roy. Soc., 1926, **B**, **100**, 293—325).—The bactericidal action of a large number of derivatives of styryl- and anil-quinoline has been examined (cf. A., 1924, i, 990). Substitution produces closely parallel effects in the two series, the styryl compound being the more powerfully antiseptic. Changes which, as a rule, increase the potency are methylation and acylation of the amino-groups, sulphonation and methods of increasing the solubility in general, and introduction of a further condensed nucleus. Removal of the styryl side-chain from the 2- to the 4-position or introduction of acidic groups in the 6-position has a depressant effect, whilst a 6-azo-group completely destroys the activity.

The following new compounds are described: the *methochlorides* of 6-chloro-, 6-bromo-, and 6-nitro-2-methylquinoline; the following acyl derivatives of 6-amino-2-methylquinoline: *formyl-*, m. p. 131—132° (*methiodide*); *propionyl-*, m. p. 146—148° (*hydrate*, m. p. 80°; *methiodide*); *butyryl-*, m. p. 134—135°; *valeryl-*, m. p. 156—158°; n-*hexoyl-*, m. p. 166—167°; *diethylacetyl-*, m. p. 165—166°; *chloroacetyl-*, m. p. 164—166°; *bromoacetyl-*, m. p. 161—163° (decomp.); *trichloroacetyl-*, m. p. 167—168°; *bromodiethylacetyl-*, m. p. 122—123°, and *benzoyl-*, m. p. 176—177°; the following derivatives of 2-(*p*-dimethylaminostyryl)quinoline methochloride: 6-*nitro-*, 6-*amino-*, 6-*chloroacetamido-*, 6-*bromoacetamido-*, 6-*trichloroacetamido-*, 6-*bromodiethylacetamido-* and 6-*azo*-(8-*amino*-α-*naphthol*-3 : 6-*disulphonic acid*); 4-(p-*dimethylaminostyryl*)-6-*methylquinoline methochloride*; the following derivatives of 2-styrylquinoline: p-*amino*-6-*acetamido- methochloride*; p-*amino*-6-*dimethylamino- methochloride* and *-methiodide*; p-*amino*-6-*amino- methochloride*; o-*nitro*-6-*methyl-*, m. p. 160—161°; o-*amino*-6-*methyl-*; m. p. 178—179° (*methochloride*, *acetyl* derivative, m. p. 188—190°); m-*nitro*-6-*methyl-*, m. p. 198—200°; m-*amino*-6-*methyl-*, m. p. 159—161° (*methochloride*, *acetyl* derivative, m. p. 167—168°); p-*nitro*-6-*methyl-*, m. p. 187—188°; p-*amino*-6-*methyl-*, m. p. 190—191° (*methochloride*, *acetyl* derivative, m. p. 247—250°); p-*acetamido*-6-*acetamido- methochloride*; mp-*dihydroxy- methosulphate*; m-p-*methylenedioxy- methosulphate*, and 6-*methyl- methochloride*; the following derivatives of 2-anilquinoline methochloride: p-*dimethylamino*-6-*nitro-*; p-*dimethylamino*-6-*azo*-(8-*amino*-α-*naphthol*-3 : 6-*disulphonic acid*), and p-*acetamido*-6-*acetamido-*. H. E. F. NOTTON.

Tautomerism of 2-aminopyridine. V. 2-Phenylpyriminazole and the conditions for the preparation of homologues of pyriminazole. A. E. TSCHITSCHIBABIN (Ber., 1926, **59**, [*B*], 2048—2055; cf. A., 1925, i, 1328; Schmid and Bangler, this vol., 848).—ω-Bromoacetophenone and 2-aminopyridine at 200—220° or in the presence of alcohol afford 2-*phenylpyriminazole hydrobromide monohydrate*, m. p. 129°, from which 2-phenylpyriminazole, m. p. 136—137°, is obtained; 2-*phenylpyriminazole chloroplatinate dihydrate*, softening at 214° but not undergoing further change below 290°, and 2-phenylpyriminazole methiodide, m. p. 220—221° (decomp.), are described. The base is identical with that considered by Palazzo and Marogna to be 2-phenacylaminopyridine (cf. A., 1913, i, 300). 1-*Phenacylpyridone*-2-*phenacylimine*, m. p. 120° [non-crystalline *hydrochloride*; *chloroplatinate*, m. p. 242° (decomp.)], is obtained as by-product of the change. Bromoacetone and 2-aminopyridine in alcoholic solution give *methylpyriminazole*, b. p. 148—150°/20 mm., $d_0^{23\cdot4}$ 1·1105, d_4^3 1·1263; the *hydrobromide* is described. Reaction proceeds less slowly than with ω-bromoacetophenone. H. WREN.

Alkhalides of 2-aminopyridine. A. E. TSCHITSCHIBABIN and R. A. KONOVALOVA (Ber., 1926, **59**, [*B*], 2055—2058; cf. Magidson and Menschikov, this vol., 844).—2-*Dimethylaminopyridine*, d_{14}^{14} 1·0157, is converted by methyl iodide at 100° into the corresponding *methiodide*, m. p. 183—184° (*picrate*, m. p. 113°), which yields 2-dimethylaminopyridine when treated with silver oxide and subsequently distilled. 1-Methyl-2-pyridonemethylimine (cf. A., 1921, i, 450) yields a *methiodide*, which is converted by treatment with silver oxide and subsequent distillation into 1-methyl-2-pyridone and decomposed by sodium hydroxide with production of dimethylamine. H. WREN.

Dyes derived from β-phenylpyridinedicarboxylic acid. J. D. TEWARI and S. DUTT (J. Indian Chem. Soc., 1926, **3**, 161—165; cf. J.C.S., 1923, **123**, 225).—β-Phenylpyridinedicarboxylic acid condenses with a series of mono- and poly-hydric phenols in presence of stannic chloride or sulphuric acid to

produce dyes analogous to the phthaleins: *phenol-β-phenylpyridophthalein*, m. p. above 305°; *resorcinol-β-phenylpyridophthalein*, m. p. 200° (decomp.) after sintering at 186°; *pyrocatechol-β-phenylpyridophthalein*, m. p. above 310°; *phloroglucinol-β-phenylpyridophthalein*, m. p. above 280°; *hydroxyquinol-β-phenylpyridophthalein*, m. p. 228—230° (decomp.); m-*diethylaminophenol-β-phenylpyridophthalein*, m. p. 193°, reddish-violet crystals giving a fluorescent solution; and m-*phenylenediamine-β-phenylpyridophthalein*, m. p. 154° (decomp.). G. M. BENNETT.

Derivatives of naphthaquinolines and naphtha*iso*quinolines. C. S. GIBSON, K. V. HARIHARAN, K. N. MENON, and J. L. SIMONSEN (J.C.S., 1926, 2247—2260; cf. *ibid.*, 1915, **107**, 1148).—α-Naphthylamine (1 mol.) and ethyl acetoacetate (1 mol.), heated together at 100°, yield only acetoaceto-α-naphthalide (cf. Conrad and Limpach, A., 1888, 503). In presence of a trace of diethylamine, ethyl β-1-naphthylaminocrotonate is readily obtained at the ordinary temperature. When heated at 240°, this compound is converted into 4-hydroxy-2-methyl-α-naphthaquinoline, which reacts with phosphorus pentachloride in tetrachloroethane solution, giving 4-*chloro*-2-*methyl*-α-*naphthaquinoline*, m. p. 92—93° (*picrate*, m. p. 196—197°). Reduction of the chloro-derivative with sodium and ethyl alcohol yields dl-2-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthaquinoline*, b. p. 202—203°/20 mm. (*benzoyl* derivative, m. p. 102—103°; *hydrochloride*, decomp. 252—253°; *sulphate*, decomp. 211—212°; *chloroplatinate*, decomp. 207—208°; *picrate*, m. p. 153—154°). When α-naphthylamine (2 mols.) is heated with ethyl acetoacetate (1 mol.) at 150—170° (cf. Knorr, A., 1884, 1198), the main product is *s*-di-α-naphthylcarbamide, accompanied by β-1-*naphthylaminocrotono*-α-*naphthylamine*. Preliminary heating at 100° increases the yield of the latter compound, which exists in two interconvertible forms, m. p. 144—145° and 167—168°, obtained by crystallisation from benzene and from absolute alcohol, respectively. Hydrolysis of the crotonyl derivative with dilute hydrochloric acid gives *acetoaceto*-α-*naphthalide*, m. p. 107°. This substance is converted by prolonged treatment with concentrated hydrochloric acid into 2-hydroxy-4-methyl-α-naphthaquinoline and thence into 2-*chloro*-4-*methyl*-α-*naphthaquinoline*, m. p. 134—135°, and dl-4-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-α-*naphthaquinoline*, b. p. 186—188°/10 mm. (*picrate*, decomp. 205—206°; *sulphate*; *chloride*; *hydrobromide*). No 2-methyl-α-naphthaquinoline could be obtained by condensation of α-naphthylamine with paraldehyde (cf. Doebner and von Miller, A., 1884, 1375). 4-Nitro- and 4-bromo-α-naphthylamine condense readily with paraldehyde, giving 6-*nitro*-2-*methyl*-α-*naphthaquinoline* (*chloroplatinate*, decomp. 229—230°; *sulphate*; *hydrochloride*; *nitrate*) and 6-*bromo*-2-*methyl*-α-*naphthaquinoline* (*chloroplatinate*, decomp. 238°; *picrate*, m. p. 185—186°; *hydrochloride*; *hydrobromide*). 3-Hydroxy-1-methyl-β-naphthaquinoline was obtained from β-naphthylamine and ethyl acetoacetate by a modification of Knorr's method (*loc. cit.*). The yield of *s*-di-β-naphthylcarbamide in the first stage was diminished by preliminary heating at 100°. Distillation of the hydroxy-compound with zinc dust gives 1-methyl-β-naphthaquinoline (*picrate*, m. p. 230—231°) in poor yield. The hydroxy-derivative was converted through 3-*chloro*-1-*methyl*-β-*naphthaquinoline*, m. p. 153—154°, into dl-1-*methyl*-1 : 2 : 3 : 4-*tetrahydro*-β-*naphthaquinoline*, b. p. 187—190°/10 mm. [*picrate*, decomp. at 162° (and at 167—168° rapid heating), accompanied by an isomeric *picrate*, m. p. 201—202°; *hydrochloride*; *sulphate*]. α- and β-Naphthaldehydes condense with acetone in presence of alkali, giving, respectively, 1-γ-*ketobutenylnaphthalene*, b. p. 200—201°/10 mm. (*oxime*, m. p. 136—137°), and 2-γ-*ketobutenylnaphthalene*, sintering at 95—96°, m. p. 102° (*oxime*, m. p. 158—160°). In the latter preparation, a trace of *di*-β-*naphthylvinyl ketone*, m. p. 241°, is formed. This compound becomes the main product when a solution of the aldehyde in acetone is treated with a drop of sodium methoxide solution. Reduction of the unsaturated ketones gives 1-γ-*ketobutylnaphthalene*, b. p. 192—195°/17 mm. (*oxime*, m. p. 96—97°), and 2-γ-*ketobutylnaphthalene*, b. p. 180—182°/8 mm. (*oxime*, m. p. 129°; *semicarbazone*, m. p. 161—162°). Treatment of the oximes of these compounds with phosphoric oxide in boiling toluene solution gives 4-*methyl*-1 : 2-*dihydro*-β-*naphtha*iso*quinoline*, m. p. 101—102° (*hydrochloride*; *chloroplatinate*; *picrate*, decomp. 221°), and 1-*methyl*-3 : 4-*dihydro*-α-*naphtha*iso*quinoline*, m. p. 36—37° (*picrate*, decomp. 207—208°).

α-*Naphthanilide* has m. p. 162—163; β-*naphthanilide* has m. p. 171°. M. CLARK.

Preparation of uracil from carbamide. D. DAVIDSON and O. BAUDISCH (J. Amer. Chem. Soc., 1926, **48**, 2379—2383).—Details are given for the preparation of uracil from carbamide, fuming sulphuric acid, and malic acid (yield, 50—55%). Hydroxymethyleneacetic acid is formed intermediately (cf. von Pechmann, A., 1884, 1124; 1891, 1457). Uracil is readily converted into 1 : 3-dimethyluracil by methyl sulphate and aqueous alkali. F. G. WILLSON.

Kinetics of the fission of diketopiperazine. H. VON EULER and E. PETTERSSON.—See this vol., 1108.

Mechanism of the action of hydrazine on α : δ-diketones with formation of 1 : 2-diazines or aminopyrroles. Absorption spectra of some 1 : 2-diazine derivatives. G. KORSCHUN and (MME.) C. ROLL (Bull. Soc. chim., 1926, [iv], **39**, 1223—1235).—The authors suggest that in all cases the first stage of the reaction between hydrazine and αδ-diketones is direct addition of one hydrazine molecule to the ketonic form of the diketone. Elimination of a molecule of water can then occur in two ways. (1) The imino-hydrogen atom is eliminated with the hydroxyl group, affording a hydrazone, which then undergoes ring closure to a 1 : 2-diazine, $\begin{matrix}CH_2\cdot CR(OH)\cdot NH\cdot NH_2\\ |\\ CHR\cdot CO\cdot R\end{matrix} \rightarrow \begin{matrix}CH_2\cdot CR{:}N\cdot NH_2\\ |\\ CHR\cdot CO\cdot R\end{matrix} \rightarrow \begin{matrix}CH_2\cdot CR=\!=\!=N\\ |\quad\quad\quad |\\ CHR\cdot CR(OH)\cdot NH\end{matrix}$; (2) the hydrogen atom of the methylene group is eliminated with the hydroxyl, giving a hydrazide, which on ring closure affords an aminopyrrole. The relative mobilities of the two hydrogen atoms will determine which reaction takes

place, and these mobilities will depend on the nature of the substituent groups present as well as on the experimental conditions. It is in accordance with this view of the mechanism of the reaction that the heats of formation of the aminopyrrole and the isomeric 4 : 5-dihydro-1 : 2-diazine should be approximately the same, as Gounder and Roll have shown for the heats of combustion of 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylic acid and 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4 : 5-dicarboxylic acid (see below). An examination of the absorption spectra of a number of 1 : 2-diazines also suggests the correctness of the above views, the 1 : 2-diazines giving spectra quite distinct from those of the pyrrole derivatives (cf. A., 1925, ii, 258); the structures assigned on chemical evidence are supported. Thus the ethyl esters of 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4-carboxylic acid and 3 : 6-dimethyl-1 : 2-diazine-4-carboxylic acid show pronounced absorption bands, and the curve is displaced towards the red as compared with that of the isomeric 1-amino-2 : 5-dimethylpyrrole-4-carboxylate. The diazine shows bands at 3053 and 3766, its dihydro-derivative a band at 3175. The ethyl esters of 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4 : 5-dicarboxylic acids and 3 : 6-dimethyl-1 : 2-diazine-4 : 5-dicarboxylic acid show similar curves with absorption bands having maxima at 3150 and at 3000 and 3469—4195, respectively. In the case of the esters of 6-phenyl-3-methyl-1 : 2-diazine-4-carboxylic acid and the corresponding 4 : 5-dihydro-derivative, the phenyl group causes a displacement towards the red, without weakening the intensity of absorption, and the dihydro-diazine derivative shows a maximum at 2750. Ethyl 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4 : 5-dicarboxylate shows no basic properties, its absorption spectra in acid and in neutral alcoholic solution being identical. R. BRIGHTMAN.

Heats of combustion of aminopyrroles and 1 : 2-diazines. A. GOUNDER and (MME.) C. ROLL (Bull. Soc. chim., 1926, [iv], **39**, 1222—1223).—Values are given for the heats of combustion of ethyl 1-amino-2 : 5-dimethylpyrrole-3 : 4-dicarboxylate, 1566·8 g.-cal., ethyl 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4 : 5-dicarboxylate, 1588·2 g.-cal., and ethyl 3 : 6-dimethyl-4 : 5-dihydro-1 : 2-diazine-4-carboxylate, 1252·5 g.-cal. R. BRIGHTMAN.

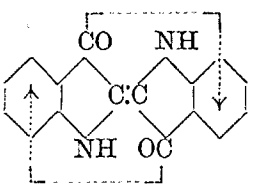
Indigotin group. VI. Action of acid chlorides on indigotin and its derivatives and the stereochemical formula for indigotin. T. POSNER [with W. STOCKENSCHNEIDER, H. NEUMANN, E. NACHRING, K. MEYER, and E. BEISSNER] (Ber., 1926, **59**, [*B*], 1799—1827).—The absorption spectrum of indigotin is so completely analogous with those of indigotin-malonic esters, indigotinphenylacetic esters, and lake-red-ciba *B*, which belong to the *trans* series, that it also must be classed as a *trans*-derivative if it be assumed that geometrical isomerism is possible.

Indigotin is converted by successive reduction and treatment with acetic anhydride into α-diacetyldihydroindigotin, whereas direct treatment with acetic anhydride and acetyl chloride affords the red *NN'*-diacetylindigotin. The latter compound is also derived by the oxidation of α-diacetyldihydroindigotin, whereby the acetyl groups migrate. Tetra-acetyldihydroindigotin is derived from *NN'*-diacetylindigotin, acetic anhydride, sodium acetate, and zinc dust, from *O*-diacetyldihydroindigotin and acetic anhydride, or from indigotin and acetic anhydride in the presence of concentrated sulphuric acid. NN'-*Dibenzoylindigotin*, m. p. 257°, is prepared from indigotin and benzoyl chloride in boiling pyridine; prolongation of the reaction leads to formation of tetrabenzoyldihydroindigotin, m. p. 242—243°. Similarly, *p*-nitrobenzoyl chloride affords successively NN'-*di*-p-*nitrobenzoylindigotin*, and *tetra*-p-*nitrobenzoyldihydroindigotin*, m. p. 281° after darkening at 270°. *O*-Dibenzoyldihydroindigotin is prepared by benzoylation of reduced indigo, but, under similar conditions, *p*-nitrobenzoyl chloride causes oxidation to indigotin. Boiling benzoyl chloride converts indigotin into a colourless compound, $C_{30}H_{17}O_3N_2Cl$ (cf. Dessoulary, Diss., Neufchâtel, 1909), which when heated or treated with cold, concentrated sulphuric acid loses benzoyl chloride (1 mol.) and gives a yellow dye, (?) $C_{23}H_{12}O_2N_2$.

7 : 7'-Dimethylindigotin is converted by acetylation in the vat into *o*-diacetyl-7 : 7'-dimethyldihydroindigotin, m. p. 247° (decomp.) after darkening at 200°, which could not be further acetylated. Contrary to the observations of Vorländer and von Pfeiffer, the substance is not converted by nitrous gases into *NN'*-diacetyl-7 : 7'-dimethylindigotin, but yields N-*nitroso*-2-*hydroxy*-N'-*acetyl*-7 : 7'-*dimethyldihydroindigotin monoenol acetate*, $C_{22}H_{19}O_6N_3$, m. p. 178°; when exposed to light, it gradually loses acetic acid and nitrous gases, with production of *N*-monoacetyl-7 : 7'-dimethylindigotin, also prepared by boiling 7 : 7'-dimethylindigotin with acetic anhydride and acetyl chloride. Oxidation of *O*-dibenzoyl-7 : 7'-dimethyldihydroindigotin similarly affords N-*nitroso*-2-*hydroxy*-N'-*benzoyl*-7 : 7'-*dimethyldihydroindigotin monoenol benzoate*, m. p. 175°, which is converted by exposure to sunlight into N-*benzoyl*-7 : 7'-*dimethylindigotin*, m. p. 216°, also prepared by benzoylation of 7 : 7'-dimethylindigotin in pyridine. Vorländer and von Pfeiffer's *NN'*-dibenzoyl-7 : 7'-dimethylindigotin does not appear to exist. Oxidation of *N*-benzoyl-7 : 7'-dimethylindigotin yields *o*-methylisatin and benzoic acid; in one instance, 2-*amino*-m-*toluoylformic acid*, m. p. 239—240°, was obtained. The resistance of 7 : 7'-dimethylindigotin to acylation is due to the proximity of the methyl and imino-groups. On the other hand, 5 : 5'-dimethylindigotin behaves similarly to the unsubstituted compound, yielding OO'-*dibenzoyl*-5 : 5'-*dimethyldihydroindigotin*, m. p. 247°, converted smoothly by benzoyl chloride and boiling pyridine into *tetrabenzoyl*-5 : 5'-*dimethyldihydroindigotin*, m. p. 236°. NN'-*Dibenzoyl*-5 : 5'-*dimethylindigotin*, m. p. 225°, is prepared directly from the parent substance and benzoyl chloride in boiling pyridine. With benzoyl chloride in boiling nitrobenzene, 5 : 5'-dimethylindigotin yields a *compound*, $C_{25}H_{18}O_2N_2$, m. p. above 300°, analogous with indigo-yellow 3*G*. ciba. Benzoylation of 5 : 7 : 5' : 7'-tetrabromodihydroindigotin affords OO-*dibenzoyl*-5 : 7 : 5' : 7'-*tetrabromodihydroindigotin*, m. p. above 325° after darkening at 300°, which could not be further benzoylated; treatment of it with nitrous fumes yields the monoenol *benzoate* of N-*nitroso*-N'-

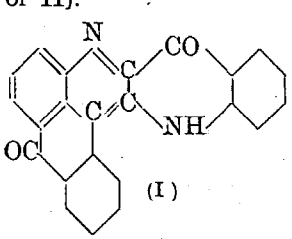
benzoylhydroxytetrabromodihydroindigotin, m. p. 123—125°. Direct benzoylation of 5 : 7 : 5′ : 7′-tetrabromoindigotin in pyridine affords *N*-monobenzoyl-5 : 7 : 5′ : 7′-tetrabromoindigotin, m. p. above 300°, and a *product*, $C_{23}H_{19}O_3N_2Br_4$,EtOH. Cautious treatment of 5 : 7 : 5′ : 7′-tetrabromoindigotin with acetyl chloride and pyridine affords a *compound*, $C_{25}H_{15}O_2N_3Br_4$,C_5H_5N, whereas more prolonged treatment gives OO′-*diacetyl*-5 : 7 : 5′ : 7′-*tetrabromodihydroindigotin*, m. p. above 300°, which could not be further acetylated. Benzoylation of indirubin in the vat yields O-*dibenzoyldihydroindirubin*, which could not be converted into a tetrabenzoyl derivative. Short treatment in pyridine converts indirubin into *N-monobenzoylindirubin*, m. p. above 300°, whereas more prolonged action leads to the *O*-dibenzoyl compound. *Ethyl indirubinmalonate*, $C_{21}H_{14}O_4N_2$, is prepared directly from its components or, more conveniently, from indirubin, ethyl malonate, and sodium hydroxide in boiling nitrobenzene. *Ethyl benzoylindirubinmalonate* is described.

The author is led to classify coloured, molecular compounds as "true halochromic" substances in which the activity of the subsidiary valencies depends on the contrast, acid to basic or metallic to non-metallic and "pseudo-halochromic" compounds in which the activity is exercised between an oxygen or a nitrogen atom and an unsaturated carbon atom. From this point of view, indigotin appears to be mainly pseudo-halochromic, the prevalent activity of the subsidiary valencies lying between the carbonyl oxygen atoms and the benzene nuclei as indicated by the annexed formula.

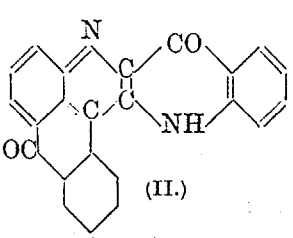


H. WREN.

Indigotin group. VII. Constitution of the vat dye, indigo-yellow 3 *G*. ciba. T. POSNER and R. HOFMEISTER (Ber., 1926, **59**, [*B*], 1827—1835).—Indigo-yellow 3*G*. ciba, m. p. 275°, prepared by the action of benzoyl chloride on indigotin in the presence of nitrobenzene and copper powder at 150—160°, has the composition $C_{23}H_{12}O_2N_2$ instead of $C_{23}H_{14}O_2N_2$ (cf. Engi, Z. angew. Chem., 1914, **27**, 144). The production of an intensely coloured vat and the stability of the dye towards oxidising agents are not compatible with the assumed indigoid structure. Protracted ebullition with concentrated nitric acid converts it into phthalic anhydride (in addition to a *substance*, $C_{14}H_6O_6N_2$, m. p. 255—258°), so that it appears to be an anthraquinone derivative (formula I or II).



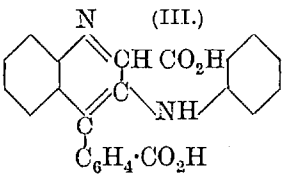
(I)



(II.)

Ciba-yellow is reduced by sodium hyposulphite and converted by benzoyl chloride and sodium hydroxide into *dibenzoyl*leuco*ciba-yellow*, m. p. 274°, whereas methylation cannot be effected by use of methyl sulphate.

Ciba-yellow is slowly dissolved by warm, dilute sodium hydroxide and the solution when acidified affords "*ciba-yellow dihydrate*," m. p. about 272—275°. The new compound readily loses water and reverts to ciba-yellow when warmed or crystallised from inert solvents. Its ready solubility in cold sodium hydroxide, sodium carbonate, or dilute ammonia solution, its inability to be benzoylated, its transformation by ethyl alcohol into the "*diethyl* ester of *ciba-yellow dihydrate*," m. p. 267°, and by methyl sulphate into "*dimethylciba-yellow monohydrate*," m. p. 178°, indicate the constitution (III). "*Acetylciba-yellow*," $C_{25}H_{14}O_3N_2$, m. p. 256°, is prepared by the action of boiling acetic anhydride on "ciba-yellow hydrate."



(III.)

H. WREN.

Velocity of formation of 3 : 5-dimethylpyrazole-4-diazonium chloride. J. REILLY and (MISS) H. E. BASTIBLE (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 343—349).—The diazotisation of 4-amino-3 : 5-dimethylpyrazole is a bimolecular reaction, the velocity constant at 0° being 0·024, identical with that for the corresponding reaction with aniline. An excess of hydrochloric acid increases the velocity. Values of K for seven temperatures up to 72° satisfy the equation $K=0{\cdot}0271\times10^{T'/30}$, where T' is the temperature (° C.). G. M. BENNETT.

Manufacture of benziminazoles. FARBENFABR. VORM. F. BAYER & Co.—See B., 1926, 850.

Tautomerism of amidines. VI. Methylation of 4-anilino-2-phenyl-6-methylpyrimidine. R. FORSYTH and F. L. PYMAN (J.C.S., 1926, 2502—2510).—Reaction between 4-anilino-2-phenyl-6-methylpyrimidine [hydrochloride, m. p. 258—259° (corr.)—lit. 240°; hydriodide, m. p. 238—239° (corr.) —lit. 231°; nitrate, $+1H_2O$, anhyd. m. p. 158—159° (corr.)—lit. 85—87°; *hydrogen oxalate*, m. p. 242—243° (decomp.; corr.); *picrate*, m. p. 195—196° (decomp.; corr.)], and methyl iodide yields a mixture of 4-*anilino*-2-*phenyl*-3 : 6(1 : 6)-*dimethylpyrimidinium iodide*, $+2H_2O$, anhyd. m. p. 220° (corr.) [*chloride*, $+H_2O$, anhyd. m. p. 231—232° (corr.).], and an *equimolecular compound*, m. p. 182—183° (corr.), of this quaternary salt with the original base. Methylation in the presence of methyl alcohol gives as main product 4-*anilino*-2-*phenyl*-6-*methylpyrimidine hydriodide*, m. p. 238—239° (corr.), together with some 4-anilino-2-phenyl-3 : 6(1 : 6)-dimethylpyrimidinium iodide (cf. Wheeler, A., 1898, i, 538). Treatment of 4-anilino-2-phenyl-3 : 6(1 : 6)-dimethylpyrimidinium chloride with aqueous sodium carbonate yields 4-*phenylimino*-2-*phenyl*-3 : 6(1 : 6)-*dimethyl*-3 : 4(1 : 4)-*dihydropyrimidine*, m. p. 193—194°, and this base heated with methyl iodide gives 4-methylanilino-2-phenyl-3 : 6(1 : 6)-dimethylpyrimidinium iodide, m. p. 215° (decomp.; corr.). This salt is also obtained by reaction of methyl iodide with 4-methylanilino-2-phenyl-6-methylpyrimidine [*hydrogen oxalate*, m. p. 182—183° (decomp.; corr.);

picrate, m. p. 174—175° (corr.)], whilst it decomposes into these two compounds when heated under reduced pressure.

It is suggested that partly cyclic amidines containing one nitrogen atom in the aromatic nucleus yield with methyl esters of inorganic acids mainly the isomerides methylated on the ring nitrogen, since they tend to react chiefly in the form in which the ring nitrogen is doubly linked, *i.e.*, as amino-derivatives of aromatic compounds rather than as the isomeric iminodihydro-derivatives. M. CLARK.

Oxidation products of some pyrrole compounds. A. PIERONI and P. VEREMEENCO (Gazzetta, 1926, **56**, 455—479).—In view of the importance, on Angeli's theory (A., 1920, i, 626), of the pyrrole-blacks in connexion with the nature of melanin, attempts have been made to obtain definite products of oxidation of comparatively simple pyrrole derivatives, using peracetic acid ("perhydrolysis"). Prolonged action of this reagent on 2 : 4-dimethylpyrrole gives an uncrystallisable syrup, but intermediately a *substance*, $C_{12}H_{20}O_5N_2$, m. p. 171° (decomp.), is formed, which hydrolyses to α-methyl-lævulic acid (phenylhydrazone, m. p. 133°; *phenylhydrazide phenylhydrazone*, m. p. 183°), and is probably $[NH_2Me{:}C(OH)\cdot CH_2\cdot CHMe\cdot CO\cdot]_2O$. 2 : 5-Dimethylpyrrole gives dark products; 2 : 5-diphenylpyrrole, acetophenone, benzoic acid, and ammonia; 1-phenyl-2 : 5-dimethylpyrrole gives yellow or brown products, but not aniline-black; 2 : 5-*dimethyl*-1-iso*amylpyrrole* (b. p. 219—221°/7·75 mm., prepared by condensing *iso*amylamine with ethyl diacetylsuccinate to give *ethyl* 2 : 5-*dimethyl*-1-iso*amylpyrrole*-3 : 4-*dicarboxylate*, m. p. 61—62°, hydrolysing to the *acid*, m. p. 219°, after reddening from 120°, and distilling) gives reddish-brown products, with the odour of valeric acid. Tetraphenylpyrrole perhydrolyses to benzoic acid and benzil, among syrupy products; triphenylmethylpyrrole to benzophenone, triphenylacetic acid, and other substances, including pyrrole-blacks which oxidise to oxalic acid and pyrrolecarboxylic acids, or to succinic acid etc. Pyrrolecarboxylic acid is attacked by peracetic acid only at temperatures high enough for it to react with the acetic acid formed.

When pyrroles are oxidised by benzoquinone, condensation products are formed. Thus 1-phenyl-2 : 5-dimethyl- and 2 : 5-dimethyl-1-*iso*amyl-pyrrole condense to give 3 : 4-*dibenzoquinone* derivatives, brownish-black solids; triphenylmethylpyrrole gives a violet-blue and 2 : 5-*dimethyl*-1-iso*amyl*-3-*triphenylmethylpyrrole* (m. p. 183°) a red colour with benzoquinone.

2-Acetyl- and 2-benzoyl-pyrrole give no dark colour on perhydrolysis, and no colour with benzoquinone.

The substances 2-*methyl*-3-*triphenylmethylindole*, m. p. 180°, and 2 : 5 : 2′ : 5′-*tetramethyl*-1 : 1′-*dipyrryl*, m. p. 62°, obtained from ethyl diacetylsuccinate, are also prepared. E. W. WIGNALL.

Syntheses by means of magnesylpyrroles. VII. Methylketolephthalein and its isomerides. B. ODDO (Gazzetta, 1926, **56**, 437—442).—Experimental details of work already published (A., 1925, i, 588). The free acid of methylketole-yellow forms red crystals with metallic reflex, m. p. 212° (*silver* salt prepared), and is considered to be identical with indophthalone (see following abstract). The isomeride described (*loc. cit.*) decomposes at 326—333°.

E. W. WIGNALL.

Syntheses by means of magnesylpyrroles. VIII. Reactions with phthalic anhydride and the constitution of indophthalone. B. ODDO and L. PEROTTI (Gazzetta, 1926, **56**, 442—445).—The interaction of equimolecular quantities of phthalic anhydride and magnesyl-2-methylindole gives a product identical with a compound to which Fischer (A., 1888, 284) attributed the constitution $C_8H_5Me{:}N\cdot CO\cdot C_6H_4\cdot CO_2H$, but this is now described as 2-methylindolidenephenylcarbinol-*o*-carboxylic acid; precipitated *silver*, *lead*, *ferric*, and *cupric* salts are obtained.

The action of phthalyl chloride on magnesyl-2-methylindole gives a product identical with the indophthalone of Renz (A., 1904, i, 534), considered to be ω-[2-methylindolidene-2-methylindolyl]-*o*-toluic acid (cf. preceding abstract). E. W. WIGNALL.

Racemic and optically active α-phenanthroline-diethylenediaminecobaltic salts and the reaction between mono- or di-amines and diethylene-diamine-dichloro- or -chloroaquo-salts. F. M. JAEGER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 559—579).—Diethylenediaminechloroaquocobaltic sulphate boiled in aqueous solution with α-phenanthroline yields dl-α-*phenanthrolinediethylenediaminecobaltic chlorosulphate*, $\left[\mathrm{Co}\begin{matrix}\alpha\ \mathrm{phen}\\ \mathrm{en_2}\end{matrix}\right]\begin{matrix}\mathrm{SO_4}\\ \mathrm{Cl}\end{matrix}, 2H_2O$, triclinic needles (*iodide*, *nitrate*, *sulphate* [$+12H_2O$], *chlorate* [$+H_2O$], and d-*tartrate* [$+9H_2O$] also described). Crystallisation of the tartrate gave no sign of a resolution of the base into its optical antipodes, but this resulted from crystallisation of the *d*-bromocamphorsulphonate together with precipitation of the *dl*-iodide, which is less soluble than the iodide of the active base. l-α-*Phenanthrolinediethylenediaminecobaltic* d-*bromocamphorsulphonate*, triclinic crystals, $+3H_2O$, is the more sparingly soluble salt (l-*base chlorate*, $+2H_2O$, also described). The optical rotatory powers for light of 16 different wave-lengths are recorded and shown graphically for the bromocamphorsulphonate and the *iodide* in aqueous solution; the specific rotation of the former vanishes at 5025 Å., and that of the iodide, which shows the Cotton effect, at 4910 Å.

In the formation of the new cobalt complex, *r*-triethylenediaminecobaltic iodide appears as a by-product. A similar production of *luteo*-triethylenediaminecobaltic salts occurs when *l*-menthylamine acts on a diethylenediamine-chloroaquo- or -dichlorocobaltic salt and when racemic or *l*-βδ-diaminopentane is heated with a solution of the chloroaquo-salt. The resolution of *dl*-βδ-diaminopentane by means of tartaric acid in aqueous acetone is described, the rhombic l-βδ-*diaminopentane di*-d-*tartrate*, $[\alpha]_D$ +26°, crystallising. Optically active or racemic α-propylenediamine gives rise in aqueous solution to the same products, but the normal product results if the anhydrous base be used. Crystallographic descriptions are given of many of the salts prepared. G. M. BENNETT.

Esters of the procaine type derived from nicotinic acid. A. W. INGERSOLL and B. H. ROBBINS (J. Amer. Chem. Soc., 1926, 48, 2449—2452).—Nicotinyl chloride, m. p. 264—265°, is obtained in 90% yield by heating nicotinic acid with a slight excess of thionyl chloride in dry benzene (cf. Meyer, A., 1901, i, 407). Treatment of nicotinyl chloride with β-diethylaminoethyl and γ-diethylaminopropyl alcohols in acetone affords *β-diethylaminoethyl nicotinate hydrochloride*, hygroscopic, m. p. 169—170° (rapidly heated), and *γ-diethylaminopropyl nicotinate hydrochloride*, similar, m. p. 172—173° (rapidly heated), respectively. Neither ester produces local anæsthesia. F. G. WILLSON.

Pyrrole and indole syntheses with [substances containing] anthracene nuclei. Q. MINGOIA (Gazzetta, 1926, 56, 446—450).—The condensation of magnesylpyrrole with anthraquinone gives probably first dipyrrylanthranol, which loses water to give 9 : 10-*di*-1′ : 2′-*pyrrylenedihydroanthracene*, $CH\langle\begin{matrix}CH{:}C\\CH{\cdot}N\end{matrix}\rangle C_{14}H_8\langle\begin{matrix}C{:}CH\\N{\cdot}CH\end{matrix}\rangle CH$, or $CH\langle\begin{matrix}CH{\cdot}C{:}C_{14}H_8{:}C{\cdot}CH\\CH{:}N\qquad\quad N{:}CH\end{matrix}\rangle CH$, dark micro-crystals, m. p. 160°, forming no acetyl, benzoyl, or silver derivatives. With magnesylmethylketole, 9 : 10-*tetra*-2-*methylindolyldihydroanthracene*, m. p. 148° (brown *silver* salt), is formed. E. W. WIGNALL.

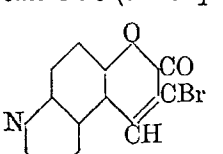
Interaction of *iso*cyanic acid and *iso*cyanates [carbimides] with some alkyl and aryl Schiff bases and with hydrazones. Addition to the CH:N linking. N. A. LANGE (J. Amer. Chem. Soc., 1926, 48, 2440—2444; cf. A., 1920, i, 399).—Phenylcarbimide reacts analogously to, but less readily than, carbimide, with *N*-alkyl Schiff bases, yielding diketohexahydrocyanidines (diketohexahydro-1 : 3 : 5-triazines), $\begin{matrix}CHR{\cdot}NR{\cdot}CO\\NPh{\cdot}CO{-}NPh\end{matrix}$, which are stable, crystalline, and unaffected by acetylating agents. The reaction is analogous to the polymerisation of cyanic acid to cyanuric acid, and to the addition of ketens to Schiff bases (Staudinger, A., 1910, i, 586; 1917, i, 666). Analogous compounds are not produced from *N*-aryl Schiff bases, the reaction products yielding, on steam distillation, the corresponding *s*-disubstituted carbamides, the formation of which may be due to hydrolysis of an unstable four-membered ring compound formed by condensation of 1 mol. of phenylcarbimide with 1 mol. of Schiff base. In glacial acetic acid, insoluble ureides are also produced, derived from condensation of aldehyde with the disubstituted carbamide. Phenylcarbimide does not add to the CH:N group in hydrazones. Treatment of phenylcarbimide with benzylidene-ethylamine in a sealed tube at 180—200° for 4 days affords 2 : 4 : 6-*triphenyl*-1-*ethyl*-2 : 4-*diketohexahydro*-1 : 3 : 5-*triazine*, m. p. 192°. Benzylidenepropylamine yields similarly 3 : 5 : 6-*triphenyl*-1-*propyl*-2 : 4-*diketohexahydro*-1 : 3 : 5-*triazine*, m. p. 156°, whilst benzylidene-ethylamine and *p*-tolylcarbimide afford 6-*phenyl*-1-*ethyl*-3 : 5-*di*-p-*tolyl*-2 : 4-*diketohexahydro*-1 : 3 : 5-*triazine*, m. p. 173°. Treatment of benzylidene-*p*-toluidine with potassium cyanate in cold glacial acetic acid affords *benzylidenedi*-p-*tolylureide*, m. p. 206—208°, which is also obtained by condensation of benzaldehyde and *p*-tolylcarbamide in the same solvent. *Benzylidenedi*-o-*tolylureide*, m. p. 199—200°, is obtained similarly. Both ureides are polymerides. F. G. WILLSON.

Constitution of osotetrazines and amino-osotriazole. R. STOLLÉ (Ber., 1926, 59, [*B*], 1742—1747).—Osotetrazines (cf. von Pechmann and Bauer, A., 1909, i, 270) are deeply coloured if phenyl residues are attached to the nitrogen atoms, whereas the corresponding acyl derivatives are colourless; the latter, therefore, are regarded as true osotetrazines, $R{\cdot}C\langle\begin{matrix}CR{=}{=}{=}N\\N{\cdot}N(COR)\end{matrix}\rangle N{\cdot}COR$, whereas the former are azo-derivatives, R·N:N·CR:CR·N:NR. In conformity with this hypothesis, " diacetylphenylosotetrazine " is readily reduced by hydrogen sulphide in boiling alcoholic solution to diacetylosazone, whereas *N*-dibenzoyl-*C*-dimethylosotetrazine is completely stable.

Benzhydrazide and *iso*nitrosoacetone afford methylglyoxaldibenzoylosazone, m. p. 252°, which is converted by mercuric oxide, magnesium oxide, and iodine in ethereal solution into *dibenzoylmethylosotetrazine*, m. p. 124°. The latter compound is transformed by boiling, aqueous-alcoholic hydrochloric acid into 1-amino-5-methyl-1 : 2 : 3-triazole, m. p. 68°, identical with the compound described by Wolff and Hall (A., 1904, i, 120; contrast Stollé, *ibid.*, 1909, i, 337). 1-*Benzamido*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 158°, is obtained in addition to the isomeric compound by the oxidation of methylglyoxaldibenzoylosazone with potassium ferricyanide and also by treatment of dibenzamidomethyltriazole with sodium carbonate. 1-*Benzamido*-4-*methyl*-1 : 2 : 3-*triazole* is converted by hydrochloric acid into 1-amino-4-methyl-1 : 2 : 3-triazole (*benzylidene* derivative, m. p. 94°). 1-*Dibenzamido*-5-*methyl*-1 : 2 : 3-*triazole*, m. p. 136°, and 1-*dibenzamido*-4-*methyl*-1 : 2 : 3-*triazole*, m. p. 152°, are described. H. WREN.

Uranium compounds of hexamethylenetetramine. E. ISNARD (Bull. Sci. pharmacol., 1925, 32, 659; from Chem. Zentr., 1926, I, 1814).—" Gelatinous needles " of a compound containing 59·65% of uranium and 11·67% of hexamethylenetetramine are obtained by mixing aqueous solutions of hexamethylenetetramine and uranyl acetate. M. CLARK.

Quinolinobromopyrones and their conversion into quinolinofurans. B. B. DEY and T. R. SESHADRI (J. Indian Chem. Soc., 1926, 3, 166—176).—3-Bromo-6-nitrocoumarin (Dey and Row, J.C.S., 1923, 123, 3379), when heated with glycerol and sulphuric acid, undergoes the Skraup reaction, yielding 3-*bromo*-5 : 6-(5′ : 6′-*quinolino*)-α-*pyrone* (I), m. p.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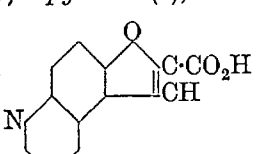
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237° [*picrate*, m. p. 255°, *sulphate*, *nitrate*, *hydrochloride*, *oxalate*, *dichromate*, *ferrocyanide*, *mercurichloride*, *chloroplatinate*, and *methiodide*, m. p. 252° (decomp.), described], which is reduced by means of tin and hydrochloric acid to its *tetrahydro*-derivative, m. p. 174° [*hydrochloride*, *chloroplatinate*, and *nitroso*-

compound, m. p. 196° (decomp.), described], and converted by boiling alcoholic potassium hydroxide solution into 5 : 6-*quinolinofuran-α-carboxylic acid* (II), not melted at 300° (*silver* salt and *ethyl* ester, m. p. 133°, described). Distillation of this acid with soda-lime yields the 5 : 6-*quinolinofuran*, m. p. 85° [*picrate*, m. p. 221°, *dichromate*, m. p. 149° (decomp.), *mercurichloride*, *mercuri-iodide*, *chloroplatinate*, and *methiodide*, m. p. 284° (decomp.), described]. 3-*Bromo*-6-*aminocoumarin*, m. p. 193°, prepared from the nitro-compound by reduction, condenses with paraldehyde in presence of hydrochloric acid to give 3-*bromo*-5 : 6-(2′-*methyl*-5′ : 6′-*quinolino*)-α-*pyrone*, m. p. 243° (decomp.) [*hydrochloride*, *nitrate*, *sulphate*, *picrate*, m. p. 210°, *dichromate*, *mercurichloride*, *mercuri-iodide*, *ferrocyanide*, *chloroplatinate*, and *methiodide*, m. p. 285° (decomp.), described] reduced to the *tetrahydro*-derivative, m. p. 163° (*hydrochloride*, *chloroplatinate*, and *nitroso*-compound, m. p. 179°, described), and converted by alcoholic potassium hydroxide into 2-*methyl*-5 : 6-*quinolinofuran-α-carboxylic acid*, not melted at 300° (*silver* salt and *ethyl* ester, m. p. 107°, described). Decarboxylation of this acid furnishes 2-*methyl*-5 : 6-*quinolinofuran*, m. p. 29° at first but after keeping 85° [*picrate*, m. p. 198°, *dichromate*, m. p. 152° (decomp.), *ferrocyanide*, *mercurichloride*, *mercuri-iodide*, *chloroplatinate*, and *methiodide*, m. p. 256° (decomp.), described].

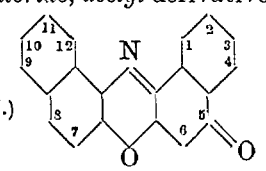
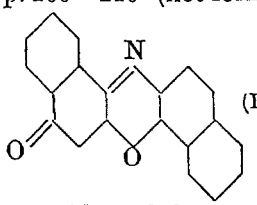
G. M. BENNETT.

Dioximes. XXXI. G. PONZIO (Gazzetta, 1926, **56**, 490—502).—The dibenzoylphenylhydroxyglyoxime of m. p. 183° (cf. this vol., 850) is considered to have the structure HO·C(=N·OBz)—(BzO·CPh)=N ; the substance, m. p. 176°, which it gives with alkali is 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole, wrongly described as "phenylhydroxyfurazan" by Gastaldi (A., 1925, i, 988). This may also be obtained from oximinophenylacetonitrile oxide (this vol., 295), which after reaction with sodium hydroxide gives on neutralisation with carbon dioxide a *substance*, m. p. 123°, and on acidification a mixture of the above oxadiazole and its 5 : 3-isomeride, whilst *phenylmetazonic acid*, CPh(:NOH)·CH:NO_2H, m. p. 166°, remains in solution, from which it is extracted by means of its *nickel* salt. The 3-hydroxy-compound is separated by means of its insoluble *copper* salt, or can be prepared pure by the action of bromine on phenylmetazonic acid, boiling off the benzonitrile formed; treated with *o*-toluidine, it gives *s*-di-*o*-tolylcarbamide.

Dibenzoylglyoxime peroxide gives similarly with alkali 3-*hydroxy*-5-*benzoyl*-1 : 2 : 4-*oxadiazole*, m. p. 123—124°. This is very stable towards acids; with aniline, it gives *s*-diphenylcarbamide and benzanilide; with *o*-toluidine, *d*-di-*o*-tolylcarbamide and benz-*o*-toluidide; the *phenylhydrazone*, m. p. 231—232° (decomp.), *aniline* salt, m. p. 135—136° (decomp.), and *sodium*, *potassium*, *silver*, and *cupric* salts were prepared. 5-*Hydroxy*-3-*benzoyl*-1 : 2 : 4-*oxadiazole*, m. p. 192—193° (*phenylhydrazone*, m. p. 196°, *sodium* and *cupric* salts), having a more soluble sodium salt, remains in solution when the above isomeride is precipitated; the corresponding tautomeric lactam formula was ascribed by Böeseken (A., 1912, i, 723) to a substance which is probably of a different nature. *Benzoylmetazonic acid*, COPh·C(:NOH)·CH:NO_2H, m. p. 166° (decomp.), is converted by hydroxylamine and sodium acetate into 4-oximino-5-keto-3-phenyl-4 : 5-dihydro*iso*oxazole (cf. Guinchard, A., 1899, i, 780).

E. W. WIGNALL.

Azoxines. II. H. GOLDSTEIN and H. RADAVANOVITCH (Helv. Chim. Acta, 1926, **9**, 776—783).—By the condensation of 1-amino-β-naphthol and 2-amino-α-naphthol with 2-hydroxy-1 : 4-naphthaquinone, 2-hydroxynaphthaquinoneimine, and hydroxyphenylnaphthaquinoneimine, the following αα′- and αβ′-dinaphthazoxine derivatives are obtained: *αα′-dinaphthazox-5-one* (I), m. p. 277—278° (*hydrochloride*); *αα′-dinaphthoxazime*, decomp. about 212° [*hydrochloride*, *acetyl* derivative, m. p. 209—210° (not formed

(I.)  (II.) 

by the condensation of acetamidonaphthaquinone with 1-amino-β-naphthol, which yields probably an unstable *iso*oxonium derivative of the ψ-base, cf. Kehrmann, Gottrau, and Leemann, A., 1907, i, 554)]; N-*phenyl-αα′-dinaphthoxazime*, m. p. 237—239° (*hydrochloride*); *αβ′-dinaphthazox-5-one* (II), m. p. 284—285°; *αβ′-dinaphthoxazime*, softens 240°, decomp. 252° (*hydrochloride*; *acetyl* derivative, m. p. 237—238°); N-*phenyl-αβ′-dinaphthoxazime*, m. p. 301° (*hydrochloride*).

J. W. BAKER.

Thiodiazines. III. Hydroxythiodiazines. P. K. BOSE (J. Indian Chem. Soc., 1926, **3**, 148—154; cf. A., 1925, i, 167, 1465).—The interaction of benzyl dithiocarbazinate (A., 1916, i, 343), ethyl chloroacetate, and alcoholic ammonia produces 5-*hydroxy*-2-*benzylthiol*-1 : 3 : 4-*thiodiazine*, OH·C(=NH·N)(—CH=)—S—C·S·CH_2Ph, m. p. 124° (*sodium* salt soluble in water; *methyl ether*, a pale brown oil). *o-Nitrobenzyl dithiocarbazinate*, m. p. 92—94°, prepared in a manner analogous to that used for the benzyl ester, gives 5-*hydroxy*-2-*o-nitrobenzylthiol*-1 : 3 : 4-*thiodiazine*, m. p. 151°, and the *p*-isomeride yields 5-*hydroxy*-2-*p-nitrobenzylthiol*-1 : 3 : 4-*thiodiazine*, m. p. 173°. With ethyl α-bromopropionate and ethyl bromomalonate in place of ethyl chloroacetate, the above reaction furnishes 5-*hydroxy*-2-*benzylthiol*-6-*methyl*-1 : 3 : 4-*thiodiazine*, m. p. 111°, and 5-*hydroxy*-2-*benzylthiol*-6-*carbethoxy*-1 : 3 : 4-*thiodiazine*, m. p. 117°, respectively. Ethyl chloroacetate acts on a mixture of hydrazine hydrate, carbon disulphide, and alcoholic potassium hydroxide to give the *disulphide* of 5-*hydroxy*-2-*thiol*-1 : 3 : 4-*thiodiazine*, m. p. 92°, which has acidic properties, whilst chloroacetic acid reacts in the same circumstances to yield the *potassium* salt, +H_2O, m. p. 253° (decomp.), of 2-*thiol*-1 : 3 : 4-*thiodiazole*-5-*thiolacetic acid*, m. p. 164°, oxidised by iodine to a *disulphide*, m. p. 180° (decomp.).

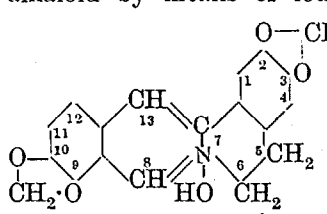
G. M. BENNETT.

***Cinchona* alkaloids. Transformations of diazotised amino-derivatives.** F. X. ERBEN, E. PHILIPPI, and O. MAULWURF (Ber., 1926, **59**, [*B*], 2150—2159).—In attempts to prepare arsino-deriv-

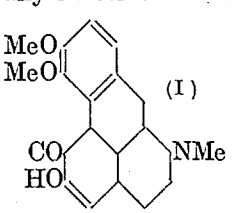
atives of the *Cinchona* alkaloids, diazotised 5-aminodihydroquinine is treated with sodium arsenite solution; arsenic-free compounds are produced from which hydrocupreine-5-diazoanhydride (cf. Giemsa and Halberkann, A., 1921, i, 582) is isolated. A similar result is obtained with 5-aminodihydroquinine-sulphonic acid, which gives *dihydroquinine-5-diazoanhydride sulphonic acid*, decomp. above 140°, and *dihydrocupreansulphonic acid*, $C_{19}H_{24}O_4N_2S$. To eliminate the possibility of the production of a diazoanhydride, further experiments were performed with 5-aminodihydrocinchoninesulphonic acid (cf. Giemsa and Halberkann, *loc. cit.*), for which (and for the corresponding nitro-compound) amended directions of preparation are given. The products obtained were *hydroxydihydrocinchoninesulphonic acid* and *dihydrocinchansulphonic acid*, each of which can be prepared separately without the use of arsenite. 5 : 8-Diaminodihydroquinine is too unstable for experiments on its diazotisation. H. WREN.

Amine-oxides of alkaloids. I. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1926, [iv], **39**, 1147—1167).—Work already published is reviewed and extended (cf. A., 1925, i, 828), the following new compounds being described: *cinchonine* N-*oxide*, m. p. 186°, $[\alpha]_D$ +165° in alcohol; *ψ-pelletierine* N-*oxide*, m. p. 160—162° [*hydrobromide*, m. p. 224° (decomp.)]; *monoacetylmorphine* N-*oxide*, m. p. 205°, $[\alpha]_D$ −144° in alcohol. It is thought that the product of the action of hydrogen peroxide on strychnine is not a peroxide (cf. Pictet and Mattisson, A., 1905, i, 816; Mossler, *ibid.*, 1910, i, 584), but a normal amine oxide containing hydrogen peroxide of crystallisation. After many recrystallisations from water, the *N*-oxide, m. p. 216°, $[\alpha]_D$ +5° in alcohol, gives no reactions for peroxide and forms a hydriodide, m. p. 266°, and a *benzoate*, m. p. 163—164°, $[\alpha]_D$ +4° in water. The authors fail to confirm the formation of the double salt, $Na_2SO_4,H_2O_2,9H_2O$ (Tanatar, A., 1902, ii, 11), the product of the interaction of sodium sulphate and hydrogen peroxide responding to no simple formula. Analogy is drawn between the constitution of this salt and that proposed for the so-called peroxide of strychnine, viz., $C_{21}H_{22}O_2N{\cdot}N{:}O,0{\cdot}75(3H_2O,H_2O_2)$. R. W. WEST.

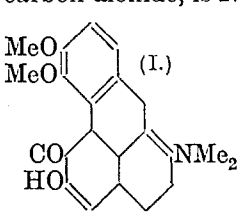
Constitution of coptisine, a new alkaloid from *Coptis japonica*. Z. KITASATO (Proc. Imp. Acad. Tokyo, 1926, **2**, 124—125).—A yellow, crystalline alkaloid *coptisine*, $C_{19}H_{15}O_5N$, found in the herb *Coptis japonica*, Mak., is purified through its *tetrahydro*-derivative, m. p. 215°, which is reoxidised to the alkaloid by means of iodine. It contains no methoxyl, and is shown to be 2 : 3 : 9 : 10-*bis-methylenedioxyprotoberberine* (annexed formula; nomenclature adopted from J.C.S., 1925, **127**, 1462) by its conversion by the action of sulphuric acid and phloroglucinol (cf. Späth and Quietensky, this vol., 82) into an unstable base which on complete methylation and reduction with zinc and sulphuric acid yields tetrahydropalmatine. G. M. BENNETT.



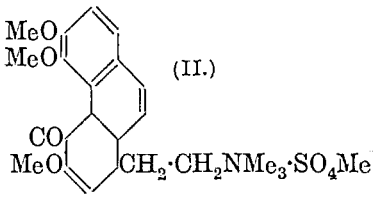
Sinomenine and dehydrosinomenine. K. GOTO (Proc. Imp. Acad. Tokyo, 1926, **2**, 7—9; cf. A., 1923; i, 1222). Sinomenine, $C_{19}H_{23}O_4N$, m. p. 162°, $[\alpha]_D^{20}$ −73·92°; contains a keto-group (*oxime*, m. p. 233°; *methylsinomenine semicarbazone*, m. p. 149—151°) and a free phenolic hydroxyl group giving rise to a greenish-blue colour with ferric chloride and a red product with benzenediazosulphonate. Reduction by hydrogen in presence of colloidal palladium furnishes *hydrosinomenine*, $C_{19}H_{25}O_4N$, m. p. 201°, $[\alpha]_D$ +193·58° [*methiodide*, m. p. 268° (decomp.); *oxime*, m. p. 211°; *semicarbazone*, m. p. 209°], which is still phenolic. Bromination of sinomenine hydrochloride yields two *monobromo*-derivatives, m. p. 153°, $[\alpha]_D^{25}$ −2·62°, and m. p. 421° (241°?), $[\alpha]_D^{25}$ +14·65°, respectively, of which the former alone still gives phenolic reactions. *Dehydrosinomenine*, $C_{19}H_{21}O_4N$, m. p. 245°, $[\alpha]_D^{25}$ −149·97° [*hydrochloride*, m. p. above 285°; *methiodide*, m. p. 261°; *oxime*, m. p. 265° (decomp.); *semicarbazone*, m. p. above 285°], occurs together with sinomenine and also results from mild oxidation of the latter. It has phenolic properties. Distillation of sinomenine with zinc dust yields phenanthrene. Boiling 66% potassium hydroxide solution acts on the alkaloid to produce methylethylamine and *sinomenol*, $C_{16}H_{14}O_4$, m. p. 176°. Sinomenine methiodide, m. p. 255° (decomp.), also yields this product together with dimethylethylamine. Sinomenol contains two methoxyl groups and two hydroxyl groups (two *dimethylsinomenols*, m. p. 115° and 240°, two *dibenzoyl* derivatives, m. p. 206° and 260°, and a *diacetyl* derivative, m. p. 149°, are described), but it has no keto-group. The dibenzoylsinomenol of m. p. 206°, which also results from the fusion of sinomenine at 180° with benzoic anhydride, is optically inactive and is oxidised to a red quinone (*phenazine* derivative, m. p. 254°). Distillation of sinomenol with zinc dust gives phenanthrene in quantity. It has the reducing properties of an *o*-dihydroxy-compound such as *apo*morphine. These facts are interpreted by the annexed formula, sinomenine (I) being a tetrahydro*iso*quinoline alkaloid of the phenanthrene group and sinomenol 3 : 4-*dihydroxy*-5 : 6-*dimethoxyphenanthrene*. G. M. BENNETT.



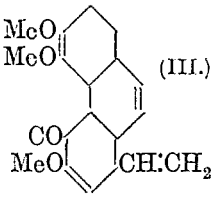
Hofmann's decomposition of sinomenine. K. GOTO (Proc. Imp. Acad. Tokyo, 1926, **2**, 167—170; cf. preceding abstract).—Sinomenine methiodide is boiled with 2% sodium hydroxide solution, when the product, isolated by saturating the solution with carbon dioxide, is N-*methylanhydrosinomeninium base*, $C_{20}H_{25}O_4N$ (I), m. p. 183°, $[\alpha]_D^{15}$ +31°, which is hydrolysed with great ease by dilute acids or alkalis, water, alcohol, or methyl iodide. Methylation of sinomenine with methyl sulphate yields *sinomenine methyl sulphate*, m. p. 245°, and *methylsinomenine methyl sulphate*, m. p. 265° (*oxime*, m. p. 252°). In



presence of cold alkali, the product is the *methyl sulphate* (II) (m. p. 213°, $[\alpha]_D^{13}$ +478°) of *α-methylsinomeninemethine*, m. p. 172° (*methiodide*, m. p. 213°), which dissolves in concentrated hydrochloric acid with



(II.)

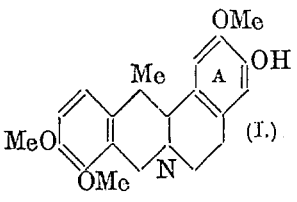


(III.)

a blue colour, together with an isomeride, *β-methylsinomeninemethine*, m. p. 263° (*methiodide*, m. p. 287°; *methyl sulphate*, m. p. 178°), which gives an orange-red colour to hydrochloric acid. At 100°, in presence of dilute sodium hydroxide solution, the base decomposes with production of 3 : 5 : 6-*trimethoxy*-4-*keto*-1-*vinyltetrahydrophenanthrene* (III), m. p. 310°, yielding on methylation *α-tetramethoxyvinyldihydrophenanthrene*, $C_{20}H_{22}O_4$, m. p. 283°, which is also obtained directly from sinomenine by the action of methyl sulphate and warm sodium hydroxide solution, together with a *β-isomeride*, m. p. 122°.

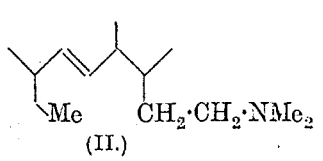
No anhydro-base could be obtained from morphine or codeine. G. M. BENNETT.

Corybulbine. J. GADAMER and K. SAWAI (Arch. Pharm., 1926, **264**, 401—409; cf. von Bruchhausen and Sawai, this vol., 185).—The following work was already in progress when Späth and Dobrowsky published results (A., 1925, i, 1085) showing that corybulbine had formula (I). The incomplete investigation confirms their conclusions, and proves that Gadamer and Bruns (A., 1904, i, 185) were right in assigning the hydroxyl group to nucleus A.

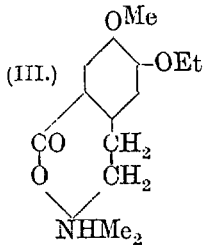


(I.)

The *methiodide* (m. p. 223—224°, decomp., or, for a second form, 240—241°, $[\alpha]_D^{20}$ +128°) of corybulbine ethyl ether (m. p. 129—130°, $[\alpha]_D^{20}$ +298·7° in alcohol; *hydrochloride*, m. p. 245—251°) is converted into the *methochloride* and boiled with methyl-alcoholic potassium hydroxide; it yields optically inactive *de*-N-*methylcorybulbine ethyl ether*, m. p. 117—118°, but much of the material remains as or is reconverted into the quaternary base. The *sulphate* corresponding with *de*-N-*methylcorybulbine ethyl ether methiodide* (m. p. 207—208°) is converted by reduction with sodium amalgam in dilute sulphuric acid solution into *dihydrode*-N-*dimethylcorybulbine ethyl ether*, m. p. 87—88°. The product is homogeneous; the ring scission has therefore taken place entirely in one



(II.)



direction (cf. II). When this compound is oxidised, as sulphate, in ice-cold aqueous solution with potassium permanganate, it is disrupted into methyl acetoveratrone (3 : 4-dimethoxy-2-methylacetophenone) and an amino-acid, precipitated by Mayer's reagent and eventually isolated as the *chloroaurate*, m. p. 192—193°, which, if Späth and Dobrowsky's conclusions are correct in detail, should have the formula III.

W. A. SILVESTER.

Formation of phosphinic acids from triarylmethoxyphosphorus dichlorides [dichlorotriarylmethoxyphosphines]. D. R. BOYD and F. J. SMITH (J.C.S., 1926, 2323—2334; cf. A., 1924, i, 1121).—The following triarylmethoxyphosphorus dichlorides were prepared by the action of phosphorus trichloride on the appropriate carbinol: p-*chlorotriphenylmethoxyphosphorus dichloride*, m. p. 161·5°; p-*bromotriphenylmethoxyphosphorus dichloride*, m. p. 163° (the carbinol has m. p. 82°; lit. 130°); *diphenyl*-p-*anisylmethoxyphosphorus dichloride*, m. p. 180°; *diphenyl*-m-*anisylmethoxyphosphorus dichloride*, m. p. 122—124°; *diphenyl*-α-*naphthylmethoxyphosphorus dichloride*, m. p. 171—172°; *diphenyl*-β-*naphthylmethoxyphosphorus dichloride*, m. p. 194°; p-*nitrotriphenylmethoxyphosphorus dichloride*, m. p. 188·5°; *diphenyl*-p-*tolylmethoxyphosphorus dichloride*, m. p. 193° (decomp.). These compounds are all stable towards cold aqueous alkali. Diphenyl-*p*-anisylphosphorus dichloride is slowly hydrolysed to phosphorous acid and diphenyl-*p*-anisylcarbinol by digestion for some hours with hot aqueous ammonia; the other chlorides are unaltered by this treatment. The behaviour of the phosphorus chlorides towards hot alcoholic potassium hydroxide varies with the "basicities" of the parent carbinols. A relatively low "basicity" favours molecular rearrangement: $CAr_3{\cdot}OPCl_2 \longrightarrow CAr_3PO(OEt){\cdot}OK$. A relatively high "basicity" leads to hydrolysis without molecular rearrangement. Thus *p*-$Cl{\cdot}C_6H_4{\cdot}CPh_2{\cdot}O{\cdot}PCl_2$ (basicity of carbinol 0·79) gives 93% of phosphinic acid. No phosphinic acid is obtained from *p*-$MeO{\cdot}C_6H_4{\cdot}CPh_2{\cdot}O{\cdot}PCl_2$ (basicity of carbinol 6·52) or from α-$C_{10}H_7{\cdot}CPh_2{\cdot}O{\cdot}PCl_2$ (basicity of carbinol 10·8). The yield of phosphinic acid obtained as a by-product in the preparation of the dichloride by the action of phosphorus trichloride on the carbinol is greater in the case of the more strongly basic carbinols. This is in agreement with the hypothesis that an additive compound is first formed: $R{\cdot}OH+PCl_3 \rightarrow RO{\cdot}PHCl_3 \rightarrow RO{\cdot}PCl_2+HCl$, or in the case of a carbinol with pronounced basic properties: $R{\cdot}OH+PCl_3 \rightarrow R{\cdot}P(OH)Cl_3 \rightarrow R{\cdot}POCl_2+HCl$. The following are described: p-*chlorotriphenylmethylphosphinic acid*, m. p. 273°; p-*bromotriphenylmethylphosphinic acid*, +AcOH, m. p. 297° (*barium* salt); *diphenyl*-p-*anisylmethylphosphinic acid*, m. p. 210°; *diphenyl*-α-*naphthylmethylphosphinic acid*, m. p. 256°; *diphenyl*-β-*naphthylmethylphosphinic acid*, +AcOH, m. p. 247·5°; *diphenyl*-p-*tolylmethylphosphinic acid*, $+H_2O$, m. p. 254°. The basicity of these acids was established by preparation of the corresponding *dipotassium* salts and by electrometric titration. Diphenyl-*m*-anisylmethylphosphinic acid could not be isolated. The ethyl ester, when boiled with acetic and hydriodic acids, was converted into m-*hydroxytriphenylmethylphosphinic acid*, $+2H_2O$,

m. p. 248° [*disodium* salt; *benzoyl* derivative, m. p. 237·5° (*disodium* and *disilver* salts)]. Methylation of this acid gave a dibasic *acid*, m. p. 197°.

M. CLARK.

Dicarboxyphenylarsinic acids. I. 2 : 3-Dicarboxyphenylarsinic acid and its anhydride. C. S. HAMILTON and R. FRAZIER (J. Amer. Chem. Soc., 1926, **48**, 2414—2416).—2 : 3-*Dicarboxyphenylarsinic acid* (*trisodium* salt), obtained from 3-aminophthalic acid by Bart's method (A., 1922, i, 1201), yields the corresponding *anhydride* when heated at 200° for several days. F. G. WILLSON.

Synthesis of polypeptide-like derivatives of arsanilic acid. G. GIEMSA and C. TROPP (Ber., 1926, **59**, [*B*], 1776—1786).—Polypeptide-like derivatives of arsanilic acid are obtained in satisfactory yield by the action of halogenoacyl chlorides diluted with ether on alkaline solutions of the arsanilic acid covered by ether and subsequent replacement of the halogen atom by the amino-group under mild conditions. Biologically, the action of the more complex derivatives is almost invariably greater than that of atoxyl, but does not exceed that of glycylarsanilic acid (cf. Jacobs and Heidelberger, A., 1920, i, 111).

The following compounds are described: chloroacetylarsanilic acid; glycylarsanilic acid; *chloroacetylglycylarsanilic acid*, slow decomp. 305°; *carbethoxyglycylarsanilic acid*, from glycylarsanilic acid and ethyl chloroformate, decomp. 275°, hydrolysed by a slight excess of *N*-sodium hydroxide to *carboxyglycylarsanilic acid*, decomp. 205°; p-*anisoylglycylarsanilic acid*, decomp. 300—302°; *diglycylarsanilic acid*, decomp. 275—280°; *chloroacetyldiglycylarsanilic acid*, decomp. 222—224°; *carbethoxydiglycylarsanilic acid*, decomp. 295—299°; *carboxydiglycylarsanilic acid*, by very cautious hydrolysis of the ethyl ester; *triglycylarsanilic acid*, decomp. 220°; *chloroacetyltriglycylarsanilic acid*, decomp. 236—237°; *carbethoxytriglycylarsanilic acid*, decomp. 259—261°; *tetraglycylarsanilic acid*, decomp. 222—224°; *α-bromopropionylarsanilic acid*, decomp. about 245° after darkening at 225°; *alanylarsanilic acid*, decomp. above 300°; *α-bromopropionylglycylarsanilic acid*, decomp. 205°; *alanylglycylarsanilic acid*, decomp. above 300° after darkening at 255°; *α-bromoisohexoylarsanilic acid*, decomp. 240—243°; *leucylarsanilic acid*, decomp. 272—275°; *α-bromoisohexoylglycylarsanilic acid*, decomp. 240—243; *leucylglycylarsanilic acid* (*calcium* salt). H. WREN.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. III. Homologues and amino-, chloro-, and cacodyl derivatives. H. BURTON and C. S. GIBSON (J.C.S., 1926, 2241—2247; cf. A., 1921, i, 371; this vol., 418).—Condensation of arsenious chloride in *o*-dichlorobenzene solution with phenyl-β-naphthylamine, *p*-tolyl-α-naphthylamine, and *p*-tolyl-β-naphthylamine yields 12-*chloro*-7 : 12-*dihydrobenzophenarsazine*, m. p. 249—250°, 7-*chloro*-9-*methyl*-7 : 12-*dihydrobenzophenarsazine*, m. p. 252—255° (decomp.), and 12-*chloro*-10-*methyl*-7 : 12-*dihydrobenzophenarsazine*, m. p. 266—267° (decomp.), respectively. Formation of 10-chloro-3-amino-5 : 10-dihydrophenarsazine from arsenious chloride and *m*-aminodiphenylamine, m. p. 66—67° (cf. Wieland and Rheinheimer, A., 1921, i, 371, m. p. 76—77°), is unaccompanied by formation of the 1-amino-derivative. The constitution ascribed to 10-chloro-2-amino-5 : 10-dihydrophenarsazine (*loc. cit.*) is established by direct synthesis from arsenious chloride and *p*-aminodiphenylamine. Nitration and subsequent reduction of phenarsazinic acid gives 1-nitrophenarsazinic acid, m. p. above 300° (*sodium* salt; *barium* salt, $+7H_2O$), and 1-aminophenarsazinic acid (*dihydrochloride*, decomp. about 260°). Reduction of an alcoholic hydrochloric acid solution of the latter with sulphur dioxide, in presence of a trace of iodine, yields 10-*chloro*-1-*amino*-5 : 10-*dihydrophenarsazine* (*hydrochloride*). Arsenious chloride condenses with *m*- and *p*-chlorodiphenylamine and with pp'-*dichlorodiphenylamine*, m. p. 71—72°, to give 3 : 10-*dichloro*-5 : 10-*dihydrophenarsazine*, m. p. 220—221° (decomp.), 2 : 10-*dichloro*-5 : 10-*dihydrophenarsazine*, m. p. 230—231° (decomp.), and 2 : 8 : 10-*trichloro*-5 : 10-*dihydrophenarsazine*, m. p. 273—274° (decomp.), respectively. Reduction of 10-chloro-5 : 10-dihydrophenarsazine in acetone–alcohol solution or of phenarsazinic acid in acetic acid solution containing a trace of iodine with hypophosphorous acid gives 10 : 10'-*bis*-5 : 10-*dihydrophenarsazine*, m. p. 304—305° (decomp.), converted by bromine in carbon tetrachloride solution into 10-bromo-5 : 10-dihydrophenarsazine and oxidised in boiling xylene suspension to the phenarsazinic acid. Similar reduction of *N*-acetylphenarsazinic acid gives 10 : 10'-*bis*-5-*acetyl*-5 : 10-*dihydrophenarsazine*, m. p. 293—294° after decomp. M. CLARK.

Mercuration of alkylphenols and alkylphenolaldehydes. T. A. HENRY and T. M. SHARP (J.C.S., 1926, 2432—2440; cf. A., 1922, i, 1080; 1924, i, 738; 1925, i, 1006).—*p-tert.*-Butylphenol and *p-iso*amylphenol, when heated in alcoholic solution with mercuric acetate and a small amount of acetic acid, afford 2 : 6-*diacetoxymercuri*-p-tert.-*butylphenol*, m. p. 224° (decomp.), and 2 : 6-*diacetoxymercuri*-p-iso*amylphenol*, +AcOH, m. p. 123—125°, respectively. These compounds are converted by treatment with ice-cold concentrated nitric acid into 2 : 6-dinitro-*p-tert.*-butylphenol and 2 : 6-dinitro-*p-iso*amylphenol (*potassium* salt). Mercuration in 50% alcohol at the ordinary temperature yields 2-*acetoxymercuri*-p-tert.-*butylphenol*, m. p. 180°, and 2-*acetoxymercuri*-p-iso*amylphenol*, m. p. 176—177° (decomp.), respectively. Mercuration of carvacrol in boiling 50% alcohol yields 4 : 6-*diacetoxymercuricarvacrol*, softening at 190°, decomp. 215°, and 4(6)-*acetoxymercuricarvacrol*, decomp. 196°. Treatment of the former compound with benzenediazonium chloride in alkaline solution gives *op*-dibenzeneazocarvacrol, m. p. 163° (lit. 158°). 2-*Hydroxy*-5-iso*amylbenzaldehyde*, b. p. 165—168°/17 mm. (*semicarbazone*, m. p. 222°; *phenylhydrazone*, m. p. 177—178°), is obtained by condensation of *p-iso*amylphenol with formaldehyde. Mercuration of this compound and of 2-hydroxy-5-*tert.*-butylbenzaldehyde by heating with mercuric acetate at 100° in the absence of solvent yields 2-*hydroxy*-3-*acetoxymercuri*-5-iso*amylbenzaldehyde*, m. p. 134—135°, and 2-*hydroxy*-3-*acetoxymercuri*-5-tert.-*butylbenzaldehyde*, m. p. 220°, respectively. Similar mercuration of

p-carvacrolaldehyde gives 4-*hydroxy*-5-*acetoxymercuri*-3-*methyl*-6-iso*propylbenzaldehyde*, +AcOH, m. p. 120°, which, with a solution of iodine in potassium iodide, gives probably 5-*iodo*-4-*hydroxy*-3-*methyl*-6-iso*propylbenzaldehyde* (?), m. p. 157°. 4-*Hydroxy*-5-*chloromercuri*-3-*methyl*-6-iso*propylbenzaldehyde* softens at 209°, decomp. about 260°. Mercuration of *p*-thymolaldehyde yields 3-*acetoxymercuri*-4-*hydroxy*-2-*methyl*-5-iso*propylbenzaldehyde*, sintering at 179°, decomp. 185°. This compound yields an iodo-derivative, probably 3-*iodo*-4-*hydroxy*-2-*methyl*-5-iso*propylbenzaldehyde*, m. p. 128—129°.

Investigation of the bactericidal properties of these substances shows that the rise in bactericidal power which accompanies increase in weight of the substituent alkyl group in phenols is retained when these products are mercurated and that the further introduction of an aldehyde group has little or no influence on the bactericidal action. M. CLARK.

Colloidal properties of complex mercury derivatives of sulphosalicylic acid. W. OSTWALD and M. MERTENS.—See this vol., 1097.

Action of mercuric acetate on *p*- and *o*-iodoaniline. L. VECCHIOTTI and A. MICHETTI (Gazzetta, 1926, **56**, 480—489; cf. A., 1925, i, 1058).—The action of mercuric acetate on *o*-iodoaniline gives 2-*iodoaniline* 4-*mercuriacetate*, m. p. 149°, since the *acetyl* derivative of the product, stable at high temperatures, is converted by iodine into 2 : 4-diodoacetanilide (cf. this vol., 720). The corresponding *hydroxide*, m. p. 152°, and *iodide*, m. p. 183°, are described. With *p*-iodoaniline, 4-*iodoaniline* 2-*mercuriacetate*, m. p. 179°, is obtained, since the *acetyl* derivative, m. p. 205°, is also converted by iodine into 2 : 4-diiodoacetanilide. The corresponding *hydroxide*, m. p. 259°, and *iodide*, decomp. 165°, are described. The action of sodium thiosulphate on the acetate gives a very unstable substance which may be *mercury di*-m-*chloro*-o-*aminophenyl*. E. W. WIGNALL.

Presence of cysteine group in protein molecules. Y. OKUDA (Proc. Imp. Acad. Tokyo, 1926, **2**, 277—279).—During the prolonged hydrolysis of proteins, cysteine is not produced from cystine, but, on the contrary, cysteine becomes oxidised to cystine. Both cystine and cysteine are primary products of the complete hydrolysis, the latter being isolated directly, provided that air is excluded by a current of carbon dioxide during the experiment. G. M. BENNETT.

Proteins. III. Action of superheated water on proteins. II. S. KOMATSU and C. OKINAKA (Bull. Chem. Soc. Japan, 1926, **1**, 151—157; cf. this vol., 853).—The titration curves and buffer value curves (Van Slyke, A., 1922, i, 893) of the solutions obtained by digesting edestin, gliadin, and casein with water at 120° are figured. The buffer action of the solution is altered by changes in the concentration and method of preparation, except in the case of gliadin, where it is apparently dependent on concentration alone. The existence in each solution of at least two complex compounds is inferred. The solutions from edestin and gliadin are flocculated on addition of dilute acetic acid. H. E. F. NOTTON.

Irradiated proteins. I. Coagulation of egg-albumin by ultra-violet light and heat. J. H. CLARK (Amer. J. Physiol., 1925, **73**, 649—660).—The final, but not the initial, actions of ultra-violet light and heat are identical; the albumin is coagulated when irradiated or heated at certain p_H values near the isoelectric point. At any other p_H value the albumin remains clear on irradiation or heating, but reacts like a globulin. A. A. ELDRIDGE.

Quantitative organic microanalysis. G. LUNDE (Biochem. Z., 1926, **176**, 157—164).—A description of modifications of the Pregl microanalytical technique used in elementary microanalysis and in the microdetermination of carbonyl and methoxyl groups. P. W. CLUTTERBUCK.

Rapid determination of organic nitrogen. G. JARAMILLO (J. Amer. Chem. Soc., 1926, **48**, 2453—2454).—The substance is heated in a copper test-tube with sodium hydroxide and crystallised sodium acetate. The ammonia evolved is collected in *N*-sulphuric acid, the last traces being expelled by the methane as the temperature rises towards the end of the distillation. The method is illustrated by analyses of wheat flour, fertilisers, and soils. F. G. WILLSON.

Micro-determination of total iodine and of iodine in organic acids. B. GROÁK (Biochem. Z., 1926, **175**, 455—460).—Details are given of a micromethod for determining iodides and organically combined iodine in liquids and solids, both in the presence and in the absence of bromine. The liquid or solid is treated with a mixture of solid sodium carbonate and potassium nitrate, dried, and fused at dull red heat in a small crucible. The mass is extracted with water, treated with a few drops of a saturated solution of permanganate and the boiling solution acidified with sulphuric acid. Potassium permanganate is added until a permanent rose-red colour is obtained, the liquid being brought to b. p. at the same time. Sodium nitrite is then added until the colour is discharged. Finally, carbamide solution and, after cooling, potassium iodide are added, and the liberated iodine is titrated with thiosulphate. When bromine is present, the permanganate treatment after acidification is continued until all the bromine is liberated and driven off in the escaping steam, and after decolorising with nitrite, more permanganate is added and the treatment continued as above. J. PRYDE.

Piperidine as reagent for quinones and dyes. W. DILTHEY and R. WIZINGER (Ber., 1926, **59**, [*B*], 1856—1858).—The colour of solutions of *o*- and *p*-hydroxypyrylium compounds, parafuchsin, crystal-violet, malachite-green, *p*-aminotriphenylmethyl perchlorate, auramine, benzaurin, aurin, phenolphthalein, fluorescein, eosin, erythrosin, rhodamine-3*B*-extra, and rhodamin-*S* is lightened or destroyed by addition of piperidine; with azines, oxazines, and thiazines, the effect is less noticeable. With chloranil, 1 : 2-naphthaquinone, 2 : 3-dichloro-1 : 4-naphthaquinone, phenanthraquinone, dibromoanthraquinone, and chrysenequinone, a bathochromic effect is observed, which is less obvious with anthraquinone, acenaphthenequinone, or benzil. Since the production of a blue colour from *spiro*dinaphthapyrans is inhibited

by the presence of piperidine, it is scarcely probable that the blue compound is an *ortho*-quinone (cf. Löwenstein and Katz, this vol., 956). H. WREN.

Detection of methylpentosan. K. OSHIMA and K. KONDO (J. Coll. Agric. Hokkaido Imp. Univ., 1926, **16**, 1—11).—The usual methods for the detection of methylpentosans are untrustworthy in the presence of hydroxymethylpentosan. 3—5 G. of material are distilled with hydrochloric acid (*d* 1·06); when 300 c.c. of distillate have been collected, 100 c.c. are returned and redistilled, 30 c.c. of the original distillate being returned every time an equal amount has been distilled; hydrochloric acid is finally employed. After treatment of 5 c.c. of the distillate with hydrochloric acid and phloroglucinol, the absorption spectrum is examined for the characteristic band of methylfurfuraldehyde. CHEMICAL ABSTRACTS.

Determination of pentosan and methylpentosan. K. OSHIMA and K. KONDO (J. Coll. Agric. Hokkaido Imp. Univ., 1926, **16**, 13—71).—3—5 G. of the material are distilled with 100 c.c. of hydrochloric acid (*d* 1·06), 30 c.c. more acid being added to replace each similar quantity distilled; distillation is continued until the distillate (about 600 c.c.) no longer becomes yellow or orange on addition of concentrated hydrochloric acid. 100 C.c. of the distillate are similarly distilled, a hydrochloric acid solution of phloroglucinol is added to the distillate, and the phloroglucide collected in a Gooch crucible. If *a* and *b* represent the mg. of furfuraldehyde phloroglucide and methylfurfuraldehyde phloroglucide (separable with hot alcohol), respectively, the mg. of carbohydrate present may be calculated as follows: arabinose, $1{\cdot}1569(a+6{\cdot}298)$; xylose, $0{\cdot}99993(a+6{\cdot}298)$; fucose or rhamnose, $2{\cdot}4443(b+7{\cdot}488)$; pentose, $1{\cdot}0798(a+6{\cdot}298)$; methylpentose, $2{\cdot}228875\times(b+7{\cdot}488)$. CHEMICAL ABSTRACTS.

Determination of diguanide. C. D. GARBY (Ind. Eng. Chem., 1926, **18**, 819).—Diguanide may be accurately determined (results within 1%) by the following method. In the absence of guanylcarbamide a weighed amount of the sample containing 0·1 g. of diguanide is dissolved in 25—30 c.c. of a 10% mannitol solution, 5 drops of trinitrobenzene solution are added, and a 25% solution of potassium hydroxide is added dropwise until the colour changes from dark red to yellowish-red. A solution of nickel nitrate (40 g. of $NiNO_3,6H_2O$, 100 c.c. of a 10% mannitol solution, 40 c.c. of concentrated ammonia, and 15 c.c. of a 25% potassium hydroxide solution) is added (0·5—3·0 c.c.), and the solution left for 2—3 hrs., filtered through a Gooch crucible, the precipitate washed with a 0·12% ammonia solution, dried at 125° for 1 hr., and weighed as $Ni(C_2H_6N_5)_2$. In the presence of guanylcarbamide, 0·2 g. of diammonium hydrogen phosphate and 0·1 g. of ammonium nitrate are added before the addition of the indicator and the alkali. J. W. BAKER.

"Formol" titration. J. H. NORTHROP (J. Gen. Physiol., 1926, **9**, 767—769).—Sørensen's original method (cf. A., 1908, i, 115) could not be used for accurate determinations of amino-acids owing to the difficulty of determining the exact end-point, and because the value obtained depended on the point at which the titration started. To overcome these objections, a method, based on theoretical grounds, has been evolved in which p_H 7 and 9 are made the starting- and the end-points, respectively, of the titration, the correct p_H being determined by comparison with given colour standards. The solution of amino-acid etc. is titrated to p_H 7, using neutral red as indicator; formalin is added, and the solution titrated to p_H 9 using phenolphthalein. The amount of alkali required to bring the solution from the "neutral" to the "alkaline" standard is the titration figure, which in the case of amino-acids and simple dipeptides agrees with the alkali equivalent determined by electrometric titration. The method is especially useful for comparative results, *e.g.*, for following the course of hydrolysis of proteins. W. ROBSON.

Determination of protein and proteose. F. B. SEIBERT (J. Biol. Chem., 1926, **70**, 265—272).—Pure proteins such as crystalline egg-albumin are precipitated from aqueous solution to the extent of at least 98% on addition of trichloroacetic acid to 16% concentration, whilst in the case of impure proteins and of Witte's peptone a part only of the nitrogenous material is precipitated by such treatment. When mixtures of equal parts of pure protein and of the non-precipitable proteoses from Witte's peptone are similarly treated, the whole of the protein together with 3·5—4% of the proteose is precipitated; this error becomes more serious if the protein concentration in the solution be higher than 1·0%. It is concluded that, if the concentration of trichloroacetic acid be raised to 16% and the protein solution be sufficiently dilute, the method of Hahn (A., 1922, i, 291) is accurate to within 1%. C. R. HARINGTON.

Umbelliferone as fluorescent indicator. R. ROBL.—See this vol., 1115.

Biochemistry.

Hæmocyanin. II. Influence of hydrogen-ion concentration on the dissociation curve of the oxyhæmocyanin from the blood of the common lobster (*Homarus vulgaris*). III. Influence of hydrogen-ion concentration on the dissociation curve of the oxyhæmocyanin from the blood of the edible crab (*Cancer pagurus*). E. STEDMAN and (MRS.) E. STEDMAN (Biochem. J., 1926, **20**, 938—948, 949—956).—II. Between p_H 7·8 and 9·65 the shape of the dissociation curve of *Homarus* hæmocyanin is modified in two directions by changes in p_H. Increase in alkalinity causes the initial portion of the curve to become steeper, whilst the upper portion simultaneously tends to approach saturation more and more asymptotically. This effect is at its maximum at p_H 9·65. The behaviour of hæmocyanin at p_H 9·65 is consonant with the view that the combination with oxygen follows the law of mass action

for true solution, and the pigment is probably present as its alkali salt at this p_H. *Limulus* hæmocyanin is different from that of *Cancer*, *Homarus*, *Maia*, and *Palinurus*. The pigments of the last four species resemble one another closely in their properties. The hæmocyanins of *Cancer* and of *Homarus* are different and the others are probably also not identical.

III. The oxygen dissociation curves of hæmocyanin from *Cancer* have been determined at p_H values ranging from 3·84 to 9·52. The affinity of the hæmocyanin for oxygen is at a minimum in the neighbourhood of neutrality. As the acidity or alkalinity of the solution is increased, the curve approaches more and more closely to the hyperbolic form. The combination of the pigment with oxygen follows, therefore, the law of mass action for homogeneous solutions, and the curve is probably controlled by the relative amounts of pigment present in the form of salt and in the uncombined state. S. S. ZILVA.

Kastle-Meyer test for blood. J. GLAISTER (Brit. Med. J., 1926, i, 650—652).—The reagent is prepared by boiling potassium hydroxide (20 g.) and phenolphthalein (2 g.) with water (up to 100 c.c.), 10—30 g. of powdered zinc being added, until the solution becomes colourless. In the presence of blood, a few drops of 20-vol. hydrogen peroxide solution, and 10—20 drops of the reagent, a deep permanganate-colour is immediately developed.
CHEMICAL ABSTRACTS.

Manoilov's reaction and its specificity. M. J. GALWIALO, G. E. VLADIMIROV, A. P. VINOGRADOV, and W. W. OPPEL (Biochem. Z., 1926, **176**, 189—197).—Manoilov's blood test for the determination of the sex of animals is not specific, and is conditioned largely by differences in the protein content of the blood. P. W. CLUTTERBUCK.

Chemico-physiological basis of Manoilov's reaction. A. A. SCHMIDT and N. O. PEREVOSSKAJA (Biochem. Z., 1926, **176**, 198—209).—Manoilov's reaction is not a reaction depending on the sex hormone, but is due to the fact that the serum of the female always contains about 8·5% more protein than that of the male. P. W. CLUTTERBUCK.

Hæmoglobin and iron in blood. G. E. SACKETT (J. Lab. Clin. Med., 1925, **10**, 1018—1020).—In Newcomer's method, 100% represents 16·4 g. of hæmoglobin per 100 c.c. of whole blood. The normal standard corresponding with 5,000,000 erythrocytes is 16·4 g. of hæmoglobin per 100 c.c. of whole blood.
CHEMICAL ABSTRACTS.

Labile sulphur in the blood. D. CAMPBELL and E. M. K. GEILING (J. Pharm. Exp. Ther., 1926, **28**, 389—394).—Boiling with 0·1*N*-sodium carbonate for 30 min. in an atmosphere of hydrogen causes a considerable proportion of the sulphur of whole blood, plasma, and washed cells to be eliminated. In experiments using solutions of different p_H, it was found that the more alkaline the solution the more hydrogen sulphide was formed. There was no essential difference between the blood of normal and diabetic humans, and the blood of dogs and pigs also showed the above phenomena. H. I. COOMBS.

Liberation of adsorbed substances from proteins. II. Effect of addition to blood of sodium oleate on non-protein nitrogen. S. M. ROSENTHAL (J. Biol. Chem., 1926, **70**, 129—133).—Addition to whole blood of 25 mg. per c.c. of sodium oleate causes an increase of 20—55% in the concentration of nitrogen in the filtrate obtained after treatment of the blood with tungstic acid; it appears, therefore, that the sodium oleate is able to release some nitrogenous compounds which are normally adsorbed by the proteins. C. R. HARINGTON.

Absorption of amino-acids by erythrocytes and its effect on the distribution of the residual nitrogen. H. HÄUSLER (Arch. exp. Path. Pharm., 1926, **116**, 173—188).—Ox and human bloods treated with fluoride do not destroy glycine when incubated with the latter at 37°, although about 1% disappears from the plasma. Ox and human corpuscles take up equal amounts of amino-acids which have been added to the plasma, the quantity increasing as the amount added to the blood is increased, but the data do not suggest an adsorption phenomenon. The adsorption of glycine by the corpuscles is accompanied by a diffusion of non-amino-nitrogen from the corpuscles to the plasma. H. J. CHANNON.

Donnan equilibrium and osmotic pressure relationship between red blood-corpuscles and serum. H. WU (J. Biol. Chem., 1926, **70**, 203—205).—It is pointed out that in a Donnan equilibrium in which ions of one sign only are indiffusible there must be osmotic inequality on the two sides of the membrane; the osmotic equality between the blood-corpuscles and serum is due to the indiffusibility both of the protein anions and of the metallic cations.
C. R. HARINGTON.

Influence of temperature on the p_H of blood. C. J. MARTIN and E. H. LEPPER (Biochem. J., 1926, **20**, 1071—1076).—The p_H of human and rabbit blood does not alter significantly when the temperature varies from 18° to 38° if the pressure of carbon dioxide remains constant (cf. Hasselbach, A., 1917, i, 490). With the concentration of total carbon dioxide constant, the p_H of human blood falls about 0·2 when the temperature is raised from 18° to 38°. If 0·2 be deducted from the p_H of the plasma determined by the colorimetric method of Cullen (A., 1922, ii, 672), Hawkins (J. Biol. Chem., 1923, **57**, 493), or the authors' micro-colorimetric method (this vol., 442) at 18°, it will give the p_H of the corresponding blood at 38°. The effect of temperature with concentration of total carbon dioxide constant is the same on the c_H of the corpuscles and the corresponding plasma.
S. S. ZILVA.

Changes in acid-base equilibrium of the blood caused by hæmorrhage. p_H of serum and plasma of dog blood. Colorimetric determination of p_H of blood plasma. M. A. BENNETT (J. Biol. Chem., 1926, **69**, 675—692, 693—696, 697—702).—Extensive hæmorrhage in dogs was followed immediately by an acidosis; this gave place to an alkalosis on the succeeding day, normal conditions being attained several days later. No difference could be detected between the p_H of the serum and that of the plasma

in normal dogs. The colorimetric method of Cullen (A., 1922, ii, 672) is not applicable with accuracy to the determination of the p_H of blood after hæmorrhage, since, under these conditions, the magnitude of the *C* correction shows large variations.

C. R. HARINGTON.

Colloidal condition and chemical and physical constitution of blood-serum. IV. L. PETSCHACHER, R. RITTMANN, and O. GALEHR (Z. ges. exp. Med., 1926, **48**, 421—443; from Chem. Zentr., 1926, I, 1835; cf. *ibid.*, 712).—An incomplete correlation is observed between the viscosity, non-protein nitrogen, calcium content, K : Ca ratio, corrected conductivity, and carbon dioxide capacity of the serum.

E. C. SMITH.

Cholesterol as prosthetic group in serum-globulin. N. TROENSEGAARD and B. KOUDAHL (Z. physiol. Chem., 1926, **157**, 62—63; cf. this vol., 634).—To get the best yield of the hydrocarbon $C_{16}H_{28}$ from serum-globulin, the acetylation must be carried out at 135°, not at 115°, as formerly given.

H. I. COOMBS.

Quantitative determination of the lipins present in proteins salted out of horse plasma. A. H. T. THEORELL (Biochem. Z., 1926, **175**, 297—317).—The proteins precipitated from horse plasma by fractional saturation with ammonium sulphate contain, even after dialysis and redissolution, considerable quantities of lipins; 89·3% of the total fatty acids and 77% of the total cholesterol of the plasma are thus precipitated. The ratios of the total cholesterol to the ether-soluble phosphorus of the fibrinogen, globulin, and albumin fractions were, respectively, 20·5, 16·9, and 9·7, an indication of the distribution of cholesterol and phosphatides between these three fractions. The Liebermann–Burchard and Liebermann reactions for cholesterol and for hydroxycholesterol are not the same, since with the latter the reaction is much more rapid in all circumstances than with the former. For the determination of the total cholesterol, different extinction coefficients must be used for the two substances. Liebermann's reaction (in the absence of chloroform) is strongly positive with pure cholesterol ester and Lifschütz's method for determining free cholesterol by means of this reaction is not recommended. J. PRYDE.

Blood-sugar. X. Distribution of dextrose in plasma and corpuscles. P. RONA and M. SPERLING (Biochem. Z., 1926, **175**, 253—267).—From a series of studies of alimentary hyperglycæmia without insulin, it is concluded that the sugar of the formed elements is lower, and increases less rapidly, than that of the plasma and of the whole blood; that an increase in corpuscular sugar takes place more slowly than a decrease, and that rabbits and humans give similar results. During the hypoglycæmic phase resulting from the action of insulin, the plasma and whole blood-sugar become lower than normal, whilst the corpuscular sugar increases, the latter becoming higher than that of the plasma. A reversal of this distribution occurs with the disappearance of the insulin effect. Small amounts of insulin increase the volume of the corpuscles, larger amounts lessen it.

J. PRYDE.

Proteolytic enzymes of the serum. III. Chemically determinable toxin–antitoxin union *in vitro*. H. J. FUCHS and M. VON FALKENHAUSEN (Biochem. Z., 1926, **176**, 92—100).—The toxin–antitoxin union is characterised chemically by the disappearance of residual nitrogen with the formation of a protein precipitable by 2·5% trichloroacetic acid. The residual nitrogen of both toxin and antitoxin takes part equally in the formation of this protein (cf. Fuchs, this vol., 536).

P. W. CLUTTERBUCK.

Action of ammonia on complement. The fourth component. J. GORDON, H. R. WHITEHEAD, and A. WORMALL (Biochem. J., 1926, **20**, 1028—1035).—Small quantities of ammonia have a specific destructive action on complement. This is due to the inactivation of a fourth, hitherto unknown, component of the complement. It is associated with the albumin fraction, is relatively thermostable (it is not destroyed at 56° for ½ hr., but is inactivated readily at 66°), and is not dialysable. The inactivation process is not immediate, and depends on the temperature and strength of ammonia. Prolonged treatment with ammonia has a general destructive action on the other components of the complement owing to the alkalinity of the solution.

S. S. ZILVA.

Calcium and complement action. J. GORDON, H. R. WHITEHEAD, and A. WORMALL (Biochem. J., 1926, **20**, 1036—1043).—The non-diffusible calcium of serum is connected with its complement activity. The calcium content of the various fractions of serum obtained by using carbon dioxide and other acids and the power to reactivate ammonia-inactivated serum (see above) show some correlation. Calcium in various forms was found ineffective in reactivating ammonia-treated serum. The calcium of the serum or any added calcium introduced as calcium oleate is found in the albumin fraction when the complement is decomposed by carbon dioxide, hydrochloric acid, or phosphoric acid. With acids giving insoluble calcium salts, the calcium is found in both fractions, and in the case of oxalic acid mainly in the globulin fraction. The fractions obtained by these acids are inactive either singly or when combined. No alteration in dialysable calcium occurs during inactivation by ammonia. S. S. ZILVA.

Fourth component of complement and its relation to opsonin. J. GORDON, H. R. WHITEHEAD, and A. WORMALL (Biochem. J., 1926, **20**, 1044—1045).—Serum in which the fourth component of complement (see preceding abstracts) had been inactivated by means of ammonia lost none of its opsonic activity. S. S. ZILVA.

Urico-oxydase of blood and the true uric acid content of the blood. FLATOW (Munch. med. Woch., 1926, **73**, 12—14; from Chem. Zentr., 1926, I, 1819).—All previously recorded figures for the uric acid content of the blood are too low, the error being due to the presence in blood of an oxydase, which, in the presence of air, destroys 90% of the uric acid before the determination is carried out. The enzyme acts most strongly in weak alkaline solution, but will also act in weak acid. It is not

removed by protein precipitants and may be detected in serum after removal of the protein. It is very stable. E. C. SMITH.

Sulphate content of blood-serum and of aqueous humour. W. HEUBNER and R. MEYER-BISCH (Biochem. Z., 1926, **176**, 184—188).—The ultrafiltrate of human blood-serum contains 3—5, of rabbit's and cow's serum 9—14, and of rabbit's aqueous humour 6 mg.% SO_4. P. W. CLUTTERBUCK.

Lactic acid content of aqueous humour. I. Relationship between the lactic acid contents of blood plasma and aqueous humour. A. WITTGENSTEIN and A. GAEDERTZ (Biochem. Z., 1926, **176**, 1—16).—The lactic acid content of the aqueous humour of dogs, cats, and rabbits is very dependent on that of the blood plasma. The resting value in the aqueous humour (20—24 mg.%) is higher than that of the plasma (15—18 mg.%). During activity, the lactic acid content of the aqueous humour increases, following the increase in that of the plasma, but never attaining the highest values of the plasma. The lactic acid content of the aqueous humour decreases more slowly to the resting value than that of the plasma, and it is not changed by exposure of the animals to intense light or to long periods of darkness. The higher values of the aqueous humour, therefore, cannot be explained in terms of the activity of the retina. Dialysis of serum against normal saline through a collodion membrane led to equalisation of the concentrations of lactic acid on the two sides of the membrane. The same result was obtained on dialysis of a solution containing gelatin with calcium or lithium lactate against normal saline. The p_H of these solutions has no influence on the distribution, and it would appear, therefore, that lactic acid of the aqueous humour behaves differently from that of the dialysate of blood plasma. P. W. CLUTTERBUCK.

Proteins of lymph and suprarenal glands. M. M. SABRY (Biochem. Z., 1926, **176**, 109—126).—Systematic fractionation of the proteins of the lymph and suprarenal glands shows that the protein fractions differ for the different glands and that the fractions for a particular gland differ considerably in coagulation point, salting out, and in their content of various groups, particularly of phosphoric acid. A protein is present in the tissues, but not in the blood, which coagulates at 41°. P. W. CLUTTERBUCK.

Proteins of the ovary. E. MEIERSDORF (Biochem. Z., 1926, **176**, 127—133).—The total dry substance, the total nitrogen and carbon contents, the globulin, albumin, pseudoglobulin, and globulin contents, the coagulation points of the individual proteins, and the content of albumose, peptone, diamino- and amino-acids arising on hydrolysis, of saline extracts of the ovary are tabulated. The protein constituents of ovary nucleoprotein contain less tryptophan and indole compounds, but more carbohydrate and amino-acids, than Witte's peptone. P. W. CLUTTERBUCK.

Constitution of the histone of the thymus gland. II. Combining capacity with acids and bases. K. FELIX and A. HARTENECK (Z. physiol. Chem., 1926, **157**, 76—90).—A method of preparation is given, the yield being 25—30 g. of histone sulphate per kg. of gland. The isoelectric point is at p_H 8·51, and a 1% solution has p_H 8·33. The ash-content was 0·9% and the total nitrogen (on ash-free substance) was 17·46%; 16·3% of the nitrogen was in the free amino-form. Figures are given for the p_H of known strengths of sulphuric acid and sodium hydroxide with and without a known quantity of the histone (cf. A., 1925, i, 1203). H. I. COOMBS.

Parathyroid glands and their iodine content. A. M. HJORT, O. M. GRUHZIT, and A. G. FLIEGER (J. Lab. Clin. Med., 1925, **10**, 979—984).—Parathyroid preparations made from the external bovine glands were not contaminated with thyroid tissue. The iodine content of the parathyroids is of no greater magnitude than that of the ovaries, pituitary, and thymus. The iodine found in these glands probably represents its normal distribution throughout the body tissues. CHEMICAL ABSTRACTS.

Occurrence of iodine in the human and animal organism. E. MAURER and S. DIEZ (Münch. med. Woch., 1926, **73**, 17—20; from Chem. Zentr., 1926, I, 1827).—The iodine content of the venous blood of women is increased during menstruation from 9·2 to $19{\cdot}3\times10^{-6}$%, there being no increase in pregnancy. In blood from the umbilical vein, a slight increase to $11{\cdot}5\times10^{-6}$% was observed. The embryo thyroid gland during the last 3 months of gestation contains iodine. The colostrum has a high iodine content during the first day after birth, but then falls to normal. E. C. SMITH.

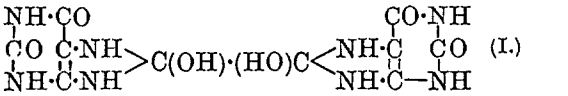
Chemical constitution of spermine. III. Structure and synthesis. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING.—See this vol., 1128.

Muscle extractives. XXV. Absence of β-alanine in the degradation products of muscle proteins. S. KAPLANSKY (Z. physiol. Chem., 1926, **158**, 19—21).—Dog muscle, carefully freed from carnosine by extraction with water, was pressed, and after hydrolysis and esterification the ester fractions, b. p. 60—80° and 80—100°, were examined for ethyl β-aminopropionate. No odour of ethyl acrylate was observed in either fraction after heating (cf. Abderhalden and Fodor, A., 1913, i, 798), nor in a "β-alanine fraction" of the copper salts. β-Alanine is therefore absent from the hydrolysate, and its presence in carnosine degradation products is possibly due to secondary formation from asparagyl- and lysyl-histidines. C. HOLLINS.

β-Hydroxybutyric acid content of muscle and liver. J. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1926, **175**, 366—370).—In normal muscle-tissue and in fresh normal liver, the authors find less β-hydroxybutyric acid than has been recorded by previous workers. Livers obtained from the slaughter-house gave higher results, in agreement with those of earlier workers. Marriott's observation that the ratio β-hydroxybutyric acid (as acetone)/acetone+acetoacetic acid+β-hydroxybutyric acid, is lower in blood than in other tissues is confirmed. J. PRYDE.

Existence of a characteristic level of nucleic phosphorus in tissues. M. JAVILLIER and H. ALLAIRE (Bull. Soc. Chim. biol., 1926, **8**, 924—933).—See this vol., 969.

Leucopterin, the white wing-pigment of the common white butterfly (*Pieris brassicæ* and *P. napi*). C. SCHÖPF and H. WIELAND (Ber., 1926, **59**, [*B*], 2067—2072; cf. A., 1925, i, 1464).—Extraction of the wings with 0·5*N*-ammonia gives an ammonium salt which very closely resembles ammonium urate in most of its reactions. Analyses of the



(I.)

leucopterin derived therefrom indicates the formula $C_5H_5O_3N_4$; it is suggested that leucopterin is a dipurine derivative (I). The *sodium*, $C_{10}H_9O_6N_8Na,2H_2O$, *potassium*, *silver*, and *barium* salts are described.

H. WREN.

Pigments of butterflies' wings. II. Occurrence of the pigment of *Melanargia galatea* in *Dactylis glomerata*. D. L. THOMSON (Biochem. J., 1926, **20**, 1026—1027).—The grass *Dactylis glomerata* contains a flavone or flavonol, which is present both free and in glucosidic combination and is identical with the pigment of the wings of the butterfly *Melanargia galatea* (cf. this vol., 424). S. S. ZILVA.

Diamino-acids of the shield of *Cheledone imbricata*. W. KEIL (Ber., 1926, **59**, [*B*], 2012—2013).—There is no essential difference in proportions of diamino-acids in the shield and in other horny substances. The difference in physical properties of the shield from those of other keratins depends probably on the differing proportions of the monoamino-acids (cf. Buchtala, A., 1911, ii, 1009).

H. WREN.

Effect of protein concentration on the chloride equilibrium between plasma and cerebrospinal fluid. F. FREMONT-SMITH and M. E. DAILEY (J. Pharmacol., 1926, **27**, Proc. 255—256).—In comparison with plasma, cerebrospinal fluid is practically protein-free, but contains chlorides in much higher concentrations. The manner in which the high chloride level in cerebrospinal fluid depends on the protein content of plasma is discussed.

CHEMICAL ABSTRACTS.

Application of the Hench-Aldrich urea index to the cerebrospinal fluid. G. S. GRAHAM and S. H. MACCARTY (J. Lab. Clin. Med., 1925, **10**, 548—551).—This method gives a rapid and fairly accurate determination of urea in cerebrospinal fluid. The normal urea index ranges from 30 to 50.

CHEMICAL ABSTRACTS.

Colloidal gold reaction using gold prepared by an electrical method. P. J. MANHEIMS and A. BERNHARD (J. Lab. Clin. Med., 1925, **11**, 235—241).—The method of preparation of colloidal gold is described. Blood in cerebrospinal fluid will precipitate colloidal gold. The same type and intensity of reaction is obtained by this gold as that prepared chemically. CHEMICAL ABSTRACTS.

Nitrogen equilibrium during secretion under normal and pathological conditions of gland innervation. D. ALPERN and L. LINDENBAUM (Biochem. Z., 1926, **176**, 62—72).—The effect of section of the sympathetic nerves with and without injection of calcium chloride and of carbamide on the total and residual nitrogen of salivary secretion leads to the conclusion that the sympathetic nerves regulate the nitrogen equilibrium of the secretions of these glands. The nitrogen is made up of the total nitrogen of the mucin arising from the gland and the residual nitrogen, which appears to be almost exclusively due to carbamide which passes into the secretion from the blood. P. W. CLUTTERBUCK.

Gastric secretion. I. Hydrochloric acid and chlorine concentration of pure gastric juice. II. Effect of strenuous work on gastric secretion. F. DELHOUGNE (Deut. Arch. klin. Med., 1926, **150**, 70—77, 78—82; from Chem. Zentr., 1926, I, 1831).—I. The hydrochloric acid concentration of gastric juice shows considerable variation, the maximum being 0·6%. The absolute amount of hydrochloric acid is constant, not altering with hyperacidity or hypoacidity.

II. The lowered alkaline reserve following muscular exercise is accompanied by an increase in the hydrogen-ion concentration of the gastric juice, which can be prevented by the injection of atropine.

E. C. SMITH.

Phosphorus content of human milk and cow's milk. E. LENSTRUP (J. Biol. Chem., 1926, **70**, 193—202).—Human milk contains, on the average, 14·2 mg. of total phosphorus per 100 c.c., composed of 2·6 mg. of acid-insoluble (caseinogen) phosphorus and 11·6 mg. of acid-soluble phosphorus; cow's milk has 95·4 mg. of total phosphorus (17·1 mg. of acid-insoluble and 78·3 mg. of acid-soluble). In cows, the organic phosphorus remains constant throughout the year, whilst the inorganic phosphorus falls when the animals are at pasture. C. R. HARINGTON.

Uric acid in human sweat. K. VOIT (Arch. exp. Path. Pharm., 1926, **116**, 320—333).—Human sweat contains volatile phenols and, perhaps, other substances which give a blue colour with the uric acid reagent of Folin and Denis. The presence of a trace of uric acid was indicated by the method of Morris (A., 1922, ii, 328), but it was not separable by the usual methods. R. K. CANNAN.

Cardiac stimulant excreted by the kidneys. E. K. FREY and H. KRAUT (Z. physiol. Chem., 1926, **157**, 32—61).—Various preparations were made from urine; 0·5 mg. of the most active had an effect on the heart equal to that of 5 c.c. of urine, which contains 75—100 mg. of dry material. The substance was also detected in blood. Most of the products gave the tests for protein, but one was obtained which did not. H. I. COOMBS.

Influence of injections of neutral, acid, and alkaline salt solutions on urine secretion. K. MISUMI (J. Biochem. [Japan], 1925, **5**, 417—439).—A study of the influence of injections of acid and alkaline phosphate solutions on the rate of secretion of urine. The blood carbon dioxide increases after the injection of disodium hydrogen phosphate and diminishes after that of sodium dihydrogen phosphate, the p_H value remaining constant. An injection of sodium hydrogen carbonate increases the carbon

dioxide content of the blood plasma much more than alkaline phosphate solution.

CHEMICAL ABSTRACTS.

Influence of calcium and magnesium chloride injections on urine secretion. K. MISUMI (J. Biochem. [Japan], 1925, **5**, 441—448).—A study of the secretory activity of the kidney. The urinary reaction in both cases is alkaline. CHEMICAL ABSTRACTS.

Comparative analyses of fæces of laying hens, with and without a calcium carbonate supplement in the diet. G. D. BUCKNER, J. H. MARTIN, and A. M. PETER (Poultry Sci., 1925, **4**, 165—170).—Hens not given oyster shells consumed the larger amount of soil and inorganic matter; the calcium content of their fæces fell; carbonate was not present, all the calcium carbonate being used for egg-shell formation. In these cases, the greater part of the calcium was present as phosphate.

CHEMICAL ABSTRACTS.

Behaviour of the urinary C : N ratio in phenylhydrazine-anæmia. T. KANAMORI (Biochem. Z., 1926, **175**, 330—334).—Anæmia produced in dogs by the injection of phenylhydrazine resulted in a small increase in the output of carbon and nitrogen in the urine, but any tendency of the C : N ratio to increase was slight, and no definite conclusions are reached.

J. PRYDE.

Glycolytic power of animal organs in carcinoma. Z. DISCHE and D. LASZLO (Biochem. Z., 1926, **175**, 412—448).—The non-carcinomatous livers of mice with an active carcinoma in another part (*e.g.*, in the pelvic muscles) show a marked increase in glycolytic power over normals, both as regards their own glycogen and added dextrose. The kidney, which in normal animals shows a much higher glycolytic power than the liver, gives a slight increase in the carcinomatous animals. It is suggested that the increased glycolysis is due to the liberation of specific substances from the carcinoma into the blood-stream. J. PRYDE.

Malignant tumours. III. SH-SS content. R. BIERICH and K. KALLE (Z. physiol. Chem., 1926, **158**, 1—6).—The ratio of reduced (SH) to oxidised (SS) glutathione in normal tissue and in the tissue of benignant tumours is less than 1; in malignant tumours, the ratio is greater than 1, and the actual SH value varies considerably. The SH and SS values are determined by the methods of Tunnicliffe (A., 1925, i, 752) and Walker (this vol., 194).

C. HOLLINS.

Calcium of the blood. VIII. Calcium content of the blood in diabetes mellitus. E. KYLIN (Zentr. inn. Med., 1926, **47**, 79—80; from Chem. Zentr., 1926, I, 1834; cf. Acta Med. Skand., **61**, 345).—The blood calcium is increased in cases of diabetes with normal blood pressure, with lowered K : Ca ratio. With high blood pressure, the calcium is increased only in exceptional cases, the K : Ca ratio being high. E. C. SMITH.

Production of conjugated glycuronic acids in depancreatised dogs. A. J. QUICK (J. Biol. Chem., 1926, **70**, 59—69).—Administration of benzoic acid or of borneol to depancreatised dogs is followed by as much excretion of conjugated glycuronic acid as in normal animals; the dextrose of the urine, however, falls by an amount corresponding with the glycuronic acid formed, which indicates that the dextrose and the glycuronic acid are derived from a common (protein ?) source. C. R. HARINGTON.

Blood sugar. II. Free and protein sugar in plasma and corpuscles of normal and diabetic individuals. Mechanism of insulin hypoglycæmia. B. GLASSMANN (Z. physiol. Chem., 1926, **158**, 113—138).—Using the micro-method previously described (this vol., 192), it is found that in normal individuals after a meal the average total sugar (*i.e.*, the sum of the "free" and the "protein" sugar) content of whole blood is 0·76%. The average for eight diabetics is 0·94%. The blood-corpuscles of both normals and diabetics contain no "free" sugar, but from 0·3 to 0·5% of "protein" sugar, chemically bound to the hæmoglobin. The "free" sugar of the plasma in normals is from 0·12 to 0·18%, in diabetics from 0·2 to 0·7%. Insulin causes an increase of the "protein" sugar at the expense of the "free" sugar. The bearing of these results on insulin hypoglycæmia is discussed. H. D. KAY.

Blood changes in convulsions, especially in epilepsy. O. WUTH (Bull. Johns Hopkins Hosp., 1926, **38**, 389—408).—Non-protein nitrogen, uric acid, creatinine, and serum-protein exhibit a non-uniform increase during or shortly after convulsions. These changes are typical of all physical exertion.

CHEMICAL ABSTRACTS.

Carbohydrate metabolism in experimental ileus. H. LANGE and H. SPECHT (Arch. exp. Path. Pharm., 1926, **117**, 87—91).—In rabbits a rise in blood-sugar up to 0·5% and a rapid decrease in liver glycogen occurred. C. RIMINGTON.

Formation of sulphur in discharges. M. LOEPER, J. DECOURT, and J. TONNET (Compt. rend. Soc. Biol., 1925, **93**, 1350; from Chem. Zentr., 1926, I, 1836).—There is a parallelism between the sulphur and amino-acids formed in inflammatory and serous exudates. E. C. SMITH.

Formation of amino-acids in discharges. M. LOEPER, J. DECOURT, and A. LESURE (Compt. rend. Soc. Biol., 1925, **93**, 1348—1349; from Chem. Zentr., 1926, I, 1837).—Amino-acids in pleural discharges are formed by proteolytic processes in the exudate, arising in sepsis from the action of bacterial and leucocytic enzymes, in aseptic cases from the enzymes of the leucocytes and of the exudate itself.

E. C. SMITH.

Congenital porphyrinuria. L. MACKEY and A. E. GARROD (Quart. J. Med., 1926, **19**, 357—374).—The pigment most abundantly present in the urine was uroporphyrin, and in the fæces coproporphyrin (stercoporphyrin). The pigment in the teeth gave a pink fluorescence with hydrochloric acid, but no absorption bands. CHEMICAL ABSTRACTS.

Behaviour of bile acids in blood and urine during pregnancy. Methods of detection and determination of bile. H. KLEESATTEL (Arch. Gyn., 1925, **123**, 638—645; from Chem. Zentr., 1926, I, 1836). E. C. SMITH.

Thiocyanates and cellular respiration. N. TARUGI (Annali Chim. Appl., 1926, 16, 281—293; cf. this vol., 190).—When a solution of a ferric salt is treated with potassium thiocyanate, the acidity increases, owing to the formation of a ferrous salt; if the red ether-soluble complex is treated with potassium oxalate, it is decolorised, and ferrous oxalate separates on adding ammonia. The resulting solution gives no colour on acidification, but if ferric chloride is then added, an intensely red solution is obtained of a substance not extracted by ether. It is suggested that a perthiocyanate is formed.

It is found that small quantities of thiocyanic acid have no effect on the oxidation of oxalic acid by excess of iodic acid, but retard oxidation when oxalic acid is in excess. E. W. WIGNALL.

Oxidation of phenols by tissues and the significance of surfaces for biological oxidation. H. HANDOVSKY (Biochem. J., 1926, 20, 1114—1124).—The effect observed by Szent-Györgyi (A., 1925, i, 93, 708, 709) is due to a displacement of lactic acid from the surface of the glass-powder present in his muscle preparations by *p*-phenylenediamine, thus enabling the acid to be oxidised. It is, therefore, not due to the activation of the oxidation of lactic acid by muscle by the presence in the system of the ice-water extract of the muscle and *p*-phenylenediamine. *p*-Phenylenediamine is oxidised by washed muscle and by charcoal, but not by coagulated muscle. Heating washed muscle at 60° for 1 hr. diminishes the activity; heating at 80° entirely destroys it. The oxidation of this compound is therefore a surface catalysis. The oxidation of quinol and pyrocatechol, on the other hand, is not accelerated by surfaces such as charcoal. *p*-Phenylenediamine accelerates aërobically and anaërobically the oxidation of reduced glutathione. Hæmoglobin and methæmoglobin catalyse the oxygen uptake of washed muscle, but do not affect lactic acid oxidation. S. S. ZILVA.

Biological value of the carbon of different proteins. O. KAUFFMANN-COSLA and J. ROCHE (Bull. Soc. Chim. biol., 1926, 8, 942—957).—Dogs were fed on a ration deficient in nitrogen and supplemented with the protein to be studied. When caseinogen was added, the urinary nitrogen, carbon, and calcium were increased. With egg-white the increase was greater, but with wheat-albumin it was absent. From the C : N ratio and the ratio of protein carbon intake to urinary carbon it was concluded that the nutritive value of these proteins was in the descending order—wheat-albumin, caseinogen, egg-white. R. K. CANNAN.

Intestinal chemistry. IV. Method for study of food utilisation. V. Carbohydrates and absorption of calcium and phosphorus. VI. Investigation of absorption in different parts of the intestinal tract. VII. Absorption of calcium and phosphorus in small and large intestines. O. BERGEIM (J. Biol. Chem., 1926, 70, 29—33, 35—45, 47—50, 51—58).—IV. See. A., 1925, i, 99.

V. Application of the author's method (*loc. cit.*) shows that, in rats on a diet lacking vitamin-*D*, the degree of absorption of calcium and phosphorus is not affected by addition to the diet of starch, dextrose, lævulose, and maltose in amounts of less than 50% of the diet and is only slightly increased by these large amounts; addition of dextrin in large amount causes a definite increase in absorption of calcium, but a much greater effect is obtained by addition of lactose in amounts of 25% of the diet and upwards. This is ascribed to the favourable effect on calcium absorption exerted by the acid reaction of the intestinal contents which is known to result from ingestion of lactose. Addition of lactose to the basal diet was not sufficient to protect against rickets in the absence of vitamin-*D*.

VI. Extended application of the author's method to examination of contents of different parts of the intestine is discussed.

VII. *Post-mortem* examination of the contents of the intestines of normal and rachitic rats on standard diets shows that both normal and rachitic animals absorb calcium from and excrete phosphorus into the small intestine; whereas, however, the normal rat absorbs calcium and phosphorus from the large intestine, the rachitic rat excretes calcium into this region and fails to absorb phosphorus therefrom. It would seem, therefore, that, in rickets, the failure is not in the absorption of calcium, but in its deposition; it is suggested that this failure is due to the low concentration of phosphates in the blood, to maintain which at the normal level may be the function of vitamin-*D*. C. R. HARINGTON.

Carbohydrate metabolism. I. Importance of phosphate in carbohydrate metabolism. I. ABELIN (Biochem. Z., 1926, 175, 274—292).—On administering carbohydrate together with disodium hydrogen phosphate to rats, a lower R.Q. is observed than when the same amount of sugar is given alone, on the average 0·8—0·85 instead of 0·9—1·0. The increased production of carbon dioxide which normally accompanies utilisation of carbohydrate is lessened by the simultaneous administration of phosphate. Hyperglycæmia and insulin hypoglycæmia are both affected by phosphates and other salts. By the simultaneous (or successive) administration of rice, sucrose, dextrose, or dihydroxyacetone as carbohydrate source, and disodium hydrogen phosphate, glycogenesis in the liver is markedly inhibited, whilst the muscle glycogen is not definitely influenced. On the other hand, the formation of glycogen in the liver is not affected by lævulose and phosphate—both lævulose alone and lævulose+phosphate considerably increase liver glycogen. Sodium dihydrogen phosphate gives results similar to those obtained with the disodium salt. A similar lowering of the R.Q. and of the carbon dioxide production occurs after ingestion of protein (raw flesh) and phosphate. It is concluded that the presence or otherwise of phosphates and certain other inorganic salts may produce great modifications in the course of carbohydrate metabolism. J. PRYDE.

Sugar in the organism. I. Breakdown of sugar under the action of dilute alkalis. F. FISCHLER (Z. physiol. Chem., 1926, 157, 1—31).—By the action of dilute alkali on dextrose solutions a substance is formed which gives an iodoform

reaction. Dilute acids do not produce this substance. The best results were obtained by the use of a solution containing 6% of crystallised sodium sulphite and 0·04*M*- or 0·02*M*-sodium carbonate. On distillation, under carefully defined conditions, of this solution mixed with a dextrose solution, methylglyoxal was proved to be present in the distillate by means of its osazone—the yield of methylglyoxal being estimated to be about 7·5%. Dextrose, galactose, maltose, and lactose all give rise to the substance giving the iodoform reaction, but sucrose, dulcitol, mannitol, and sorbitol do not. This is probably due to their having no aldehydic group.

H. I. Coombs.

Carbohydrate metabolism. IX. Influence of insulin and muscle-tissue on dextrose *in vitro*. X. Occurrence of insulin complement in muscles of warm- and cold-blooded animals. XI. Occurrence of "new glucose" in fermentation of αβ-glucose. XII. Properties of insulin complement. C. Lundsgaard, S. A. Holbøll, and A. Gottschalk (J. Biol. Chem., 1926, **70**, 71—77, 79—82, 83—87, 89—95; cf. A., 1925, i, 1494; this vol., 861).—IX. For the production of "new glucose" from ordinary dextrose the action of the insulin and that of the muscle-tissue must be simultaneous; the substance in muscle-tissue which takes part in this reaction is designated insulin complement.

X. Insulin complement has been demonstrated in the muscles of the rat and rabbit, and in those of the frog, the cod, and the lobster; in the case of the cold-blooded animals, the insulin complement was active at 20°.

XI. No evidence could be obtained of the formation of "new glucose" during fermentation of dextrose by yeast; the latter process must therefore be regarded as of a nature different from the catabolism of dextrose in the animal body.

XII. Insulin complement could not be detected in the expressed juice of muscle; it could not be removed from muscle by washing with water and it was destroyed by brief heating at 70°; it cannot, therefore, be identical with the muscle co-enzyme of Meyerhof (A., 1918, i, 242, 464).

C. R. Harington.

Physiology of plain muscle. V. Influence of caffeine on lactic acid formation. C. L. Evans (Biochem. J., 1926, **20**, 893—901).—In the presence of caffeine in concentrations from 0·002 to 0·4%, the rate of lactic acid formation in plain muscle under anaërobic conditions is diminished. This diminution is also observed in phosphate solutions of p_H 4·5 and p_H 9·0. This effect is merely a delay, and is not due to the early death of the muscle, since the lactic acid maximum is reached ultimately. The oxidative recovery process is not affected by caffeine, nor is the oxygen usage of the fresh tissue altered. The effect of arsenates in accelerating lactic acid formation is reduced by the presence of caffeine.

S. S. Zilva.

Fate of amino-acids injected into the blood. H. Schlossmann (Arch. exp. Path. Pharm., 1926, **117**, 132—136).—Intravenously introduced amino-acids disappear very rapidly, except for a small quantity, from the blood-stream. Extirpation of the kidneys does not affect the process, but exclusion of the liver from the circulation renders the disappearance less rapid.

C. Rimington.

Catabolism of amino-acids. I. Fate of γ-aminobutyric and δ-aminovaleric acids in the phloridzinised dog. R. C. Corley (J. Biol. Chem., 1926, **70**, 99—108).—Administration to phloridzinised dogs of γ-aminobutyric acid leads to excretion of extra dextrose equivalent to three carbon atoms of the amino-acid; after feeding δ-aminovaleric acid, on the other hand, small amounts only of extra dextrose are excreted. Since all other possible degradation products are known to give rise to extra dextrose under these conditions, the latter acid must be oxidised through the stage of β-aminopropionic acid or of glutaric acid; γ-aminobutyric acid is probably oxidised through the stage of succinic acid which gives rise to extra dextrose.

C. R. Harington.

Intermediary metabolism of histidine. I. S. Edlbacher (Z. physiol. Chem., 1926, **157**, 106—114).—In the liver, an enzymic cleavage of histidine takes place, giving rise to ammonia, but no carbamide. The optimum reaction for the activity of the enzyme is at p_H 9·0. The enzyme is still active at p_H 5·0, but not at p_H 2·0. It is stable at 50°, but its activity is diminished by heating for 10 min. at 70° and destroyed by heating for a similar period at 90°. In several animals which were investigated, the enzyme was present only in the liver. The maximum yield of ammonia from the histidine was 58—62% and the author suggests that two of the three atoms of nitrogen of each molecule are eliminated in the form of ammonia.

H. I. Coombs.

Methylation. N. J. Novello, B. Harrow, and C. P. Sherwin (J. Pharm. Exp. Ther., 1926, **27**, Proc., 242—243).—Glyoxaline was largely destroyed in the body, but was not detoxicated by methylation; it yielded ammonia, some carbamide, and a considerable amount of uric acid and allantoin. Pyridine was qualitatively, but not quantitatively, methylated in the organism of the dog. Piperidine was extremely toxic, but was partly excreted as an ethereal sulphate. Quinoline yielded a pyridine derivative. 2-Methylquinoline yielded some acetamidobenzoic acid. Glyoxalinepyruvic acid can to some extent replace histidine in the diet; glyoxalinelactic and -acrylic acids are less efficient.

Chemical Abstracts.

Is the degradation of uric acid by man an established fact? S. J. Przylecki (Bull. Soc. Chim. biol., 1926, **8**, 804—811).—Uricase is absent from the tissues of man and numerous vertebrates and invertebrates. The administration of uric acid and purines to man does not increase the amount of excreted allantoin, and allantoin is excreted quantitatively when administered. Hence uric acid is regarded as the end-product of purine metabolism in man.

H. J. Channon.

Effect of lack of inorganic salts on man. F. Thielmann (Arch. exp. Path. Pharm., 1926, **116**, 261—271).—Determinations were made of the sodium,

potassium, calcium, phosphorus, and chlorine in the urine and fæces during a period of 11 days on a diet containing insignificant quantities of inorganic salts. The sodium, potassium, and chlorine excretion fell in 4 days to a low level, which was thereafter maintained. Over the whole period there was a loss of 7·95 g. of chlorine, 3·2 g. of sodium, and 4·2 g. of potassium from the body. The excretion of calcium and phosphorus was less regular, but a total negative calcium balance was disclosed. There was no evidence of acidosis or increased protein catabolism. The effect on the chief constituents of the serum was followed. R. K. CANNAN.

Calcium ionisation in physiological solutions. L. JENDRASSIK and E. MOSER (Biochem. Z., 1926, **175**, 461—470).—The electrical conductivity of solutions containing calcium chloride and sodium hydrogen carbonate shows a gradual diminution. After 24 hrs., the decrease is usually less than that calculated from the formula of Rona and Takahashi on the basis of a precipitation of calcium carbonate. The action of a Tyrode solution, which had been kept for 24 hrs., on the rabbit's intestine is such as would be expected had its calcium content diminished. It is concluded that in physiological solutions containing hydrogen carbonate and calcium the calcium-ion concentration diminishes slowly whether or not a solid phase (calcium carbonate) is being formed. J. PRYDE.

Effect of lipins in interchanges between cells and the environment. D. T. MACDOUGAL (Carnegie Inst. Wash. Yearbook, 1922, **21**).—Evidence on the occurrence of lipins and phosphatides in cells indicates that the external layer of protoplasm is essentially a deposit of these fatty substances. CHEMICAL ABSTRACTS.

Alkalosis produced by ingesting urea. E. F. ADOLPH (Amer. J. Physiol., 1925, **72**, 185—186).—When urea, ammonium hydrogen carbonate, or ammonium citrate is ingested by man, the alkalinity of the blood increases, probably owing to the formation of ammonia. A. A. ELDRIDGE.

Influence of glutathione on the oxidation of fats and fatty acids. E. N. ALLOTT (Biochem. J., 1926, **20**, 957—964).—In studying the influence of glutathione on the oxidation of linseed oil and of linolenic acid, it was found that the reaction depended mainly on two variables, viz., the condition of the oil or fatty acid and the iron content of the system. The results obtained by Hopkins (A., 1925, i, 1499) in this connexion are therefore not always reproducible. The behaviour of the fatty acid was found to be much more like that of the glyceride. Some samples of oil were less "active" than others, but the "activity" increased on storage, and could also be enhanced by aërating the oil. Linolenic acid and some samples of linseed oil took up oxygen in aqueous suspension without the addition of glutathione. The "double uptake" observed by Hopkins with fatty acids at p_H 7·5 appears to depend mainly on the lack of spontaneous activity of the fatty acid and on the iron content of the system. S. S. ZILVA.

Biological significance of *cis-trans*-isomerism. E. A. COOPER and S. H. EDGAR (Biochem. J., 1926, **20**, 1060—1070).—The dibasic unsaturated *trans*-acids are superior to the *cis*-isomerides in bactericidal action, although they are weaker acids. The *trans*-compounds precipitate proteins and inhibit enzymes more readily than the *cis*-isomerides. The latter are, however, absorbed by protein in larger amounts. The uptake of the two isomerides by protein is probably an adsorption process, since there is no evidence of chemical interaction with protein or amino-acid. Fumaric acid, which is a weaker poison than maleic acid to the higher animals, is a better disinfectant than its *cis*-isomeride. S. S. ZILVA.

Narcosis. Partition coefficients of hypnotics between water and organic solvents, particularly those possessing double linkings. L. VELLUZ (Bull. Soc. Chim. biol., 1926, **8**, 751—764).—The distribution of a number of sulphones, malonylcarbamides, and hydantoins between water and hydrocarbons, fats, fatty substances plus lanolin, fatty acids, and essential oils has been studied. For fats, the partition coefficient increases with the degree of unsaturation of the fat. Only sulphonal, trional, and gardenal give a coefficient with hydrocarbons. In general, it is the presence of the hydroxyl and carboxyl groups and of double linkings in lipins which influences the solubility of hypnotics in these substances. The addition of cholesterol and its esters affects the partition only in so far as it modifies the degree of unsaturation of the lipin. H. J. CHANNON.

Blood fibrin and lævulose tolerance in acute and chronic carbon tetrachloride intoxication. P. D. LAMSON and R. WING (J. Pharm. Exp. Ther., 1926, **28**, 399—408).—Approximately 0·25 c.c. of carbon tetrachloride, given orally, per kg. body-weight for dogs is necessary to produce a fall in blood fibrin. Maximum oral doses of alcohol alone do not produce changes in blood fibrin, nor does simultaneous administration of alcohol and carbon tetrachloride reduce the threshold dose of the latter. A single dose of carbon tetrachloride causes derangement of liver function, *e.g.*, increase of bile pigments in blood, reduced tolerance to lævulose, drop in blood fibrin, and disturbance of the phenoltetrachlorophthalein liver function test. However, dogs chronically poisoned with large doses for long periods, although showing great pathological changes in the liver, give normal values for all the above liver function tests. H. I. COOMBS.

Blood cholesterol during ether anæsthesia. A. MAHLER (J. Biol. Chem., 1926, **69**, 653—659).—During ether anæsthesia, the cholesterol content of the blood shows an increase which runs parallel with an increase in the content of dextrose; both increases are prevented if insulin be administered previous to the anæsthesia. C. R. HARINGTON.

Relation of phosphate metabolism to anæsthesia. A. BOLLIGER (J. Biol. Chem., 1926, **69**, 721—731).—Provided that the condition be not complicated by asphyxia or the occurrence of excessive muscular activity, anæsthesia, whether caused by ether, chloroform, or ethylene, is accompanied by a diminution in the inorganic phosphorus of the blood; this is further observed during recovery from anæsthesia, at which time also the urinary excretion

of phosphorus is very low. In depancreatised animals, no change in the phosphorus of the blood is observed during anæsthesia. C. R. HARINGTON.

Effects of acetaldehyde, ether peroxide, ethyl mercaptan, ethyl sulphide, and dimethyl, methyl ethyl, and diethyl ketones when added to anæsthetic ether. W. BOURNE (J. Pharm. Exp. Ther., 1926, **28**, 409—432).—The effects of certain chemicals (which might be present as impurities in ether) during and after prolonged anæsthesia were studied. 0·5% of acetaldehyde does not produce any significant changes, but 1% causes marked respiratory embarrassment and consequent effects on blood pressure. The animals recover well. 0·5% of ether peroxide causes a decided lowering of the blood pressure and pronounced respiratory disturbance, but 0·3%, even after prolonged administration, does not noticeably affect the animal. 1% of ethyl mercaptan, although having a very objectionable odour, does not cause any noticeable effect, nor do diethyl, methyl ethyl, or dimethyl ketones in concentrations up to 5%. 1% of ethyl sulphide causes an extremely severe gastro-enteritis, but with 0·3% no such effect is caused and the blood pressure and respiration are not altered. H. I. COOMBS.

Toxicological properties of certain thiocarbamine compounds. J. V. SUPNIEWSKI (J. Pharm. Exp. Ther., 1926, **28**, 317—323).—The toxicity of dithiopiperazine, thiohippuric acid, and ethyl thiohippurate appears to be proportional to the quantity of sulphur in their molecules. They cause a depression of the central nervous system, which leads very often to paralysis of the respiration, which is the cause of death of warm-blooded animals. The toxic dose of dithiopiperazine decreases the blood-sugar of animals, which seems to depend on the general depression of the animal. The injection of a small dose of dithiopiperazine or thiohippuric acid causes a slight increase of the blood pressure. Toxic doses of these compounds decrease the blood pressure and depress the respiration. H. I. COOMBS.

Transformation of ergotinine into ergotoxine in lactic acid solution. R. HAMET (Bull. Soc. Chim. biol., 1926, **8**, 765—769).—By physiological tests, it is shown that ergotinine in cold dilute lactic acid solution increases in pharmacological activity due to the production of ergotoxine. H. J. CHANNON.

Contributions of the individual principles of *Digitalis* to the action of the complete drug. E. DE GIACOMI (Arch. exp. Path. Pharm., 1926, **117**, 69—86).—The essential difference between digitoxin and digitalis-leaf extracts is that the cardio-inhibitory action of the latter is reversible, whilst that of the former is not. Of the six substances isolated from the leaf extracts, digitoxin is the most active, gitalingenin and bigitalingenin the least so, but the action of the last is four to six times as rapid, and is entirely removed by washing the heart with Ringer solution, the preponderance of the genin substances in the crude leaf-extracts giving these also the character of reversibility. The glucosides are more poisonous and slower in action than the genins. C. RIMINGTON.

Effects of quaternary ammonium compounds on the autonomic nervous system. R. HUNT (J. Pharm. Exp. Ther., 1926, **28**, 367—388).—The toxicity of the tetra-alkylammonium compounds decreased from methyl to ethyl and then increased, the *n*-butyl compound being three times as toxic as the methyl compound. The toxicity of the mixed alkyl compounds was determined by the individual alkyl groups present, but was not strictly parallel to their relative numbers. Typical "muscarine" effects were produced only by tri- and tetra-methyl compounds. The most marked stimulating nicotine action on the ganglion cells of the autonomic nervous system resulted from the methyl compounds. A paralysing "nicotine" action on the ganglion cells of the autonomic nervous system resulted from a great variety of the alkyl "onium" compounds. H. I. COOMBS.

Trypanocidal action of arsenicals. F. M. DURHAM, J. MARCHAL, and H. KING (J. Pharm. Exp. Ther., 1926, **28**, 341—349).—Various substituted aminobenzoyl derivatives of *p*-aminophenylarsinic acid show trypanocidal activity *in vivo*, but their sulphonamide analogues are inactive. As a type of the latter, aminotoluenesulphonylaminophenylarsinic acid and its reduction products, oxide, and arseno-compound, have been closely examined. All three were inactive *in vivo* and the only one active *in vitro* was the oxide, which rendered trypanosomes non-infective at dilutions of 1 in 10,000 and 1 in 40,000 in 30 min. and 5 hrs., respectively. The results are interpreted on the view that the reduction potential of the tissues is insufficient to reduce the sulphonamide type of arsinic acid to the active oxide, and conversely injected oxide is inactivated by oxidation to the acid. H. I. COOMBS.

Micrurgical studies in cell physiology. II. Action of chlorides of lead, mercury, copper, iron, and aluminium on the protoplasm of *Amœba proteus*. P. REZNIKOFF (J. Gen. Physiol., 1926, **10**, 9—21; cf. *ibid.*, 1925—26, **8**, 369).—Experiments are described on the toxicity and penetrating powers of lead chloride, mercuric chloride, copper chloride, ferric chloride, ferrous chloride, and aluminium chloride towards *Amœba proteus*. The cell-membrane appears to be permeable only to aluminium chloride and possibly to cupric chloride. W. O. KERMACK.

Enzyme problem. C. NEUBERG (Z. physiol. Chem., 1926, **157**, 299—315).—A critical examination of Kostytschev's views (this vol., 756) on the constitution of enzymes and the nature of enzymic activity. H. D. KAY.

Inhibition of *Cypridina* luminescence by light. E. N. HARVEY (J. Gen. Physiol., 1926, **10**, 103—110).—Eosin, erythrosin, rose-bengal, cyanosin, acridine, and methylene-blue inhibit the luminescence of *Cypridina* luciferin–luciferase solution in green, yellow, orange, or red light, according to the position of the absorption band of the dye. This inhibition, like that which occurs without dye in bluish-violet light, does not occur in the absence of oxygen. Certain similarities exist between the behaviours of

the luciferin–oxyluciferin system and of the methylene-white–methylene-blue system.
W. O. KERMACK.

Autolysis. VI. Autoproteolysis of entire animal bodies under various conditions. O. STEPPUHN, G. PEWSNER, and A. TIMOFEJEWA (Biochem. Z., 1926, **175**, 471—481).—Autolysis of entire mice from which the gastro-intestinal tract had been removed proceeds more rapidly in the presence than in the absence of the animal's own pancreas and spleen. The mixture was buffered at p_H 7·1, the optimum for tryptases. At the same p_H, autolysis after starvation is increased, and this increase therefore cannot be due to tissue acidity. The presence of thyroid substance in the autolysate increases the extent of the process in both acid (p_H 3·8, the optimum for pepsinases) and alkaline media. After phosphorus poisoning, autolysis is increased only in alkaline ranges. Work also increases the activity of the autolytic tryptases. J. PRYDE.

Effect of fat on the tryptic digestion of protein *in vitro*. M. MAUGHAN (Biochem. J., 1926, **20**, 1046—1051).—Unhydrolysed olive oil in the form of an emulsion does not retard the action of trypsin *in vitro* on albumin previously digested with pepsin.
S. S. ZILVA.

Coagulation [of milk] by rennin. II. Action of heat. A. DE DOMINICIS and L. LA ROTONDA (Annali Chim. Appl., 1926, **16**, 294—299).—Results described in Part I (Annali R. Scuola Sup. d'Agricoltura in Portici, 1922, **17**) threw doubt on theories that calcium salts are concerned in the change in behaviour towards rennin of milk after heating; it was agreed that calcium salts could increase the activity of the rennin, as could acids. It is now found that if the caseinogen in separated milk is filtered out by a Chamberland candle, and then redispersed in the whey, coagulation by rennin is normal, as it is when the whey is intermediately boiled and cooled and when water is used instead of the whey for redispersion. When, however, the caseinogen is filtered out, dispersed in water, and boiled and filtered, no coagulation results on adding rennet, whether the boiled caseinogen is redispersed in water or in whey. Thus phosphates and soluble calcium salts have no action in the coagulation of milk by rennin; the action of heat is merely on the caseinogen. E. W. WIGNALL.

Enzymic cleavage of dipeptides. II. H. VON EULER and K. JOSEPHSON (Z. physiol. Chem., 1926, **157**, 122—139).—The optimum reaction for the action of erepsin on glycylglycine is p_H 7·9—8·0. Addition of glycine or of alanine to the mixture inhibits the hydrolytic action, and this inhibition is more marked at an alkaline p_H than at neutrality. The inhibitory action of these two amino-acids is about equal. Glycine anhydride also inhibits the action, but urea does not. Aceturic acid, hippuric acid, and benzoylglycylglycine do not inhibit the reaction and, like glycine anhydride, none of these three substances are themselves hydrolysed by erepsin. The biuret base of Curtius, although having no free carboxyl group, is, however, hydrolysed, but Witte's peptone is not. The presence of the peptone has a distinct inhibitory effect on the action of erepsin on glycylglycine. H. I. COOMBS.

Effect of substrate concentration on the hydrolysis of starch by the amylase of germinated barley. G. S. EADIE (Biochem. J., 1926, **20**, 1016—1023).—The relation of velocity of hydrolysis of starch by the diastase of germinated barley to the concentration of starch differs from the relation previously described for other enzymes. Salts in large concentration have a slight effect on this hydrolysis, insufficient, however, to account for loss of activity on dialysis. The velocity of hydrolysis is directly proportional to the enzyme concentration and has no effect on the shape of the curve of reducing power (calculated as dextrose) per min. against concentration of substrate. Change in the hydrogen-ion concentration of the medium affects mainly the slope of the curve and only very slightly the point where the zero value is reached. Change in temperature has a similar effect, and the temperature coefficient of the reaction varies from 3 to infinity, according to the concentration of the starch used. The affinity of the diastase for glycogen is much less than for starch. S. S. ZILVA.

Applicability of law of mass action to enzymic sugar and glucoside cleavage. K. JOSEPHSON (Z. physiol. Chem., 1926, **157**, 115—121).—A theoretical discussion in answer to Hedin (this vol., 756).
H. I. COOMBS.

Enzymes and inactivators. K. MYRBÄCK (Z. physiol. Chem., 1926, **158**, 160—301).—The conditions governing the process of inactivation of invertase by a number of reversible and irreversible inhibitors have been investigated with the view of determining the chemical nature of the groups concerned, both in formation of the enzyme–substrate complex and in the hydrolytic process itself.

Invertase purified by the usual adsorption–elution technique has been partly inactivated by the addition of very small quantities of silver nitrate, and the effect of change of c_H on this inactivation studied. The view that invertase is a weak acid (K_a=about 3×10^{-7}) the enzymic activity of which is due to the undissociated molecules is supported by the results. A slightly dissociated inactive silver salt is formed, which may be decomposed by hydrogen sulphide to regenerate active invertase. By adding silver in increasing amounts, the alkaline end of the activity–p_H curve of invertase may be simulated. The amount of substrate present does not affect the equilibrium between silver and invertase. From the amount of silver required at a definite c_H to diminish the activity of the invertase by 50% it is possible to calculate the total quantity of silver-binding substance, *i.e.*, active+inactive enzyme, in a given preparation, and thence the apparent equivalent weight of the enzyme (about 5000). In addition to the known inactivating metallic ions—Ag, Hg, and Au, those of $Cu^{\cdot\cdot}$, $Pb^{\cdot\cdot}$, $Zn^{\cdot\cdot}$, and $Cd^{\cdot\cdot}$ in minute concentration also inactivate invertase in a similar manner. On the other hand, $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, and $Cr^{\cdot\cdot\cdot}$ display little affinity for the enzyme. The silver-inactivated or mercury-inactivated enzyme

is less readily adsorbed by aluminium hydroxide than the active invertase.

A second class of invertase inactivators differs from the type just mentioned in that the magnitude of the inactivating effect diminishes as the substrate concentration increases. In this class, the enzyme is divided between substrate and inactivator. Such inactivators are picric and phosphotungstic acids, which react characteristically with organic bases, and, in a similar way, unite with the basic groups of the invertase molecule to form weakly dissociated salts. Nitrous acid, which reacts more specifically with primary amino-groups, also belongs to this class. Increasing concentrations of sucrose increasingly protect the enzyme from the action of nitrous acid, as do dextrose and lævulose, which are actually known to react with amino-groups. The combination between invertase and sucrose is, at least in part, a link between a primary amino-group of the enzyme (K_b=about 10^{-11}) and a hydroxyl group of the substrate. The inactivation of invertase by $Hg^{\cdot\cdot}$ differs from that of most other metallic ions in that there is a combination of this metal with the amino-group of invertase. The mercury-inactivated enzyme, if pure, does not "regenerate" on keeping, but if gelatin or sodium cyanide be added, reactivation is slowly effected. The speed of "regeneration" depends on the acidity.

The equation to the activity-p_H curve of the invertase–sucrose hydrolysis may be expressed in terms of the ionisation constants of the acid and basic groups of the amphoteric invertase molecule and that of the enzyme–substrate compound, and the concentrations of substrate and of hydrogen ion as follows: Relative activity$=1/(1+K_a/[H^{\cdot}])\{1+K_m/[S]\cdot[1+K_b/[OH']]\}$. Invertase is rapidly inactivated by free chlorine, bromine, or iodine in very small concentrations. With very small amounts of iodine, an enzymically active compound of iodine and invertase is immediately formed, which has 60% of the enzymic activity of the pure invertase. Further addition of iodine leads to complete inactivation. Osmium tetroxide in small concentrations rapidly inactivates invertase.

The dissociation constants of aniline and a number of its mono-substitution products have been redetermined. Aniline inactivates invertase reversibly. The group in the enzyme molecule with which the aniline combines is one which is unaffected by the acidity, and since both the enzyme and the enzyme–substrate compound combine with aniline, it is also not the one concerned in the binding of the substrate. The amine-combining group in the invertase molecule is probably an aldehyde group. The inactivating power of aniline depends on the fact that the amine–enzyme–substrate compound does not decompose. The aniline–invertase compound resembles a Schiff's base. With substituted anilines, the inactivating power is found to be dependent on the dissociation constant of the amine. Of the *o*-, *m*-, and *p*-isomerides of a substituted aniline, the *m*- is the most powerful inactivator.

The affinity of a simple aldehyde such as formaldehyde for the same series of substituted anilines is of a different nature, since it is independent of their dissociation constants. The aldehyde group in invertase is of a special kind, probably, as experiments on the combination between lactose and the same series of amines show, part of an aldose structure. In agreement with this view, phenylhydrazine after a short induction period (the formation of glucosazone at high dilutions is a time reaction) powerfully inactivates invertase.

Hydrocyanic acid is only a very weak inactivator. Aminoguanidine, which reacts fairly readily with aldoses, has a considerable inactivating effect on invertase, the free base being the agent. Sulphurous acid, which reacts readily and quantitatively with true aldehydes, but not with aldoses, has only the slightest inactivating effect on invertase. The aldose portion of the invertase molecule, which is not concerned in the formation of the enzyme–substrate complex, is more nearly connected with the hydrolysis process. H. D. KAY.

Enzyme action. XXXVIII. Ester-hydrolysing actions of the whole eel. H. M. NOYES, I. LORBERBLATT, and G. K. FALK (J. Gen. Physiol., 1926, **10**, 1—8).—The hydrolysing actions of various preparations of the whole eel on ten esters are described and also the separation in some cases of the active material into enzyme and co-enzyme. W. O. KERMACK.

Catalase and its relationship to biological oxidations. S. HENNICHS (Biochem. Z., 1926, **176**, 155—156).—A supplementary note to the author's paper (this vol., 756). P. W. CLUTTERBUCK.

Xanthine oxydase. VIII. Oxidation-reduction potential of the oxydase system. K. KODAMA (Biochem. J., 1926, **20**, 1095—1103).—Hypoxanthine and aldehyde do not give reduction potentials when activated by xanthine oxydase, whether the enzyme is introduced as fresh milk or as a purified preparation. This is not in agreement with Clark's results (U.S. Pub. Health Rep., 1925, Reprint No. 1017). If methylene-blue or oxygen is present in the system, a reduction potential is obtained. In the former case, it is due to the potential of the dye itself, in the latter to the formation of hydrogen peroxide (cf. Thurlow, A., 1925, i, 743). The amount of hydrogen peroxide formed has been determined by potential measurements. The oxidation–reduction indicators of Clark (A., 1923, ii, 677, 726) are reduced by xanthine oxydase and hypoxanthine and the reduced forms then give their respective reduction potentials. S. S. ZILVA.

Purification of xanthine oxydase. M. DIXON and K. KODAMA (Biochem. J., 1926, **20**, 1104—1110; cf. A., 1924, i, 1380).—By coagulating the proteins of milk with rennin, more xanthine oxydase is found in the whey than in the original milk. The enzyme can be precipitated from the whey by adding an equal volume of ammonium sulphate. Charcoal removes considerable quantities of protein from these xanthine oxydase preparations; kaolin, on the other hand, adsorbs the enzyme. The most favourable p_H for the adsorption of the enzyme is 5·0. Xanthine oxydase thus adsorbed can be removed from the adsorbent by extraction with a 1% sodium carbonate

solution. A loss of about 45% of the enzyme is incurred by this adsorption procedure. There is, however, a considerably greater proportionate fall in the protein content. The most active preparations are obtained by combining both methods of adsorption.
S. S. ZILVA.

Oxidising enzymes in the peel of *Citrus* fruits. S. G. WILLIMOTT and F. WOKES (Biochem. J., 1926, **20**, 1008—1012).—Peroxydase is fairly uniformly distributed throughout the peel of the orange, lemon, and grape fruit. As the lemon matures, the peel and juice become more acid, reaching a maximum after about 4 months. The outer pigmented portion and the inner portion of the peel behave similarly in this respect. S. S. ZILVA.

Oxidising enzymes. IX. Mechanism of plant oxydases. M. W. ONSLOW and M. E. ROBINSON (Biochem. J., 1926, **20**, 1138—1145).—The authors confirm Szent-Györgyi's observation (this vol., 99) that if an enzyme preparation from the potato tuber acts on pyrocatechol in potassium dihydrogen phosphate solution, an oxidised product is formed which remains in the solution after removing the enzyme by precipitation. This product causes blueing of guaiacum. Unlike Szent-Györgyi, the authors were unable to precipitate the enzyme entirely with methyl alcohol, but were successful in doing so with colloidal ferric hydroxide or picric acid. Hydrogen peroxide appears to be formed during the autoxidation of pyrocatechol and probably also during its oxidation by oxygenase. Oxygenase does not oxidise pyrocatechol anaërobically in the presence of hydrogen acceptors such as methylene-blue, *o*-cresol-2 : 6-dichloroindophenol, *o*-cresolindophenol, 2 : 6-dibromophenolindophenol, or *o*-chlorophenolindophenol.
S. S. ZILVA.

Peroxydase. I and II. H. W. BANSI and H. UCKO (Z. physiol. Chem., 1926, **157**, 192—213, 214—221).—I. Various theories of oxydase activity are briefly discussed, and previous methods of determining peroxydase activity are summarised. Of the reactions concerned, three, viz., the pyrogallol, cresol, and guaiacol colour reactions have been examined. On the whole, the method founded on the guaiacol–hydrogen peroxide colour reaction has been found to be most convenient, since the standard solutions are stable, the colours obtained are colorimetrically comparable, and the method can be applied over a wide range of conditions.

II. The above three methods have been applied to the evaluation of peroxydase activity of a solution of this enzyme at various stages during purification. It is found that the guaiacol value is 5—15% higher than the pyrogallol or cresol value with a crude preparation, but that it diminishes during purification to about one half of the pyrogallol or cresol figure. (Throughout the purification process the last two values change together.) The guaiacol oxidation is facilitated by the presence of certain impurities, possibly iron compounds, in the crude preparation. In spite of its convenience, the guaiacol method is not satisfactory for the evaluation of the true peroxydase activity of an enzyme preparation.
H. D. KAY.

Oxygen transport in the living cell. R. WILLSTÄTTER (Ber., 1926, **59**, [*B*], 1871—1876).—The rapid decline in the action of peroxydase towards hydrogen peroxide is due to the restrictive action of the latter substance; if the concentration of the substrate is considerably increased, the peroxidic action recommences. The peroxydase adds hydrogen peroxide with formation of a compound in which the peroxidic oxygen is more active than in hydrogen peroxide whilst, also, at least one compound is produced in which the oxygen is inactive. Contrary to the views of Warburg, iron is not an essential component of the enzyme molecule, but the obstinate tenacity of iron compounds appears to indicate that peroxydase is active in a system containing iron.
H. WREN.

Enzymic decomposition of hexosemonophosphoric acid due to bone extract. Influence of sodium hexosemonophosphate on bone fracture. M. FUJIHARA and I. KOKEN (Okayama Igakkai Zashi, 1925, No. 425, 603—611)—Neuberg's hexosemonophosphoric acid is hydrolysed by extracts from the rabbit femur and humerus. Subcutaneous injection caused increase of body-weight, but did not influence the healing of a broken fibula.
CHEMICAL ABSTRACTS.

Effect of natural carbonate and sulphate waters on urease. M. LOEPER, A. MOUGEOT, and V. AUBERTOT (Bull. Soc. Chim. biol., 1926, **8**, 958—969).—Natural waters may increase or diminish the activity of a standard preparation of soya-bean urease. The favourable action is attributed to the calcium present in the form of the unstable hydrogen carbonate. This may be balanced by the inhibitory effect of certain other ions also present.
R. K. CANNAN.

Recrystallisation of urease. J. B. SUMNER (J. Biol. Chem., 1926, **70**, 97—98; cf. this vol., 1061).—The highly active crystalline globulin obtained from Jack bean (*loc. cit.*) can be recrystallised by solution in water, addition of acetone to 30% concentration, and gradual treatment of the ice-cold solution with a solution of potassium dihydrogen phosphate of p_H 6·1. The nitrogen content and the enzymic activity of the preparation are not changed by recrystallisation. C. R. HARINGTON.

Enzymes, co-enzymes, and catalysing systems in yeast rich in coproporphyrin. I. The zymase and the oxido-reductase system. H. VON EULER, H. FINK, and R. NILSSON (Z. physiol. Chem., 1926, **158**, 302—322).—If yeast is grown in a nutrient medium rich in sugar, but free from oxygen, formation of coproporphyrin is observed. Bottom yeasts treated in this way undergo changes in their enzyme systems which bring them nearer in properties to top yeasts. An outstanding example of this is that whereas co-zymase is readily removed from "bottom yeast H" by washing, it cannot be removed from "coproporphyrin-bottom yeast H" by this process. On growing the coproporphyrin yeast again on beer wort, the organism reverts to its original state. H. D. KAY.

Fermentation of galactose by *Saccharomyces cerevisiæ*. N. L. SÖHNGEN and C. COOLHAAS (Zentr. Bakt. Parasitenk., 1925, II, **66**, 5—11; from Chem. Zentr., 1926, I, 1826).—The rate of fermentation of galactose is restricted by the formation of new yeast-cells. The enzyme which causes the fermentation of dextrose will not bring about the fermentation of galactose under conditions antagonistic to reproduction even when, as is normally the case in yeast extract, biocatalysts are present. E. C. SMITH.

Dependence of alcoholic fermentation on hydrogen-ion concentration. V. E. HÄGGLUND and T. ROSENQVIST (Biochem. Z., 1926, **175**, 293—296).—The cell-free fermentation of dextrose by yeast juice proceeds with practically uniform speed between p_H 5·5 and 8·0, with a possible slight optimum at the neutral point. In all cases, a period of "induction" was observed before the maximum rate of fermentation was reached. J. PRYDE.

Action of nitrogenous substances on yeast fermentation. V. H. ZELLER (Biochem. Z., 1926, **176**, 134—141).—Glycine, histidine hydrochloride, creatine, creatinine, and glucosamine hydrochloride are without effect on yeast fermentation, glucosamine, however, being inhibitory in high concentrations. Aspartic acid, alanylalanine, and Witte's peptone cause an optimal increase in fermentation of 33%, alanine and tryptophan one of 50%, and asparagine and ereptone one of 100%. Protein-containing liquids are precipitated by living yeast during the course of fermentation and partly carry down the yeast with them, thus inhibiting fermentation. At the beginning of the fermentation, however, most proteins cause an increase of fermentation. The following were investigated: caseinogen, meat extract, milk, hæmoglobin, serum, erythrocytes, intestinal juice, pepsin, trypsin, edestin, and ricin. Adrenaline has no effect, but insulin in small doses increases and in large doses inhibits fermentation.

P. W. CLUTTERBUCK.

Increase of yeast fermentation by urine. VI. H. ZELLER (Biochem. Z., 1926, **176**, 142—154).—Addition of urine causes an increase in fermentation of 200%, the increase diminishing as the concentration of yeast increases. The increase is conditioned by three components, first, a smaller effect due to ammonium salts, secondly, a larger effect due to a substance soluble in alcohol and precipitable by insulin, and thirdly, an inhibitory substance. The same increases could not be obtained with vitamin-*B* of Gigon and Odermatt nor with Euler's biocatalyst-*Z*. P. W. CLUTTERBUCK.

Nitrogen equilibrium in the yeast-cell. H. VON EULER and H. FINK (Z. physiol. Chem., 1926, **157**, 222—262).—If yeast is allowed to ferment a sugar solution which contains, in addition to the necessary inorganic salts, an amino-acid (glycine or alanine), it takes up nitrogen from this source. In absence of nitrogen, yeast fermenting an otherwise similar solution gives up an average of some 5% of its total nitrogen to the solution, mainly as amino-nitrogen. Exchange of amino-nitrogen with the medium is greatest when the yeast is encroaching on the nutrient limits of the system. On the whole, the ratio amino-nitrogen : total nitrogen in the yeast itself remains constant. This is also true of the ratio amino-nitrogen : peptide-nitrogen. The tryptophan content of yeast per gram of dried cells diminishes some 20% during 48 hrs.' fermentation. The formation of the tryptophan ring lags behind protein synthesis.

It is doubtful whether, during the growth, in nutrient broth, of *Bacillus prodigiosus* (which has been stated to be a tryptophan builder), there is any increase in the tryptophan content of the solution.

H. D. KAY.

Effect of lactic acid bacteria on the acetone-butyl alcohol fermentation. E. B. FRED, W. H. PETERSON, and M. MULVANIA (J. Bact., 1926, **11**, 323—343).—The growth of, and production of lactic acid by, cereal lactic acid bacteria in a mash inoculated with *Granulobacter pectinovorum* is favoured by the presence of the latter, which hydrolyses starch to fermentable carbohydrates and exercises a proteolytic effect on nitrogenous compounds. The association is, however, harmful to *G. pectinovorum*. In decreasing inhibiting effect on the butyl alcohol fermentation are *Lactobacillus leishmanni*, *L. mannitopœum*, *L. gracile*, and *L. intermedium*. A vigorous fermentation with *G. pectinovorum* favours the longevity of lactic acid bacteria by producing buffer substances and maintaining relatively small amounts of acid. The growth of *G. pectinovorum* is inhibited by a p_H of 4·7—4·8. CHEMICAL ABSTRACTS.

"Strict" anaërobes. I. Relationship of *Bacillus sporogenes* to oxygen. J. H. QUASTEL and M. STEPHENSON (Biochem. J., 1926, **20**, 1125—1137).—*Bacillus sporogenes* after being exposed to oxygen or dilute concentrations of hydrogen peroxide exhibits a long latent period in its anaërobic growth in tryptic broth. The latent period is diminished or almost entirely abolished by the introduction of cysteine or other thiol compounds in the medium. This treatment will also induce good aërobic growth of *B. sporogenes*. It is suggested that the latent period exhibited by the organism is the time of incubation required for the inoculated non-proliferating cells to produce a certain minimum quantity of a given substance from the medium in order to establish the limiting reduction potential necessary for its proliferation. Neither oxygen nor hydrogen peroxide in low concentration is lethal to *B. sporogenes*; their inhibitory influence is due to raising the potential of the medium. S. S. ZILVA.

Physiological significance of deamination in relation to oxidation of dextrose. H. B. SPEAKMAN (J. Biol. Chem., 1926, **70**, 135—150).—During the oxidation of dextrose by *Bacillus granulobacter pectinovorum* in a maize mash medium there are produced, in addition to volatile fatty acids, *l*-leucic acid (cf. Peterson and others, A., 1924, i, 1270) and *p*-hydroxyphenyl-lactic acid; the production of these acids runs parallel with the oxidation of the dextrose and is at its height when vegetative growth of the organism has almost ceased. In spite of the fact that these acids must presumably be formed by deamination of leucine and tyrosine, the smallest traces of ammonia only can be detected in the medium. Addition to the medium of tyrosine or of ammonium

phosphate accelerates the oxidation of the dextrose. From these results, it is concluded that the ammonia, liberated by the deamination of the amino-acids, acts as an endocellular oxidative catalyst. It is pointed out that, by extension to the animal organism, this hypothesis could be made to account for the "specific dynamic action" of proteins and amino-acids. C. R. HARINGTON.

Utilisation of sugars by protozoa. J. COLAS-BELCOUR and A. LVOV (Compt. rend. Soc. Biol., 1925, **93**, 1421—1422; from Chem. Zentr., 1926, I, 1824).—The utilisation of mannitol, arabinose, xylose, lævulose, dextrose, galactose, maltose, sucrose, lactose, inulin, and starch by four species of ciliates and flagellates has been investigated. Dextrose and lævulose were utilised by all the species; one ciliate species utilised maltose and sucrose. E. C. SMITH.

Utilisation of the salts of organic acids by the colon-aërogenes group. S. A. KOSER (J. Bact., 1926, **11**, 409—416).—A study of the utilisation of various di- and tri-carboxylic acids by *Bacillus coli*, *B. aërogenes*, and related types. CHEMICAL ABSTRACTS.

Urease formation by bacteria in the absence of urea. L. RUBENTSCHIK (Biochem. Z., 1926, **175**, 482—490).—Two types of urobacillus, two of urobacterium, and one urosarcina are all capable of forming urease in the absence of urea from the culture medium. After ten successive 10-day sub-cultures in urea-free media, the urease was still present in undiminished amount. In each culture, the urease reaches a maximum in from 3 to 7 days. Thus an enzyme continues to be produced when there is no need for its formation. J. PRYDE.

Dehydration and polymerisation products of β-hydroxybutyric acid. LEMOIGNE (Bull. Soc. Chim. biol., 1926, **8**, 770—782).—From autolysed *B. megatherium* there has been isolated a *compound*, $[C_4H_6O_2]_n$, in which n is probably 6; m. p. 120°, $[\alpha]_D$ −5·89° (chloroform); when heated, it decomposes, yielding crotonic acid; saponification produces crotonic and β-hydroxybutyric acids. From the fresh cultures, a substance of the same empirical composition, but of higher mol. wt. (n may be 24) has been obtained; on heating and saponification, this yields the same products as the first compound; it has m. p. 156°, $[\alpha]_D$ −1·94°. It is insoluble in boiling alcohol and is transformed by it into a substance of the same empirical composition and chemical properties, but melting at a lower temperature. It is suggested that the compounds are both polylactides of β-hydroxybutyric acid. H. J. CHANNON.

Chemical composition of the active principle of tuberculin. I. Non-protein medium suitable for the production of tuberculin. II. Precipitation with acetic and other acids. III. IV. Ammonium sulphate precipitation of the proteins of tuberculin. E. R. LONG and F. B. SEIBERT. **V. Effect of proteolytic enzymes on tuberculin proteins and the activity of tuberculin.** F. B. SEIBERT. **VI. Acid hydrolysis of tuberculin.** E. R. LONG. **VII. Evidence that the active principle is a protein.** E. R. LONG and F. B. SEIBERT (Amer. Rev. Tuberculosis, 1926, **13**, 393—453).—The medium contains asparagine 5, ammonium citrate 5, potassium dihydrogen phosphate 3, sodium carbonate 3, sodium chloride 2, magnesium sulphate 1, ammonium citrate 0·05, glycerol 50, and water 1000 parts. Acetic, phosphoric, or hydrochloric acid yields a protein precipitate, maximum precipitation coinciding with the isoelectric point (p_H 4·0) found for a protein present by electrophoresis. Complete precipitation of the active principle can be effected by ammonium sulphate; of the three proteins obtained, one is insoluble in water and non-coagulable, one is soluble in water and non-coagulable, and one is soluble in water and coagulable. The active substance of the second fraction is probably the whole protein molecule, since treatment with trypsin and sodium carbonate, but not with trypsin in neutral solution, or erepsin, causes loss of activity. Preparations heated for 4 hrs. at 120° with hydrochloric acid lost their activity when the acidity was $N/6$ or $N/3$, but not when it was 0·01N, 0·05N, or 1·0N. It is concluded that the active principle of tuberculin is a whole protein, although activity persists after partial disintegration of the molecule.

CHEMICAL ABSTRACTS.

Tuberculosis. VII. Active principles of tuberculin prepared from non-protein substrates. F. EBERSON (Amer. Rev. Tuberculosis, 1926, **13**, 454—462).—The medium contained ammonium succinate, 0·5 g.; dipotassium hydrogen phosphate, 0·5 g.; magnesium sulphate, 0·25 g.; calcium chloride, 0·125 g.; and water, 100 c.c., 2% of glycerol being added to one portion. Of the tuberculin fractions, one (4·6%) was insoluble in alcohol, one (2·3%) was insoluble in ether, and one (non-protein; 0·5%) was soluble in ether.

CHEMICAL ABSTRACTS.

Effect of oxygen on tetanus toxin. A. BERTHELOT, G. RAMON, and G. AMOUREUX (Bull. Soc. Chim. biol., 1926, **8**, 940—941).—Cultures of *Bacillus tetani* in media of p_H 5—7 developed toxin even when a slow current of oxygen was bubbled through the culture. R. K. CANNAN.

Energetics of growth. VII. Efficiency of various forms of nitrogen for the growth of micro-organisms. R. BONNET, P. DUQUÉNOIS, and G. VINCENT (Bull. Soc. Chim. biol., 1926, **8**, 970—975).—The mycelium growth of *Aspergillus niger* was studied on dextrose–salt media containing various sources of nitrogen and compared with the nitrogen metabolism. The efficiency was 0·61 for asparagine, 0·58 for ammonia and amino-acids, and 0·53 for nitrates. R. K. CANNAN.

Energetics of growth. VIII. Efficiency of glucose and various organic acids for the growth of *Aspergillus niger*. E. F. TERROINE and R. BONNET (Bull. Soc. Chim. biol., 1926, **8**, 976—981; cf. preceding abstract).—When dextrose was replaced by malic, citric, or tartaric acid as the sole source of nutrient carbon in the medium, the efficiency of growth fell from 0·58 to 0·53. The reduction of the organic acids to dextrose does not, therefore, require much energy, and the low efficiency of the utilisation of protein for growth must be attributed to the energy lost in the metabolism of the nitrogen, since only a small part seems to be required

for the conversion of the deaminised residues into sugar. R. K. CANNAN.

Exit of dye from living cells of *Nitella* at different p_H values. M. IRWIN (J. Gen. Physiol., 1926, **10**, 75—102).—The rate of exit of brilliant-cresyl-green from the sap of the living cells of *Nitella* depends on the hydrogen-ion concentration of the surrounding medium. The results support the view that this dye exists in two forms, that which penetrates the cell membrane most readily being the one the existence of which is favoured by increase of p_H. W. O. KERMACK.

Influence of light, temperature, and other conditions on the ability of *Nitella* cells to concentrate halogens in the cell sap. D. R. HOAGLAND, P. L. HIBBARD, and A. R. DAVIS (J. Gen. Physiol., 1926, **10**, 121—146).—The cell of *Nitella* is able to absorb bromine from the surrounding medium up to concentrations much greater than that existing in the medium, and at the same time chlorine is lost from the sap. The process, which is dependent on a supply of light energy, is slow. The temperature coefficient is characteristic of a chemical process. W. O. KERMACK.

Catalysis of oxidations by adrenaline. J. ROEST (Biochem. Z., 1926, **176**, 17—19).—Adrenaline, 1/10,000, in faintly alkaline solution, gradually uses oxygen (0·3—0·5 mm.^{3}/min.), forming probably a diketoquinone. *p*-Phenylenediamine under similar conditions uses 0·1 mm.^{3}/min. If the two are mixed, oxygen consumption is considerably increased (10 mm.^{3}/min. for 20 min.), an amount much greater than that required to oxidise the adrenaline. Increasing the concentration of the diamine has no influence on the rate of oxygen utilisation. It is concluded that molecular oxygen is carried catalytically to the diamine by adrenaline. The biological significance of this reaction is discussed. P. W. CLUTTERBUCK.

Mineral content of the blood. I. Effect of adrenaline on the blood-calcium. E. PULAY and M. RICHTER (Z. ges. exp. Med., 1926, **48**, 582—589; from Chem. Zentr., 1926, I, 1834).—Adrenaline intoxication in rabbits causes acidosis, an increase in the total calcium and the free (*i.e.*, ultrafilterable) calcium of the blood, and usually a decrease in the potassium content. E. C. SMITH.

Nature of the internal secretion of the pancreas and mechanism of its action. A. CHOAY (Bull. Soc. Chim. biol., 1926, **8**, 843—889).—A lecture delivered on May 18, 1926.

Altered metabolism of normal animals under insulin treatment. E. E. HAWLEY and J. R. MURLIN (Amer. J. Physiol., 1925, **75**, 107—130).—The characteristic action of insulin consists of shifting of the metabolism from fat and protein to carbohydrate. With rabbits, in the period terminating 1·75 hrs. after insulin, there is an abrupt change in metabolism from fat to carbohydrate, *i.e.*, from no carbohydrate to 1·36 g. per hr. and from 0·8 g. of fat to 0·06 g. Glycogen must be supplied from the liver and other organs as the main source of the carbohydrate oxidised after insulin. CHEMICAL ABSTRACTS.

Action of repeated doses of insulin. K. WALTNER (Biochem. Z., 1926, **176**, 246—250).—Daily repeated injection of a non-toxic but relatively high dose of insulin causes a continually increasing sensitivity to insulin accompanied by an increasing fall of blood-sugar and eventually resulting in symptoms of insulin poisoning (cf. Langecker and Stross, this vol., 205). P. W. CLUTTERBUCK.

Influence of insulin on acetaldehyde formation in the animal organism. J. V. SUPNIEWSKI (J. Biol. Chem., 1926, **70**, 13—27).—The formation of acetaldehyde by excised tissues under sterile conditions *in vitro* was increased by addition of insulin; the concentration of acetaldehyde in the tissues of normal animals was raised by simultaneous administration of insulin and of dextrose, and, in the blood, after administration of insulin and alcohol. In depancreatised animals, the acetaldehyde of the blood and urine is increased and administration of insulin causes it to fall to the normal level; similarly, insulin increases the rate of disappearance from the blood of acetaldehyde after an injection of the latter substance. C. R. HARINGTON.

Identification of acetaldehyde in normal blood, and its concentration in the blood of normal and diabetic dogs. A. H. GEE and I. L. CHAIKOFF (J. Biol. Chem., 1926, **70**, 151—165).—The presence of acetaldehyde in normal blood has been confirmed by isolation of its condensation product with dimethylhydroresorcinol (cf. Neuberg, A., 1923, i, 171). The results of Supniewski (cf. preceding abstract) are criticised on the ground that he neglected the error introduced by the presence of acetone in the blood of diabetic animals. A modification of the method of Bougault and Gros (A., 1922, ii, 666) is described, which indicates that normal dog blood contains 0·02—0·06% of acetaldehyde, these figures being in good agreement with the weight of the above-mentioned condensation product actually prepared from blood. No significant variations from the normal were found in the acetaldehyde content of the blood of depancreatised dogs. C. R. HARINGTON.

Co-enzymic nature of insulin. T. BRUGSCH and H. HORSTERS (Z. physiol. Chem., 1926, **157**, 186—191).—The criticism of Euler and Myrbäck of the conclusions of the authors (Biochem. Z., 1925, **158**, 144), that insulin is an activator or co-enzyme for phosphatese, is unjustified. These critics assume (*a*) that yeast phosphatese and muscle phosphatese are identical, (*b*) that the hexosephosphate of yeast and that of muscle are identical, neither of which assumptions can be accepted. Insulin is the co-enzyme of muscle phosphatese and is not identical with the co-zymase of yeast fermentation. H. D. KAY.

Insulin and co-zymase. K. FREUDENBERG and W. DIRSCHERL (Z. physiol. Chem., 1926, **157**, 64—75).—The activation of *Bacillus casei* ε by insulin, observed by Virtanen (A., 1925, i, 753; this vol., 435), is thought by the authors to be due to an amount of co-zymase occurring as an impurity in the insulin, because the insulin can be freed from

activating substance by suitable methods of purification. H. I. COOMBS.

Action of insulin on the blood-sugar *in vitro*. E. MÜLLER (Biochem. Z., 1926, **175**, 491—495).—The permeability of the erythrocytes of the goose to dextrose and to chloride ions is not influenced by insulin. During insulin hypoglycæmia, the tissue sugar also drops. Blood glycolysis in the presence of muscle pulp is not influenced by insulin.

J. PRYDE.

Effect of muscle and insulin on dextrose *in vitro*. M. M. HARRIS, M. LASKER, and A. I. RINGER (J. Biol. Chem., 1926, **69**, 713—719).—The experiments of Lundsgaard and Holbøll (A., 1925, i, 208) could not be repeated (cf. also Barbour, this vol., 435). C. R. HARINGTON.

Rotatory power of dextrose–insulin solutions in contact with muscle-tissue *in vitro*. H. H. BEARD and V. JERSEY (J. Biol. Chem., 1926, **70**, 167—171).—The results of Lundsgaard and Holbøll (A., 1925, i, 1494) could not be confirmed.

C. R. HARINGTON.

Albino rat in insulin standardisation. Normal blood-sugar and glycogen content of the liver and muscles. L. KARCZAG, J. J. R. MACLEOD, and M. D. ORR (Trans. Roy. Soc. Canada, 1925, **19**, [v], 57—61).—The liver glycogen of rats, starved for 24 hrs. previous to death, varies only between narrow limits, whilst the muscle glycogen shows a remarkable constancy. The relation existing between the weight of the liver and its glycogen content in normal and starved animals shows that the increase of weight during digestion is dependent mainly on factors other than glycogen deposition. It is not possible to predict the glycogen content from the liver weight.

The blood-sugar of the albino rat exhibits a greater constancy than that of rabbits, which renders this animal suitable for the standardisation of insulin preparations. C. RIMINGTON.

Preparation, physiological properties, and standardisation of a parathyroid hormone. J. B. COLLIP and E. P. CLARK (Trans. Roy. Soc. Canada, 1925, **19**, [v], 25—26).—The glands are removed and frozen soon after death. They are then digested at 100° with 5% hydrochloric acid for 1 hr. After dilution, fat is removed and the p_H brought to 8 by addition of 10% sodium hydroxide, and then sufficient dilute hydrochloric acid added to produce flocculation. The precipitate is filtered off, dissolved in alkali, and reprecipitated twice. The combined filtrates are made acid to Congo-red, sodium chloride is added to saturation, and the precipitate collected. The salting-out process is repeated, the precipitate being finally precipitated at its isoelectric point (p_H 4·8), first from alkaline and then from acid solution. It is treated with alcohol and ether and dried in a vacuum.

The preparation causes a rise in serum calcium of both normal and parathyroidectomised dogs, and is a specific for parathyroid tetany. In excess, it causes typical symptoms culminating in death. It may be standardised by the use of normal dogs, and contains 15·5% of nitrogen and traces of iron and sulphur, but no phosphorus.

The Molisch reaction is negative (cf. A., 1925, i, 754, 1017; this vol., 206). C. RIMINGTON.

Action of parathyroid extract on blood- and cerebrospinal fluid-calcium. A. T. CAMERON and V. H. K. MOORHOUSE (Trans. Roy. Soc. Canada, 1925, **19**, [v], 39—43).—Injection of parathyroid extract into parathyroidectomised animals leads to a rise in the calcium of the serum and plasma, these values approximately coinciding. The whole blood calcium rises correspondingly and the cerebrospinal fluid shows a delayed rise.

Injection into normal animals causes death with characteristic symptoms, whilst the calcium values rise in an analogous manner (cf. A., 1925, i, 857).

C. RIMINGTON.

Action of parathyroid extracts on guanidine. F. D. WHITE and A. T. CAMERON (Trans. Roy. Soc. Canada, 1925, **19**, [v], 45—52).—Vine's method for determining the activity of parathyroid extracts is not trustworthy, as it appears to depend on the inhibitory effect of certain substances such as arginine or nucleic acid derivatives on the precipitation of guanidine picrate. Collip's extract when tested by this method shows negligible activity.

C. RIMINGTON.

Pathological variations in the serum calcium. G. H. PERCIVAL and C. P. STEWART (Quart. J. Med., 1926, **19**, 235—248).—The normal range is 9·4—9·9 mg. per 100 c.c. of serum. The effect on the serum calcium of administration of parathyroid and calcium salts is described. CHEMICAL ABSTRACTS.

Influence of diets rich in vitamins and poor in minerals on metabolism and on the urinary C : N ratio. T. KANAMORI (Biochem. Z., 1926, **175**, 318—329).—From experiments on dogs, it is concluded that a diet poor in salts results in an initial considerable fall in body-weight, followed by a less regular loss. Absorption of foodstuffs is generally unaffected, but slight disturbances associated with diarrhœa may occur. The nitrogen balance is sometimes negative, sometimes positive, whilst the urinary carbon output varies in the same way, so that the C : N ratio of the urine retains its normal value.

J. PRYDE.

Relation of rate of growth to diet. I. T. B. OSBORNE and L. B. MENDEL (J. Biol. Chem., 1926, **69**, 661—673).—Considerably more rapid early growth in male albino rats than has hitherto been observed has been obtained by modification of the diets previously used. The significant alterations appear to be inclusion of a larger proportion of protein and the use of "natural" foods (*e.g.*, green leaves and yeast) as supplements. C. R. HARINGTON.

Accessory growth-factors. IX. H. VON EULER and M. RYDBOM (Z. physiol. Chem., 1926, **157**, 163—170).—By adding small amounts of meat to a diet somewhat deficient in vitamin-*A* and -*D*, almost normal growth may be obtained, with young rats, for 9 or 10 weeks. It is suggested that this addition assists the animal in the first stage—sterol formation—of the autogenous elaboration of vitamins. Chol-

esterol in the relatively large amounts of 0·1 g. of pure cholesterol per rat per day, given *per os* with or without coincident ultra-violet irradiation of the animal, maintains rats on a diet deficient in vitamin-*A* and -*D* at a steady rate of growth for at least a month. An irradiated vegetable oil (arachis) of which 10 mg. daily are sufficient to provide the vitamin-*D* necessary for one rat, when fed in 80 times the minimal dose brings about almost as striking an increase in the rate of growth as the feeding of excessive amounts of cod-liver oil. H. D. KAY.

Colorimetric investigations of oils containing vitamins-*A* and -*D* and of irradiated oils. H. VON EULER, K. MYRBÄCK, and S. KARLSSON (Z. physiol. Chem., 1926, **157**, 263—282).—Certain colour reactions of cod-liver oil and of normal and irradiated cholesterol have been studied, in the hope of finding a satisfactory colour reaction specific for vitamin-*A* or -*D*. One of the most hopeful reactions is that described by Fearon (this vol., 207), using pyrogallol and trichloroacetic acid. This colour reaction permits of quantitative study. Cod-liver oil reacts in a way quite dissimilar from that shown by irradiated vegetable oils. The influence of the addition of benzoyl peroxide to the reaction mixture is described. It is concluded that the value of such colour reactions cannot be decided until more tests have been carried out with material of known vitamin-*A* and -*D* content. H. D. KAY.

Colour tests suggested for vitamin-*A*. O. ROSENHEIM and T. A. WEBSTER (Lancet, 1926, ii, 806—807).—Fearon's pyrogallol test is shown to have no relation to vitamin-*A*, since it is negative when applied to the unsaponifiable fraction of cod-liver oil, which contains the vitamin. Moreover, the soaps obtained on saponifying cod-liver oil, which contain no vitamin, give a strongly positive Fearon's test. The chromogen of the reaction is associated with the unsaturated fatty acids. The arsenious chloride test may be specific for vitamin-*A*, all experimental evidence obtained so far being compatible with this assumption. The chemical findings are supported by the results of feeding experiments. H. W. DUDLEY.

Comparison of results obtained with the rat and the pigeon in testing for the antineuritic vitamin. A. SEIDELL (Bull. Soc. Chim. biol., 1926, **8**, 746—750).—Better recovery of rats which had been maintained on a diet deficient in vitamin-*B* was obtained when, in addition to a vitamin-*B* concentrate, autoclaved yeast was given. The addition of the yeast alone had no curative effects. With pigeons, administration of yeast in addition to the concentrate did not increase the curative effect of the latter. Hence it is suggested that for the testing of vitamin-*B* the rat is best suited, whilst the pigeon should be used for the testing of the antineuritic vitamin. H. J. CHANNON.

Cholesterol content of the organs of the guinea-pig on a scorbutic diet. MOURIQUAND and LEULIER (Compt. rend. Soc. Biol., 1925, **93**, 1314—1315; from Chem. Zentr., 1926, I, 1838).—The cholesterol content of the suprarenal gland is diminished in vitamin-*C* deficiency. No effect is observed in the case of the liver, lung, or spleen. E. C. SMITH.

Antiscorbutic fraction of lemon juice. IV. C. G. DAUBNEY and S. S. ZILVA (Biochem. J., 1926, **20**, 1055—1059).—The behaviour of inorganic constituents of lemon juice in the various stages of the preparation of concentrated antiscorbutic fractions from lemon juice has been studied (cf. A., 1924, i, 588, 901; 1925, i, 1220). Nickel, cobalt, and boron were found to be absent, phosphorus and iodine to be present in the purest fractions. The iodine present in the purest fraction is separable from the active principle by diffusion. S. S. ZILVA.

Vitamin-*C* of lemon rind. S. G. WILLIMOTT and F. WOKES (Biochem. J., 1926, **20**, 1013—1015).—Alcoholic extracts of the outer pigmented portion of ripe lemons contain only small amounts of vitamin-*C*. S. S. ZILVA.

Factors influencing calcification processes in the rabbit. M. MELLANBY and E. M. KILLICK (Biochem. J., 1926, **20**, 902—926).—Diets are described which promote good growth and general good health in rabbits, but produce very defective calcification of bones and teeth. The degree of abnormal calcification is related to the growth of the animal. The worst calcification is obtained in rabbits on the deficient diet when the calcium–phosphorus content of the diet approximates to the amounts which were found to be satisfactory in the production of rickets in rats. Calcification in rachitic rabbits is produced in the usual way, either by increasing the calcifying vitamin in the diet or by exposing the animal or the food to ultra-violet rays. Vegetable foods are mostly deficient in the anti-rachitic vitamin. Grass, especially summer-grown grass, is more active than cabbage. Carrots and swedes are richer in the vitamin than white turnips. S. S. ZILVA.

Phosphorus and calcium metabolism of young rachitic rats fed on a calcium-rich diet and treated with ultra-violet rays, cod-liver oil, and phosphates. P. SCHULTZER (Compt. rend. Soc. Biol., 1925, **93**, 1005—1007; from Chem. Zentr., 1926, I, 1838).—In all cases of improvement of the rachitic condition, by whatever treatment, the retention of calcium and phosphorus is increased. An alteration in urinary phosphorus excretion occurs only when phosphates are administered. In other cases the fæcal phosphorus only is affected. E. C. SMITH.

Effect of various methods of treatment on the calcium and inorganic phosphorus of the serum of rachitic rats. P. SCHULTZER (Compt. rend. Soc. Biol., 1925, **93**, 1008—1010; from Chem. Zentr., 1926, I, 1838).—Treatment with phosphate is again differentiated from that with ultra-violet light or cod-liver oil by its effect on the serum-phosphate (cf. preceding abstract). E. C. SMITH.

Photoactivity. V. Relation between photographic and antirachitic activity. H. VOLLMER and J. SEREBRIJSKI (Biochem. Z., 1926, **176**, 84—91).—Compounds which are photoactive under the

action of ultra-violet rays readily take up oxygen, giving peroxides or ozonides. Compounds which are active in the unirradiated state often owe this fact to their hydrogen peroxide content, and others which become active on irradiation to the production of hydrogen peroxide by the breakdown of oxidation products arising during irradiation. The antirachitic activation by ultra-violet rays is an oxidation, peroxidation, or ozonisation of readily oxidisable compounds. Hydrogen peroxide, taken by the mouth, is antirachitically inactive. Material taken by the mouth can be active only when it can pass the digestive tract unchanged and give up its active oxygen to the cell. P. W. CLUTTERBUCK.

Antirachitic value of irradiated cholesterol. II. Separation into active and inactive fractions. A. F. HESS, M. WEINSTOCK, and E. SHERMAN (J. Biol. Chem., 1926, **70**, 123—127).—The complete loss of antirachitic activity, previously observed (this vol., 546) in the attempt to separate an active fraction from irradiated cholesterol by treatment with digitonin, has been avoided by carrying out the precipitation and filtration in an atmosphere of nitrogen; the filtrate is mixed with linseed oil and the alcohol removed in a vacuum. The whole of the active material was then found in the filtrate, and amounted to 4% of the original cholesterol. On extraction of irradiated cholesterol with liquid ammonia, 4% of the material was dissolved; the insoluble residue was inactive, whereas the soluble portion protected rats against rickets when administered in daily doses of 2·5 mg. In spite of the apparent chemical similarity between vitamin-*D* and the ovarian hormone (cf. Doisy, A., 1924, i, 1387), preparations of the two substances show no physiological properties in common. C. R. HARINGTON.

Permeability in plant-cells. D. T. MACDOUGAL (Carnegie Inst. Wash. Yearbook, 1922, **21**).—Pentosans and lipins predominate in the outer layers of plant cells, in which the proteins may play a subordinate part only. CHEMICAL ABSTRACTS.

Mechanism of photosynthesis and the internal factor. H. A. SPOEHR (Carnegie Inst. Wash. Yearbook, 1922, **21**).—It is considered that photosynthesis and respiration are interdependent. CHEMICAL ABSTRACTS.

Carbohydrate-amino-acid relation in the respiration of leaves. H. A. SPOEHR and J. M. MCGEE (Carnegie Inst. Wash. Yearbook, 1922, **21**).—The supply of carbohydrate and free amino-acids is influenced by light. CHEMICAL ABSTRACTS.

Temperature coefficients and efficiency of photosynthesis. H. A. SPOEHR and J. M. MCGEE (Carnegie Inst. Wash. Yearbook, 1922, **21**). CHEMICAL ABSTRACTS.

Carbohydrate metabolism of leaves. H. A. SPOEHR (Carnegie Inst. Wash. Yearbook, 1922, **21**). CHEMICAL ABSTRACTS.

Influence of various sugars on respiration. H. A. SPOEHR and J. M. MCGEE (Carnegie Inst. Wash. Yearbook, 1922, **21**).—When dextrose is fed to leaves, the carbohydrate content is maintained or increased, but the rate of respiration is not dependent only on the amount of available carbohydrates. The influence of amino-acid on leaves given sucrose is not so great as when dextrose is given. Lævulose is more easily oxidised than any of the other hexose sugars. *d*-Mannose produces in higher plants a relatively high rate of respiration. CHEMICAL ABSTRACTS.

Utilisation of various materials in plant respiration. G. KLEIN and K. PIRSCHLE (Biochem. Z., 1926, **176**, 20—31).—The percentage increase of respiration of wheat germ as measured by aldehyde formation for the following substances is: dextrose, 84; galactose, 77·8; lævulose, 56·1; sucrose, 54·6; maltose, 49·5; lactose, 39; methyl alcohol, 0; ethyl alcohol, 120·5; *iso*propyl alcohol, 58·4; glycerol, 34·7; mannitol, 69·5; acetic acid, 127·5; propionic acid, 48·5; lactic acid, 31·6; pyruvic acid, 500 (quantitative); oxalic acid, 77·9; malic acid, 0; tartaric acid, 85·2; citric acid, 9·5; alanine, 13·9; asparagine, 28·3; dihydroxyacetone, 165·2. P. W. CLUTTERBUCK.

Nutrition of plants with aldehydes. VII. Increase of the carbohydrate content of *Elodea canadensis* by acetaldehyde. T. SABALITSCHKA and H. WEIDLING (Biochem. Z., 1926, **176**, 210—224).—By addition of acetaldehyde to the nutritive solution, the starch content of *Elodea canadensis*, R. and M., is increased both in light and in darkness. The concentration of aldehyde optimal for starch formation is 0·032%. This concentration is not, although concentrations of 0·064% and 0·128% are, injurious to plant enzymes during prolonged action. P. W. CLUTTERBUCK.

Activation of plant enzymes by ions, in relation to nutrition. I. Amylase of sugar beet poor in potash. G. DOBY and R. P. HIBBARD (Biochem. Z., 1926, **176**, 165—177).—Sugar-beet amylase is activated by both anions (Cl', F', NO_3') and cations ($K^{\cdot}$, $Na^{\cdot}$), but most powerfully by Cl'. Amylase of beet grown in sand devoid of potash is more strongly activated by Cl' than amylase of plants supplied with the normal amount of alkali. The concentration of the enzyme decreases with progressive growth of the plant more quickly in plants receiving normal nutrition than in those the nutrition of which is devoid of potash. P. W. CLUTTERBUCK.

Physiological function of iodine in synthetic and working metabolism of cells poor and rich in chlorophyll. J. STOKLASA (Biochem. Z., 1926, **176**, 38—61).—Iodine is assimilated by all living organisms of the soil and plays on important rôle in those showing greater respiratory activity (bacteria) as iodine-oxydase. Siphonogams (phanerogams) assimilate iodine by means of roots and leaves, but to differing extents. The greatest power of absorption is found in halophytes, hygrophiles, hydrophytes, and certain mesophytes. When the soil contains 0·5 g./kg. iodine, this escapes, due to the dissimilatory action of bacteria. It is concluded that the respiratory process in plants is considerably assisted by iodine, especially in presence of iron and by α-rays of radium emanation. The power of iodine to decrease the p_H of plant organisms is very important in view of the decrease of enzymic activity and the

destruction of chlorophyll resulting from accumulation of organic acids. The chlorophyll apparatus of plants always contains a greater amount of iodine than the root system. Iodine is assimilated and converted into an organic form by many plants.
P. W. CLUTTERBUCK.

Nitrogenous extractives from etiolated *Lupinus luteus* seedlings. A. TOKAREWA (Z. physiol. Chem., 1926, **158**, 28—31).—The water extract from 17·3 kg. of 8-day seedlings of *Lupinus luteus* is shown to contain no carnosine, but much asparagine, with traces of creatinine and betaine. C. HOLLINS.

Nitrogenous constituents of the cauliflower bud. I. Protein fractions. M. C. MCKEE and A. H. SMITH (J. Biol. Chem., 1926, **70**, 273—284).—By extraction of the edible portion of the cauliflower with water there was obtained a heat-coagulable protein, and by further extraction of the residue with 0·3% sodium hydroxide and acidification of the extract with acetic acid, a second protein fraction was obtained. Both preparations gave reactions for carbohydrate; figures are given for the elementary analysis and distribution of nitrogen determined by the method of Van Slyke. The two preparations formed 4·8 and 1·7% of the total solids, and represented 11·3 and 3·1%, respectively, of the total nitrogen of the original material.
C. R. HARINGTON.

Composition of *Salix triandra*, L. Rutoside, asparagine, and a new glucoside. M. BRIDEL and C. BÉGUIN (Bull. Soc. Chim. biol., 1926, **8**, 901—914). —See this vol., 983.

Isolation from the flowers of *Ulex europæus*, L., of a new glucoside hydrolysed by rhamnodiastase. M. BRIDEL and C. BÉGUIN (Bull. Soc. Chim. biol., 1926, **8**, 895—900; cf. this vol., 201).—The alcoholic extract of the flowers was concentrated and the aqueous residue extracted with ether and concentrated in a vacuum. The crystals separating during 9 months were recrystallised from boiling water, 30% and 70% alcohol. The product, *ulexoside*, m. p. 247°, was almost insoluble in cold water, $[\alpha]_D$ −51·92° in 70% alcohol. Hydrolysis with rhamnodiastase gave an unidentified reducing sugar and a crystalline product (*ulexogenol*). This and the original glucoside gave colour reactions with sodium hydroxide reminiscent of rhamnicoside.
R. K. CANNAN.

Biochemical hydrolysis of robinoside (robinine). Robinose—a new triose. C. CHARAUX (Bull. Soc. Chim. biol., 1926, **8**, 915—923).—Robinoside is hydrolysed by rhamnodiastase to a triose, *robinose*, which is composed of 1 mol. of galactose and 2 mols. of rhamnose, being isomeric with rhamninose. During the hydrolysis a gel is first formed which slowly liquefies as the robinose separates. The latter is hygroscopic and exhibits mutarotation, $[\alpha]_D$ +1·94°. The flowers of *Robinia* contain an enzyme capable of hydrolysing the triose into its constituent hexoses. R. K. CANNAN.

Sucrose formation in potatoes during drying. I. C. J. DE WOLFF (Biochem. Z., 1926, **176**, 225—245).—The formation of sucrose in potato slices on drying at an optimum temperature (Waterman, Chem. Weekblad, 1914, **11**, 332) is due, not to an effect of temperature, but to the loss of water. When the loss in weight on quick drying exceeds 53%, sucrose formation stops. Potato pulp does not form sucrose on drying. P. W. CLUTTERBUCK.

Pectic substances of plants. IV. Pectic substances in the juice of oranges. F. W. NORRIS (Biochem. J., 1926, **20**, 993—997).—The substance in orange juice is identical with the trimethylated derivative of pectic acid (pectinogen) described by Norris and Schryver (A., 1925, i, 1226). It is derived from the cell-wall by the action of the acids and enzymes in the juice, since the yield is increased if the fruit is macerated before expression of the juice in order to allow the juice to come into intimate contact with the cell-wall. The pectic substance of the juice is converted into the insoluble gel of pectic acid on keeping, unless the fruit is boiled before treatment. S. S. ZILVA.

Fat content of breads and cereals. G. A. CORMACK (Biochem. J., 1926, **20**, 1052—1054).—Bread previously digested by pepsin gives a higher fat yield on extraction with ether than before digestion. Similarly, a somewhat higher yield of fat is obtained when flours are previously digested. A Soxhlet ether extraction with repeated trituration of the flour in the course of extraction secures a very complete removal of the fats and gives a higher result than Soxhlet extraction after digestion or by extraction in a separator after peptic digestion.
S. S. ZILVA.

Pigment in tegument of seeds of *Phaseolus vulgaris*. M. SKALINSKA (Compt. rend. Soc. Biol., 1925, **93**, 780—782; from Chem. Zentr., 1926, I, 1821).—Flavones are present, which can be converted into anthocyanins. E. C. SMITH.

Yellow chromatophoric pigments of the higher plants. H. KYLIN (Z. physiol. Chem., 1926, **157**, 148—162).—By dipping strips of filter-paper into 1-day cold alcoholic extracts of *Achillea millefolium* four bands of colour were obtained. If a boiling extract were made, only three were obtained. This was thought to be due to the destruction of chlorophyllase. The time necessary to obtain the fourth band is a function of the amount of enzyme present in the leaves. It is probable that in all the higher plants there are two xanthophyll modifications, that which turns green with hydrochloric acid being called phylloxanthin. In the higher plants, there is also a red pigment, rhodoxanthin.
H. I. COOMBS.

Electrode potentials of hermidin, the chromogen of *Mercurialis perennis*. R. K. CANNAN (Biochem. J., 1926, **20**, 927—937).—*Mercurialis perennis* contains a chromogen (hermidin) which on exposure to oxygen turns into a blue pigment (cyanohermidin) and ultimately becomes irreversibly oxidised to a yellow pigment (chrysohermidin) (cf. Haas and Hill, A., 1925, i, 759; Ann. Bot., **39**, 861). By titrating hermidin with an oxidising agent such as benzoquinone or with a reducing agent such as sodium hydrosulphite, a typical oxidation–reduction curve is obtained. Electrode potentials of the system

hermidin–cyanohermidin over the range p_H 2·0–8·0 are given. When the titration is continued beyond the end-point of the first stage of oxidation, another region of poised potentials is obtained. Only in the region of p_H 7—8 can equilibrium potentials be recorded, since rapid drifts in potential are observed outside these limits, possibly due to the subjection of the true oxidant to an irreversible change at those reactions. Electrometric data are given of the rates of oxidation of hermidin and cyanohermidin by a stream of oxygen diluted with nitrogen.

S. S. ZILVA.

Polarographic methods in biology. S. PRAT (Biochem. Z., 1926, **175**, 268—273).—A discussion of the applicability of the dropping mercury cathode (cf. Heyrovský, A., 1925, ii, 673) to the quantitative determination of small amounts of metals in solutions of physiological importance. J. PRYDE.

Blood-gas analyser. C. C. GUTHRIE (J. Lab. Clin. Med., 1926, **11**, 565—567).—A modification of the Haldane apparatus and a new method are described for the determination of the carbon dioxide and oxygen content and capacity of the blood.

CHEMICAL ABSTRACTS.

Apparatus for determination of methane in metabolism experiments. T. M. CARPENTER and E. L. FOX (J. Biol. Chem., 1926, **70**, 115—121).—A gas analysis apparatus of the Haldane type is provided with a special combustion chamber which makes possible the accurate determination of small amounts of methane, such as occur in the expired air of ruminants. C. R. HARINGTON.

Determination of bile-acids in blood. F. ROSENTHAL and L. WISLICKI (Arch. exp. Path. Pharm., 1926, **117**, 8—23).—Whole blood or serum (50 c.c.) is extracted with three times the volume of boiling absolute alcohol and, after filtration, the coagulum is further extracted until the Pettenkofer reaction is negative. The extracts are evaporated to dryness and the residue is extracted with ether so long as colouring matter is removed. The residue is then treated with a magnesium sulphate solution (130 g. in 100 c.c. water) at 70° and the precipitate filtered into a Gooch crucible (through which the ether extracts have previously been passed) and washed with the warm magnesium sulphate solution. The precipitate is then thoroughly extracted with boiling absolute alcohol until the Pettenkofer reaction is negative and the alcoholic extract evaporated to dryness. The residue is taken up in a measured volume of water. Half this solution is hydrolysed by heating at 100° with an equal volume of 16% potassium hydroxide for 6 hrs., and the amino-nitrogen determined gasometrically in the two portions. The difference multiplied by 33·12 gives the amount of bile acids reckoned as glycocholic acid.

In icterus, the bile acid of the serum constitutes 5—12 mg. per 100 c.c. When bile salt is added to whole blood, the distribution between corpuscles and serum is in the ratio of approximately 59 : 41.

C. RIMINGTON.

Blood uric acid. Comparative results by three methods, and technique necessary for accurate determinations. W. P. HOLBROOK and H. D. HASKINS (J. Lab. Clin. Med., 1926, **11**, 377—381).—A slight modification of the Folin procedure.

CHEMICAL ABSTRACTS.

Micro-Folin–Wu method of blood-sugar determination using 0·1 c.c. of blood. T. L. BYRD (J. Lab. Clin. Med., **11**, 1925, 67—75).

CHEMICAL ABSTRACTS.

Apparatus for the determination of cholesterol. S. L. LEIBOFF (J. Lab. Clin. Med., 1925, **10**, 857—861). CHEMICAL ABSTRACTS.

Determination of albumin in urine. W. G. EXTON (J. Lab. Clin. Med., 1925, **10**, 722—735).—2—3 C.c. of a filtered solution containing 50 g. of sulphosalicylic acid, 10 g. of sodium sulphate, and 25 c.c. of saturated aqueous phenol-blue in 1 litre are mixed with an equal volume of urine, the mixture is kept for 5 min., gently warmed, and the opacity compared with sealed standard tubes prepared from fresh sheep-serum of known Kjeldahl value, sodium chloride, and gum arabic. Allowance is made for the opacity of cloudy urines. Alkaline urines and those containing much carbonate are first acidified with acetic acid. CHEMICAL ABSTRACTS.

Urea distillation by the Folin–Wu method. H. E. BUTKA and F. E. MEISNER (J. Lab. Clin. Med., 1925, **10**, 937—938). CHEMICAL ABSTRACTS.

Micro-colorimetric method for the determination of phospholipins in seeds. N. B. GUERRANT (J. Amer. Chem. Soc., 1926, **48**, 2185—2190).—The dried material (1 g.) is dissolved in 25 c.c. of ether–alcohol (20 : 80), insoluble matter removed by centrifuging, and 5 c.c. of the clear solution are evaporated to small volume; 1 c.c. of 12·5*N*-sulphuric acid is added, and the mixture heated. Hydrogen peroxide (30%) is added continuously to prevent the solution from darkening, and when all colour is removed the temperature is raised until the container (35 c.c.) is half-filled with acid fume, and maintained at this point for 6 min. to expel excess of oxidising agent. After cooling, the mixture is diluted to 10 c.c. with water, boiled for 10 min., cooled, shaken with 1 c.c. of 5% ammonium molybdate solution, and then with 1 c.c. of 1 : 2 : 4-aminonaphtholsulphonic acid reagent. The blue colour developed is then compared, after suitable dilution, with that developed from a known amount of standard monopotassium phosphate solution (1 mg. of phosphorus per c.c.), prepared simultaneously, and identically from the stage of heating with sulphuric acid. The aminonaphtholsulphonic acid reagent is prepared by adding to 1 g. of purified acid 225 c.c. of 20% sodium hydrogen sulphite and then 20% sodium sulphite until the acid is in solution. The solution is then diluted to 250 c.c. The results obtained compare satisfactorily with those given by the gravimetric method requiring 100 g. of material.

F. G. WILLSON.

BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1926.

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General, Physical, and Inorganic Chemistry.

Characteristic low-frequency series of oxygen and nitrogen. Spectrographic junction between *X*-rays and the extreme ultra-violet. A. DAUVILLIER (Compt. rend., 1926, **183**, 656—658).—The author has used his method (this vol., 875) to investigate the characteristic low-frequency spectra of oxygen and nitrogen with thorium, an element of high atomic weight and complete internal electronic structure, as cathode. A strong line was obtained at 45·3 Å. ($N\beta$) coincident with the $K\alpha$ line of carbon, but due to thorium. This was proved by measurements of the critical potentials, and by the failure to obtain the line when other elements were used. Less intense lines were obtained at 48·2, 71·0, and 121·0 Å., and a strong line at 51·5 Å. These correspond with the $O\delta$, $O\gamma$, $O\beta$, and $N\alpha$ lines, respectively. A link is thus established with the optical spectra obtained by Millikan in the extreme ultra-violet.

J. GRANT.

Optical instruments for the infra-red and ultra-violet. C. LEISS (Z. Physik, 1926, **39**, 465—472).—Three instruments are described: (1) an infra-red spectrometer with rock-salt prism for the region 0·3—15 μ; (2) a quartz monochromator with automatic focussing for the region 0·2—4·2 μ; (3) a double monochromator for the region 0·2—0·5 μ.

E. B. LUDLAM.

Organic absorption media as colour screens in the ultra-violet. T. M. DAHN (Physical Rev., 1925, [ii], **25**, 285).—If the concentration or the length of cell is adjusted so that $I/I_0(=e^{-kcx})$ is less than e^{-1}, the transmission of nearby lines will fall off more rapidly than k rises. Values of the "gradation constant" have been found such that adjacent strong lines of the mercury spectrum may be transmitted with 20% and less than 0·2% of the unabsorbed values. A. A. ELDRIDGE.

Secondary standards of wave-length in the spectra of neon and iron. G. S. MONK (Physical Rev., 1925, [ii], **26**, 284).—The recommended values of the lines 5852 and 5881 are questionable. In the spectrum of the standard iron arc, 110 lines have been compared with the spectrum of neon; in the red, the results are about 0·002 Å. lower than those of the Bureau of Standards. It is considered that the system of standards should be based on the iron arc at atmospheric pressure. A. A. ELDRIDGE.

Reversal in vacuum tube spectra. T. R. MERTON (Phil. Mag., 1926, [vii], **2**, 975—978).—Reversal of the D_3-line of helium has been observed, not only in long end-on tubes, but also perpendicular to the capillary of a vacuum tube of ordinary pattern so long as the current density is sufficiently high. When an echelon grating of thirty-five plates of glass each 15 mm. thick in optical contact was used to analyse the end-on spectrum from a tube 25 cm. long and 5 mm. bore containing helium at 5—10 mm. pressure, reversal was seen with moderate currents. When currents of about 100 milliampères were passed, the reversal was very distinct and was quite definitely asymmetrical, the intensity on the more refrangible side being somewhat greater. Similarly, when heavy currents were passed through an ordinary tube containing helium at a few mm. pressure and the spectrum was examined perpendicular to the capillary, similar results were obtained. The resolving power of the echelon was above 500,000. The phenomenon could not be observed with a Lummer–Gehrcke plate with a resolving power of 200,000. It is suggested that since very high current densities are required, the presence of a layer of less strongly excited gas close to the walls of a vacuum tube is not sufficient to explain reversal phenomena. A. E. MITCHELL.

Low-voltage arc oscillations in nitrogen and in mixtures of hydrogen and nitrogen. C. ECKART, C. T. KWEI, and K. T. COMPTON (Physical Rev., 1925, [ii], **25**, 889).—Oscillations were observed (cf. Eckart and Compton, *ibid.*, 1924, [ii], **24**, 97) in nitrogen at low pressures, or in hydrogen mixed with a slight excess of nitrogen, but not in pure hydrogen. The oscillations commenced at 17 volts, and were maximal at 20 or 22·5 volts, according to the strength of the thermionic current. A. A. ELDRIDGE.

Stripped atoms of the first long period. R. C. GIBBS and H. E. WHITE (Proc. Nat. Acad. Sci., 1926, **12**, 598—601).—The first lines of the diffuse spectral series for the above atoms have been identified (cf. this vol., 874), and the irregular doublet law has been shown to hold good. It seems that with all these elements the d electron is the most tightly-bound electron. The location of the $5^2D_{2,3}-6^2P_{1,2}$ lines in La III shows that here the d electrons are bound more tightly than either the p or the s electrons. R. CUTHILL.

Ground terms of the spectra of the first and second long periods. O. LAPORTE (Z. Physik, 1926, **39**, 123—129).—An empirical rule is given by means of which the deeper terms of the spark spectra and their distances apart can be calculated from the arc spectra, and conversely of the arc spectra from those of the spark. E. B. LUDLAM

Series and multiplets in sulphur and chlorine. J. J. HOPFIELD (Physical Rev., 1925, [ii], **26**, 282—283).—Sulphur series previously described (A., 1923, ii, 708) have been confirmed; the frequencies are given by the equations: $\nu=83554-R/(n+1{\cdot}05086-0{\cdot}13386/n+0{\cdot}05425/n^2)^2$; $n=1, 2, \ldots$; $\nu=83554-R/(n+0{\cdot}53341+1{\cdot}06794/n-0{\cdot}82152/n^2)^2$; $n=2, 3, \ldots$ The lines of sulphur, unassigned in Fowler's report, have been arranged in series. Two multiplets having shortest wave-lengths 1381·60 and 1473·00, respectively, are attributed to a two-electron transition. By analogy with S I the ionising potential of Cl II is provisionally calculated as 18·32 volts; hence that of Cl I is about 9·16 volts. A. A. ELDRIDGE.

Series in the arc spectrum of argon. K. W. MEISSNER (Z. Physik, 1926, **39**, 172—190).—Ten series have been established in the red argon spectrum which are analogous to the 10*p*-series of neon. These series fall into two groups having two different limits, of which the distance apart is 1423 cm.$^{-1}$ E. B. LUDLAM.

Structure of the spectra of the rare gases. W. M. HICKS (Ann. Physique, 1926, [x], **6**, 294—309).—The theory advanced by Bloch, Bloch, and Déjardin (A., 1924, ii, 286) to explain the spectra observed when the rare gases are subjected to electron collisions and to the alternating current electrodeless discharge is criticised. Their criticism of the author's classification of such spectra is considered unfounded, because the arc spectra have been confused with those of neutral atoms and the spark spectra with those of ionised atoms. R. W. LUNT.

Explanation of the spectra of metals of the second group. M. SAHA (Nature, 1926, **118**, 695).—A brief account of work to be published in detail. A. A. ELDRIDGE.

Multiplets in the spectrum of ionised vanadium. W. F. MEGGERS (Z. Physik, 1926, **39**, 114—122; cf. A., 1925, ii, 913).—Further examination of the arc spectrum of vanadium has resulted in the observation of quintuplet and triplet series. The ground term of V^+ is not a ^5F, but a ^5D term. The "raies ultimes" are discussed, and it is shown that extreme caution must be exercised in reaching conclusions as to the ground term of a spectrum from them. E. B. LUDLAM.

Selective dispersion of mercury vapour at the absorption line 2536 Å. F. E. KLINGAMAN (Physical Rev., 1926, [ii], **28**, 665—671).—The shifts of the interference fringes of seven iron lines close to the mercury absorption line 2536·7 Å. were measured for mercury vapour pressures of 0·0015—0·113 mm. That of the line closest to the absorption line is proportional to the density of the vapour; the shifts for lines further from the absorption line increase less rapidly, but it is not considered that this is due to the presence of complex mercury molecules. Molecular refractive indices were determined as follows: 2536·9 Å., 1·068; 2538·4 Å., 1·006; 2535·6 Å., 0·988. Cuthbertson and Metcalfe's value of the refractive index for the line 6560 Å. (A., 1908, ii, 545; 1910, ii, 85) is about 3% too low. A. A. ELDRIDGE.

Structure of the arc spectrum of lead. H. GIESELER and W. GROTRIAN (Z. Physik, 1926, **39**, 377—390).—The spectrum was obtained by passing a current of about 100 milliampères at 2000 volts through lead vapour, using a hollow cathode. The lines are grouped in singlet and triplet series. Higher members of the secondary series were found and anomalies noticed both in the intensities of the lines and the magnitude of the terms. E. B. LUDLAM.

Soft *X*-rays. Improvements in technique and new results for carbon, copper, and tungsten. K. T. COMPTON and C. H. THOMAS (Physical Rev., 1926, [ii], **28**, 601—612).—Thirty-one new critical potentials for copper between 66·9 and 276·7 volts are tabulated (cf. Thomas, this vol., 104), as well as 62 critical potentials for carbon between 8·95 and 155·1 volts. The "fine structure" of the critical potentials is believed to be real, and suggestions are offered for its interpretation. A method of exaggerating discontinuities in the ordinary $E/I-V$ curve is demonstrated for the soft *X*-radiation curve of tungsten. A. A. ELDRIDGE.

***K* *X*-Ray absorption of calcium in calcite, gypsum, and fluorite.** G. A. LINDSAY and G. D. VAN DYKE (Physical Rev., 1926, [ii], **28**, 613—619).—The wave-lengths of the *K* *X*-ray absorption edges, *A*, *B*, *C*, and *D*, respectively, of calcium are: calcite, 3060·3, 3050·2, 3037·9, 3023·3; gypsum, 3059·1, 3047·5, 3035·3, —; fluorite, 3059·9, 3047·8, 3034·6, 3025·3 X. Kossel's suggestion that the electron ejected from the *K*-orbit stops in some of the exterior unoccupied orbits is probably correct. A. A. ELDRIDGE.

***X*-Rays scattered by molybdenum.** P. A. ROSS (Physical Rev., 1925, [ii], **26**, 281—282).—The radiation scattered by the molybdenum cathode cup of a Coolidge tube was measured at scattering angles of 110° and 160°; the observed shifts were $0{\cdot}035\pm0{\cdot}002$ and $0{\cdot}047\pm0{\cdot}002$ Å., respectively, the corresponding computed values being 0·0345 and 0·0469. The scattering of tungsten *K*-radiation from molybdenum was also observed; at a scattering angle of 160° the line was shifted by $0{\cdot}047\pm0{\cdot}001$ Å. A. A. ELDRIDGE.

Separation and relative intensity of the components of the *K*β line in the *X*-ray spectrum of molybdenum. S. K. ALLISON and A. H. ARMSTRONG (Physical Rev., 1925, [ii], **25**, 882).—The doublet is a so-called "relativity doublet," the transitions involved being $\beta_1=K-M_{III}$; $\beta_3=K-M_{II}$; $\Delta\lambda$ (observed)$=0{\cdot}000566\pm0{\cdot}000014$ Å.; (calculated) $=0{\cdot}000564$ Å. (cf. A., 1925, ii, 1015). A. A. ELDRIDGE.

***X*-Ray spectra of the lower elements. II.** R. THORÆUS (Phil. Mag., 1926, [vii], **2**, 1007—1018; cf. this vol., 329).—The earlier work on the lower *L*-series showed only two main lines with one satellite. The newer examination has proved that both the main lines are more complicated and have at least two satellites each. These have been measured for the elements bromine (35) to copper (29). Below zinc (30) the satellites become very diffuse and impossible to measure. The *Lα* lines of zinc, copper, and nickel have been examined for the following substances: zinc, zinc oxide, zinc sulphide, copper,

cuprous and cupric oxides, cupric sulphide, nickel, nickel sulphide, and nickelous oxide. With zinc, all the $L\alpha$ lines are alike. For metallic copper and cuprous oxide, they are alike, comprising a broad band with diffuse edges; for cupric oxide and cupric sulphide, they consist of two lines clearly separated; for nickel, the metallic and bivalent atoms behave similarly and the tervalent atom gives a separated $L\alpha$ line. The $\sqrt{\nu/R}$ values of the M-levels have been calculated. When these are plotted against the atomic numbers, a break in the slope occurs at copper (29) corresponding with the changes in the structure of the L spectra observed.

A. E. MITCHELL.

Polarisation of X-rays. J. B. BISHOP (Physical Rev., 1926, [ii], **28**, 625—632).—It is concluded that molybdenum $K\alpha$ lines are at least partly polarised.

A. A. ELDRIDGE.

Stark effect from the point of view of Schrödinger's quantum theory. P. S. EPSTEIN (Physical Rev., 1926, [ii], **28**, 695—710).—Mathematical. A theory of the Stark effect based on Schrödinger's conception of characteristic oscillations in the atom (Ann. Physik, 1926, [iv], **79**, 361, 489, 734) has been worked out. Simple intensity formulæ are derived which give values in better agreement with observation than Kramers' expressions derived from Bohr's correspondence principle. A. A. ELDRIDGE.

Compton effects. S. K. ALLISON and W. DUANE (Physical Rev., 1925, [ii], **25**, 235—236).—When small radiators are used, broad peaks appear on the curves in positions in substantial agreement with Compton's equation. A. A. ELDRIDGE.

Compton effect with hard X-rays. D. L. WEBSTER and P. A. ROSS (Physical Rev., 1925, [ii], **25**, 714).—Compton's theory is confirmed within the limits of error (cf. A., 1925, ii, 1034).

A. A. ELDRIDGE.

Spectrograms of tungsten K-series rays scattered by graphite. M. C. MAGARIAN (Physical Rev., 1925, [ii], **26**, 282).—The shifted line was much more intense than the unshifted line; the wave-length shift agreed with Compton's relation within the probable errors. A. A. ELDRIDGE.

Ratio of intensity of the Compton lines. P. A. ROSS (Physical Rev., 1925, [ii], **26**, 282).—Values of the shift (10^{-3} Å.) and intensity ratio for a scattering angle of 90° are respectively as follows for molybdenum $K\alpha$-radiation: graphite, $23{\cdot}6\pm0{\cdot}3$, 1·7; aluminium, $24{\cdot}4\pm0{\cdot}1$, 0·7; sulphur, $24{\cdot}0\pm0{\cdot}5$, 0·29; copper, $24{\cdot}4\pm0{\cdot}2$, 0·32; silver, $23{\cdot}8\pm0{\cdot}2$, 0·21; lead, $24{\cdot}0\pm0{\cdot}2$, 0·024. Similarly, for molybdenum $K\beta$-radiation, aluminium, $24{\cdot}2\pm0{\cdot}1$, 1·0. For molybdenum $K\alpha$-radiation incident on graphite, $3{\cdot}0\pm1$, $0{\cdot}2$; $12{\cdot}0\pm0{\cdot}1$; 0·95 for scattering angles of 30° and 60°, respectively. A. A. ELDRIDGE.

Disappearance of the unmodified line in the Compton effect. G. E. M. JAUNCEY and R. A. BOYD (Physical Rev., 1926, [ii], **28**, 620—624).—Experiments on the scattering by carbon of X-rays of wave-lengths 0·41 and 0·47 Å. give curves, exhibiting the variation of the ratio of the modified to total scattering as a function of the angle of scattering, which decrease in slope at those angles at which Jauncey's theory requires the disappearance of the unmodified ray. The theory cannot, however, be applied to scattering by L_1 electrons.

A. A. ELDRIDGE.

Longitudinal asymmetry in the direction of ejection of photo-electrons by X-rays. O. K. DE FOE (Physical Rev., 1925, [ii], **25**, 581).—About 20% of the tracks were at about 90° to the beam; nearly all were within 45° of the plane normal to the beam. The experimental and theoretical ratios of the forward to the backward photo-electrons are 2·89 and 3·08, respectively. A. A. ELDRIDGE.

Reaction constants, life-periods, recombinations, interchange numbers in gas flames, and saturation potentials. E. MARX (Ann. Physik, 1926, [iv], **81**, 454—492).—The employment of the relation $xy/\sqrt{A}=$constant (y is degree of dissociation of an alkali salt, x degree of dissociation of the metallic atoms into electrons and positive ions, and A is the atomic weight of the alkali metal) makes possible considerable developments of the author's earlier work (*ibid.*, 1925, **76**, 737). With x, y, and $(C_p)_{\text{salt}}$ as unknowns and three equations consisting of (*a*) the Nernst reaction isotherm as used by Saha for the primary dissociation of alkali salt into atoms, (*b*) a similar isotherm for the formation of charged carriers, and (*c*) the relation given above, mathematical investigation permits the equilibrium in the flame to be analysed. The number of atoms existing in the equilibrium in various states and the life-period in those states are evaluated. For the sodium atom in its normal state, the latter is $2{\cdot}61\times10^{-3}$, whilst in the $2p$ state it is $1{\cdot}35\times10^{-8}$ sec. From the flame temperature and the constants governing the emission of the D-line, the mathematical treatment leads to conclusions on the lines indicated by the title.

R. A. MORTON.

Depolarising influence of a rapidly changing magnetic field on the resonance radiation [of mercury]. G. BREIT and A. ELLETT (Physical Rev., 1925, [ii], **25**, 888—889).—The influence of an alternating field of the order of 2 gauss becomes negligible when the frequency is 10^7 cycles per sec., but pronounced at 5×10^6 cycles per sec., indicating that the life of the excited atom is approximately 10^{-7} sec. A. A. ELDRIDGE.

Interaction between radiation and a quadrupole atom. I. I. PLACINTEANU (Z. Physik, 1926, **39**, 276—298).—Mathematical. The energy radiated by a quadrupole atom in a given time is very much less than that by a dipole; the period of duration of the excited state of the quadrupole is about a million times that for the dipole. E. B. LUDLAM.

Ionisation potential and periodic system of the elements. L. ROLLA and G. PICCARDI (Gazzetta, 1926, **56**, 512—531; Chim. et Ind., 1926, **16**, 531—543).—A review. Ionisation potentials determined by the authors (A., 1925, ii, 1018, 1105; this vol., 3, 769), and by others, are plotted against atomic number to give a periodic curve more satisfactory than those from other properties. Considering the values in relation to Bohr's orbital distribution of

electrons, it is suggested that ionisation potential is a function of the atomic structure (especially at the periphery), in quantitative relation to the chemical character of the elements. Characteristic recurrent periods are observed: (1) for alkali and alkaline-earth metals, (2) for the elements of types boron to neon, (3) for the types scandium to nickel, (4) for the types copper and zinc, and (5) for the rare earths.

E. W. WIGNALL.

Ionisation potentials of nitrogen and hydrogen on iron and other metals. G. B. KISTIAKOWSKY (J. Physical Chem., 1926, **30**, 1356—1363).—The positive-ion current produced by slow-moving electron impacts on metal surfaces has been measured by a method similar to that of Wolfenden (this vol., 217). On iron, nickel, copper, and platinum, positive ionisation starts at 11 and at 13 volts, ascribed to adsorbed nitrogen and adsorbed hydrogen on the metal surface, respectively. Theoretically, the ionisation at 11 volts cannot belong to molecular nitrogen, but is due to the nitrogen atom or to an excited nitrogen molecule. The ionisations occurring at 17 and at 16 volts belong to molecular nitrogen and molecular hydrogen, respectively. The work of Wolfenden (*loc. cit.*) is critically discussed, but is found to be in substantial agreement with the above. Olmstead's work (A., 1923, ii, 367, 820) affords no evidence that the ionisation at 11 volts is to be ascribed to the process $H_2 \longrightarrow H_2^+ + \ominus$.

L. S. THEOBALD.

Critical potentials and spectra of oxygen. L. L. LOCKROW (Astrophys. J., 1926, **63**, 205—217).—The "O I" and "O II" line spectra and the band spectra of oxygen in the visible and ultra-violet regions were observed. Ionisation occurs at 16·1 volts. Dissociation of the molecule and ionisation of an atom occur at 19·5 volts as the result of a single electronic encounter. A potential of 50 volts is sufficient for the production of doubly-ionised oxygen atoms. The dissociation potential of the oxygen atom is approximately 6 volts, corresponding with an energy of dissociation of 138,000 g.-cal./g.-mol. The three energy levels found for the band spectra were 21, 19·2, and 16·1 volts.

A. A. ELDRIDGE.

Relation between absorption coefficients, refractive indices, and photo-electric thresholds. R. HAMER (Physical Rev., 1925, [ii], **25**, 894; cf. this vol., 1073, and following abstracts).—Values of absorption coefficients and refractive indices show changes at wave-lengths approximately corresponding with observed photo-electric thresholds. Electrons in metals are evidently not free, but so bound in quantum orbits that they respond best to certain critical frequencies.

A. A. ELDRIDGE.

Reflecting powers of elements in the ultra-violet and the photo-electric thresholds. R. HAMER (Physical Rev., 1925, [ii], **26**, 285).—There is a change in the reflecting power at a wave-length coinciding approximately with the threshold, the reflecting power generally being decreased. Electrons in metals are not free, but bound.

A. A. ELDRIDGE.

"Raies ultimes" and photo-electric thresholds. R. HAMER (Physical Rev., 1925, [ii], **26**, 286).—A study of the energy values indicates that the photo-electric threshold is equal to the difference between the ionisation potential and the energy of a prominent "raie ultime"; hence the ionisation potentials and the corresponding terms or thresholds can be predicted for certain elements.

A. A. ELDRIDGE.

Compound photo-electric effect. P. AUGER (Ann. Physique, 1926, [x], **6**, 183—253).—The electron emission from gases exposed to *X*-radiation has been examined by Wilson's track method. Tertiary and quaternary β-ray emission has been investigated in mixtures of hydrogen and the rare gases as a function of the frequency of the exciting radiation, and of the atomic number of the absorbing atoms. A theory, in agreement with the Klein–Rossland transformation, is advanced to relate the observed phenomena on the hypothesis that an irradiated atom either fluoresces, giving *X*-radiation characteristic of the atom, or ejects electrons. A mechanism is suggested whereby the energy of an excited atom is degraded to energy of agitation. The experimental data are shown to support Whiddington's law relating the path of ejected electrons to their velocity. A complete description is given of the experimental procedure.

R. W. LUNT.

Emission of electrons from cold metals. F. ROTHER (Ann. Physik, 1926, [iv], **81**, 317—372).—A technique is described in detail whereby the electron emission between tantalum electrodes of various shapes has been investigated. Currents of the order of 10^{-10} ampère were obtained using continuous potentials from 2 to 12 kilovolts. In order to obtain reproducible data, the electrode material must be melted in a high vacuum and then highly polished, and the determinations carried out at a pressure not greater than 10^{-6} mm. The fields necessary to produce electron emission under such conditions are from 2 to 9×10^6 volts/cm., which is in agreement with the value 10^7 predicted by Schottky's theory (Z. Physik, 1923, **14**, 63). Some experiments were carried out on phenomena observed by Lilienfeld and on the scintillations recorded by Lilienfeld and by Cunradi. A correlation is proposed between these phenomena and the observed electron emission.

R. W. LUNT.

Theory of the thermionic effect. N. VON RASCHEVSKY (Z. Physik, 1926, **39**, 159—171; cf. A., 1925, ii, 920).—Thermionic emission has been treated as a problem of the behaviour of electrons in the interior of a substance, and also as a surface phenomenon; comparison of the mathematical and thermodynamical consequences of either point of view shows that they give the same result. The conditions for the universality of Richardson's constant are discussed. An approximate calculation of the surface difference of potential is made and a relationship indicated with the theory of metallic conduction.

E. B. LUDLAM.

Thermionic emission of tungsten, molybdenum, thorium, zirconium, and hafnium. C. ZWIKKER (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 792—802).—Measurements of the thermionic emission of tungsten, molybdenum, thorium, zirconium, and hafnium at high temperatures indicate that the value of *A* in the formula for the saturation

current, $i=AT^2 10^{-b/T}$ (cf. von Raschevsky, A., 1925, ii, 920), is in the neighbourhood of 60·2 for a pure metal surface, i being in ampères per cm.^{2} The much higher values found for zirconium and hafnium are attributed to the presence of a superficial layer of oxide. A. B. MANNING.

Effect of a hydrogen atmosphere on the velocity distribution among thermionic electrons. C. DEL ROSARIO (Physical Rev., 1926, [ii], **28**, 769—780).—For filament temperatures of 1520—1990 Abs., and pressures of hydrogen from 0 to 0·25 mm., the distribution of velocities among the electrons in a vacuum and in hydrogen follows Maxwell's law. The hypothesis that the thermionic electrons are in thermal equilibrium with the hot source is confirmed, and it is hence concluded that the collisions between the thermionic electrons and the hydrogen molecules are highly elastic. A. A. ELDRIDGE.

Electrodeless discharge in hydrogen. M. SCHLESINGER (Z. Physik, 1926, **39**, 215—225).—An oscillatory discharge was sent round six turns of copper wire inside of which was placed the bulb containing the hydrogen, the wave-length of the circuit being 300 metres. The relative intensities of the red and blue lines were measured for different pressures of the gas; lowering the pressure increased the relative intensity of the blue line at first, but it reached a maximum at 0·19 mm. and then diminished. The presence of mercury produced a marked effect. The conductivity of the gas during the discharge was measured. No phosphorescent glow was observed. E. B. LUDLAM.

Electron affinity of the hydrogen atom. G. Joos and G. F. HÜTTIG (Z. Physik, 1926, **39**, 473; cf. Kasarnovski, this vol., 876).—If the authors had used the same value as Kasarnovski for the molecular volume of sodium hydride, 15·15, obtained by extrapolation, instead of Moissan's experimental value, 26·1, they would also have obtained a negative value instead of +23 kg.-cal. Their own determination of the density of sodium hydride is in agreement with Moissan's. E. B. LUDLAM.

Passage of electrons through small apertures. G. F. BRETT and R. WHIDDINGTON (Proc. Leeds Phil. Lit. Soc. Sci. Sec., 1926, **1**, 65—69).—When electrons, accelerated by a potential V, pass through a small aperture, only a small proportion of them emerge with the maximum energy eV (cf. Lehmann and Osgood, Proc. Camb. Phil. Soc., 1925, **22**, 731). The magnetic spectrum consists of a series of well-marked lines. Among other possible explanations, it is suggested that the lines are probably the result of " reflexion " of electrons from the sides of the slit, energy differences being thus introduced equivalent to radiation and ionisation potentials. M. S. BURR.

Blackening of photographic emulsions by low-speed electrons. K. COLE (Physical Rev., 1926, [ii], **28**, 781—793).—The blackening of an unoiled emulsion by low-speed electrons is probably due to the production of radiation at the surface of impact of the charged particles, and is a discontinuous function of the electron speed. Schumann plates are particularly sensitive. For plates having a thin film of fluorescent lubricating oil on the emulsion, the electron sensitivity is 50—100 times as great as for the unoiled plates, and is still approximately proportional to the light sensitivity. A. A. ELDRIDGE.

Ionisation of hydrogen chloride. H. A. BARTON (Physical Rev., 1925, [ii], **25**, 890).—Determinations of the value m/e for ions formed from hydrogen chloride in the presence of a hot filament from which electrons are accelerated by a known field suggest the formation of ions HCl,H^+ or $(HCl)_2,H^+$; H^+ and H_2^+ ions are also present, and negatively charged chlorine ions or hydrogen chloride molecules. A. A. ELDRIDGE.

Energy of combination of gaseous ions. J. H. HILDEBRAND (Physical Rev., 1925, [ii], **26**, 284).—Calculated values for the combination of gaseous ions of the alkali metals with gaseous halide ions to form the solid halides approximate to those of Born and Landé. The stability of the compounds is discussed. A. A. ELDRIDGE.

Structure of the atomic magnet and the mechanical effects of magnetisation. R. FORRER (Compt. rend., 1926, **183**, 738—741; cf. this vol., 878).—The author's theory of multiplets supports the magnetostriction phenomena observed for iron and nickel. With iron, positive and negative magnetostrictions are obtained in weak and strong fields, respectively, owing to the normal position of the orbit being such that rotation of the triplet brings the orbits of the neighbouring atoms close together. With nickel, the strong negative magnetostriction obtained in weak fields, which increases in stronger fields, is due to the doublet nature of the nickel multiplet, and the approaching together of the constituent doublets as the field increases. The inverse phenomenon of the variation in magnetisation due to elastic deformation is explained by the same hypothesis. It is more marked for nickel than for iron. J. GRANT.

Atomic moments of ferromagnetics. E. C. STONER (Proc. Leeds Phil. Lit. Soc. Sci. Sec., 1926, **1**, 55—64).—Theoretical. Different values for the magnetic moments per atom of iron, cobalt, and nickel are deduced from the experimental data for the variation in susceptibility with temperatures above the Curie point and the saturation intensities of magnetisation at low temperatures, respectively. This difference can be explained on the basis of the quantum theory. The constitution of the ions present in the solid state is unknown, but they are not necessarily similar, and transfer and sharing of electrons may take place among groups of atoms. The magnetic properties may be assumed to be due to ions which have the same moments as those found from measurements on paramagnetic solutions and solid salts. The conditions are discussed under which ions with a magnetic moment may continue to manifest paramagnetic properties when united in solids. M. S. BURR.

Magneto-electric orientation effect. A. HUBER (Physikal. Z., 1926, **27**, 619—627).—Paramagnetic molecules possessing an electric moment should exhibit electric polarisation in a constant magnetic field if the Langevin model is valid. Attempts to

demonstrate the orienting effect (Perrier, Arch. Genève, 1922, **4**, [v], 373) have not been successful, although Szivessy (A., 1925, ii, 1123) has observed the converse magnetic effect. Nitric oxide was chosen as a dipolar paramagnetic gas suitable for investigation, but no electric polarisation was observed, although 1/700 of the expected effect could have been detected. Ferric chloride vapour (300—450°) gave no effect. Liquid and solid nitric oxide, solid ferric chloride, powdered nickel sulphate, nickel sulphate single crystal, and solid potassium ferrocyanide all gave completely negative results. The suggestion that the failure to observe electrical polarisation may be due to the existence of enantiomorphs is regarded as improbable. The physical significance of the results is discussed. R. A. MORTON.

New residual rays and overtones of residual rays. O. REINKOBER (Z. Physik, 1926, **39**, 437—443).—Powdered crystals of rubidium chloride were subjected to a pressure of 2000 atm. and the surface was polished; light from a Nernst filament was reflected from three surfaces and passed through a copper wire diffraction grating. The wave-length of the residual rays was 74 μ. For lithium fluoride, the wave-length 17·1 μ was obtained, with overtones at 8·6 and 5·8 μ. Determination of the absorption bands for sylvine in the short infra-red region gave the wave-lengths 3·20 and 6·90 μ. E. B. LUDLAM.

Atomic weight of silver by the direct ratio of silver to oxygen in silver oxide. H. L. RILEY and H. B. BAKER (J.C.S., 1926, 2510—2527).—An apparatus is described for the preparation of very pure silver oxide. This compound is much more stable than has hitherto been supposed. Provided that organic matter and carbon dioxide are rigidly excluded, pure air may be passed over it for a week, at 120°, without decomposition, and a white chloride is also obtained from it by treatment with hydrochloric acid. The pure oxide has a brown colour and is apparently insensitive to light when not exposed to the atmosphere; the action of light on it when exposed to the atmosphere is discussed. The ratio of silver to oxygen was determined by heating the oxide in a silica tube in a current of pure dry air at 350—400°. The mean value of the atomic weight of silver from the results of six complete experiments is 107·864 ± 0·0013. M. S. BURR.

Precipitation of radium-*F* from solutions on silver, copper, gold, copper–gold and silver–gold alloys. G. TAMMANN and W. RIENÄCKER (Z. anorg. Chem., 1926, **156**, 275—287).—The amounts of radium-*F* precipitated on plates of silver, copper, gold, and of the alloys copper–gold and silver–gold are compared, using the gold leaf electroscope. The effect of varying the hydrogen-ion concentration in the solutions is discussed. M. CARLTON.

Isolation of two positive substances in thorium active deposit. H. A. ERIKSON (Physical Rev., 1925, [ii], **25**, 890—891).—Mobility experiments show that there are two positive active substances in thorium active deposit, the mobilities being the same as for the actinium active deposit. It is presumed that the swifter carries a double charge.
A. A. ELDRIDGE.

Energetics of radioactive emission. H. T. WOLFF (Physikal. Z., 1926, **27**, 640—642).—According to observations on the scattering of α-particles, Coulomb's law is valid down to 3×10^{-12} cm. from the centre of the atom (A., 1921, ii, 7). For radioactive substances, this leads to high values for the velocity of α-particles. The probable explanation is that when the particle leaves the nucleus it displaces electrons into new orbits of higher energy. In returning to their stable orbits, these electrons should emit γ-radiation. For radium, the calculated wave-length may be $4\cdot9\times10^{-11}$ and even 3×10^{-11} cm., corresponding with the hardest known γ-radiation and the very penetrating radiation. All primary β-rays have velocities very near to that of light.
R. A. MORTON.

Attempt to affect artificially the rate of radioactive disintegration. B. WALTER (Z. Physik, 1926, **39**, 337—340).—Uranium-X_1 was subjected to hard *X*-rays in the hope that they would eject an electron from the *K*-ring and that this would be replaced by one from the nucleus and increase the amount of β-radiation; the result, however, was negative. E. B. LUDLAM.

Distribution of the range of α-particles from radium-*A* and radium-*C*. (MLLE.) I. CURIE and M. P. MERCIER (J. Phys. Radium, 1926, [vi], **7**, 289—294).—The experiments were carried out by a method previously described (A., 1925, ii, 834). It is found that the ranges of the α-particles are distributed according to a probability law of coefficient α, in agreement with the theories of Bohr (Phil. Mag., 1913, [vi], **25**, 10; 1915, [vi], **30**, 581) and of Flamm (Sitzungsber. Akad. Wiss. Wien, 1914, **123**, 1393; 1915, **124**, 597). The value of $\rho(=\alpha/l$, l the most probable range), in agreement with theory, is independent of temperature and gas pressure. For radium-*A*, $\rho=1\cdot25\times10^{-2}$, $\alpha=0\cdot59$ mm.; for radium-*C*, $\rho=1\cdot1\times10^{-2}$, $\alpha=0\cdot76$ mm. in air at 15° and 760 mm. The ratio l_C/l_A was found to be 1·471. It is concluded that the variations in range are in agreement with the assumption that α-particles lose energy according to the laws of classical electrodynamics by the action of the electrons and nuclei of the atoms of the gas through which they pass. R. W. LUNT.

Effect of α-particles on supersaturated solutions. W. J. RICHARDS (Compt. rend., 1926, **183**, 598—600).—An attempt has been made to apply Wilson's α-particle track method to supersaturated solutions, in which local precipitation of the solute is brought about by either ionisation, heating effect, or mechanical shock due to the α-particle. Inconclusive results were obtained, except with solutions of sucrose and certain electrolytes in water, and of molten phenyl salicylate, which were definitely negative. Bubble formation was produced in solutions of gases after a sudden reduction of pressure, but not corresponding with any particular paths of the α-particles. J. GRANT.

Direction of emission of secondary β-rays. H. FRÄNZ (Z. Physik, 1926, **38**, 92—105).—The asymmetry of the secondary β-radiation produced by the action of γ-rays from radium-*C* on lead was examined by means of a Geiger counter, and the

distribution in different directions of the electrons ejected from lead and carbon was determined. For lead, the asymmetry was about 2, contrary to the result obtained by the ionisation method. For carbon, mainly recoil electrons were found, whereas for lead the result was influenced by the photo-electric effect, this deduction being confirmed by absorption measurements. E. B. LUDLAM.

Ranges of secondary β-rays. J. M. NUTTALL and E. J. WILLIAMS (Phil. Mag., 1926, [vii], **2**, 1109—1116).—The Wilson track method has been used to photograph the secondary β-rays produced by a homogeneous beam of *X*-rays of known wave-length in oxygen, nitrogen, argon, and hydrogen. Measurements of stereoscopic photographs of the β-ray tracks has allowed of the calculation of the ranges of the β-rays at *N.T.P.* For any one gas, Whiddington's law holds over a range of energies from 4800 to 27,190 volts. For equal atomic concentrations, the range of the β-rays is proportional to the reciprocal of the atomic number of the gas. Thus $R=KV^2/N$, where K is a constant equal to $1{\cdot}42\times10^{-8}$ when R is the range in a gas at atomic concentration equal to that of a diatomic gas at *N.T.P.* A. E. MITCHELL.

Artificial disintegration of elements. J. CHADWICK (Phil. Mag., 1926, [vii], **2**, 1056—1075).—The conflicting nature of the results obtained by Rutherford and Chadwick (A., 1921, ii, 293, 671) and by Kirsch and Pettersson (A., 1924, ii, 227, 380) in investigations of the disintegration of elements by collisions with α-particles, is pointed out. The optical systems in use by Rutherford and Chadwick have been examined and shown to be satisfactory for the observation of scintillations produced by any H-particles likely to be emitted in the disintegration of a nucleus. Re-examination of the elements lithium, beryllium, carbon, and oxygen has shown no evidence of the disintegrations reported by Kirsch and Pettersson. It is suggested that the procedure adopted by these authors in distinguishing between scintillations due to α-particles and those due to H-particles by the difference in brightness may have led to error. This may be particularly so in their work on aluminium. A. E. MITCHELL.

Occurrence of helium and neon in vacuum tubes. E. C. C. BALY and R. W. RIDING (Nature, 1926, **118**, 625—626).—Earlier results (A., 1925, ii, 925) have been repeated. Helium and neon have been obtained by passing the discharge between a concave aluminium mirror as cathode and a magnesium anode through a mixture of oxygen and nitrogen under reduced pressure, but not if the discharge is passed in the opposite direction. The rare gases are also produced when the condensed discharge is passed between aluminium wire electrodes through mixtures of oxygen and nitrogen, but not in the absence of the condenser; helium was also evolved when tungsten electrodes were heated. It is believed that the gases arise from the disintegration of the nitrogen atom.
A. A. ELDRIDGE.

Structure of aluminium. H. COLLINS (Chem. News, 1926, **133**, 257—262).—Speculative.

Sub-electron. E. REGENER (Z. Physik, 1926, **39**, 247—250).—Durau's evidence (this vol., 898) in favour of the sub-electron is regarded as vitiated by the presence of adsorbed gas films on his particles (cf. following abstract). E. B. LUDLAM.

Measurements of the charge on evaporating particles. R. SANZENBACHER (Z. Physik, 1926, **39**, 251—275).—The charge on particles of mercury evaporating in air or in carbon dioxide was found to possess the normal value. Lower values were found for particles which were not maintaining a fresh surface, and this is due to surface effects.
E. B. LUDLAM.

Polarisabilities of atomic cores. (MISS) B. SWIRLES (Proc. Camb. Phil. Soc., 1926, **23**, 403—411).—The polarisability of the core (Born and Heisenberg, A., 1924, ii, 434) has been obtained on the assumption that the series electron occupies an orbit with quantum numbers n and k such that the radius vector r joining it to the centre of the core is large enough for the field to be treated as homogeneous in the region of the core and equal to e/r^2. The theory has been applied with success to elements of the aluminium group and ionised silicon, and sodium and the corresponding stripped atoms.
R. A. MORTON.

Interaction of radiation with matter. Fluorescence exciting power. E. H. KENNARD (Physical Rev., 1926, [ii], **28**, 672—683).—A theoretical discussion based on Einstein's theory of emission and absorption. The distribution of energy in an enclosure containing quantised particles is indeterminate unless there is thermal or other non-radiative interaction between the particles. Fluorescence cannot lower the entropy of the system. There is no sharp distinction between thermal emission and fluorescence.
A. A. ELDRIDGE.

Orbits and radiation of hydrogen electrons. T. ENGSET (Ann. Physik, 1926, [iv], **81**, 572—576).—Mathematical (cf. this vol., 991).

Ionisation equilibrium of a radiating atomic system. B. GERASIMOVIČ (Z. Physik, 1926, **39**, 361—376).—A formula is deduced for equilibrium of a radiating atomic system under the influence of external radiation which, in the case of thermodynamic equilibrium, reduces to Saha's formula. The theory is applied to the planetary mist (atomic hydrogen chiefly) and gives its temperature as 12,000°, or, if the ground orbit of hydrogen is the two quantum orbit, 2000°. E. B. LUDLAM.

Equilibrium between matter and radiation in Einstein's closed universe. W. LENZ (Physikal. Z., 1926, **27**, 642—645; cf. Stern, A., 1925, ii, 926, 1021).

Number of dispersion electrons in [Schrödinger's] wave mechanics. F. LONDON (Z. Physik, 1926, **39**, 322—326).—By using Schrödinger's wave formula, the Thomas–Kuhn summation rule is deduced and the wave theory of density of electric charge is supported. E. B. LUDLAM.

Interpretation of Wood's iodine resonance spectrum. E. C. KEMBLE and E. E. WITMER (Physical Rev., 1926, [ii], **28**, 633—641).—A reanalysis of the resonance series described by Mecke (A., 1922, ii, 177; 1923, ii, 669), using the formulæ

developed by Kratzer and Sudholt (A., 1925, ii, 839). The moment of inertia and internuclear distance characteristic of the normal electronic level are $8{\cdot}1\times10^{-38}$ g. cm.^{2} and $2{\cdot}78\times10^{-8}$ cm., respectively; corresponding mean values for vibrational quantum numbers 26—29 are $12{\cdot}5\times10^{-38}$ and $3{\cdot}5\times10^{-8}$.

A. A. ELDRIDGE.

Quantum theory of band spectra. R. T. BIRGE (Physical Rev., 1925, [ii], **25**, 240).—When the intensity distribution among the various bands of a group is examined in relation to the assignment of vibrational quantum numbers, the band groups fall into two distinct classes. The aluminium bands are a characteristic example of the predominant class, and the iodine bands of the remainder.

A. A. ELDRIDGE.

Spontaneous non-radiating quantum processes. A. SMEKAL (Ann. Physik, 1926, [iv], **81**, 391—406).

Rotational energy of the polyatomic molecule as an explicit function of the quantum numbers. E. E. WITMER (Proc. Nat. Acad. Sci., 1926, **12**, 602—608).—The rotational energy of molecules possessing three different moments of inertia has been calculated. The method used is not the same as that used by Lutgemeier (this vol., 991), but leads to a result which is probably essentially the same.

R. CUTHILL.

Dielectric constant of symmetrical polyatomic molecules on the new quantum mechanics. R. DE L. KRONIG (Proc. Nat. Acad. Sci., 1926, **12**, 608—612).—Mathematical. Dennison's calculation of frequencies and amplitudes for a rigid polyatomic molecule with an axis of symmetry (this vol., 994) has been utilised to compute the dielectric constant of such a molecule having a permanent electric moment. As with diatomic molecules (cf. *ibid.*, 993), the permanent moment of the molecules is related to the part of the dielectric constant due to it by Debye's equation, provided that the temperature is sufficiently high.

R. CUTHILL.

Heisenberg's quantum mechanics. N. VON RASCHEVSKY (Z. Physik, 1926, **39**, 153—158).

Emission from the Bunsen flame. J. W. ELLIS (Physical Rev., 1925, [ii], **26**, 283—284).—The emission band of the Bunsen flame at $2{\cdot}7\,\mu$ is resolved with maxima at 2·58 and $2{\cdot}76\,\mu$; a weaker doublet appears at 1·79, $1{\cdot}99\,\mu$, and a broad band at $1{\cdot}40\,\mu$.

A. A. ELDRIDGE.

Transformation of a line spectrum into a continuous spectrum by transmission through a solution of certain critical densities. S. RAY (Physikal. Z., 1926, **27**, 627—630).—When radiation from the sodium flame or a neon tube is photographed through various solutions of rhodamine the lines suffer changes in position at certain critical concentrations. The changes may take the form of apparent shifts in wave-length, bending of lines, or extension as a continuous spectrum on one or both sides of the parent lines.

R. A. MORTON.

Absorption bands in nitrogen. H. SPONER (Nature, 1926, **118**, 696).—A band system has been photographed having frequency differences of the same values as those of the final state of the first positive group; the first positive group arises from the first excited state of the molecule. The o—o band of the new system corresponds with an excitation potential of 8 volts.

A. A. ELDRIDGE.

Excitation of the ultra-violet band of ammonia. C. T. KWEI (Physical Rev., 1925, [ii], **25**, 887—888).—The current–voltage curve in a two-electrode tube containing a mixture of hydrogen and nitrogen was correlated with spectroscopic observations. The so-called ultra-violet band of ammonia at about 2360 Å. was distinct only after the second break, at 22·5 volts. It is assumed that, at this potential, ammonia is formed in increased amounts, probably owing to the presence of atomic nitrogen.

A. A. ELDRIDGE.

Absorption spectra and heat of dissociation of halogen molecules. H. KUHN (Z. Physik, 1926, **39**, 77—91).—The edges of the absorption bands of bromine and chlorine have been measured and arranged in series. The bands increase in intensity from the red to the green and pass into a continuous band for shorter wave-lengths. The separations of the corresponding edges of the different series give the oscillation quanta of the normal molecule, those of the adjacent edges of a series give the oscillation quanta of the excited molecule. Two kinds of constant differences were sought for: (*a*) those between the edges of the same series—along the series, and (*b*) those between corresponding members of a different series—cross differences. The differences, however, show a systematic diminution, since the force holding the molecules together diminishes, for the halogens, with increasing amplitude. For bromine, the bands converge at 5107 Å.; the magnitude of the first oscillation quantum in the excited state is given by the frequency difference 160 cm.$^{-1}$, that of the normal state by 325 cm.$^{-1}$ For chlorine, the values are for 4785 Å., 180 cm.$^{-1}$, and 559 cm.$^{-1}$, respectively. The temperature was varied from 20° to 550°, the density remaining the same; for bromine, the shortest wave-length series diminished in intensity, all the others gained, hence the absorption in this series is due to the non-vibrating molecule (as with iodine also). For chlorine, however, the absorption increased right through the point of convergence and into the continuous region, hence in chlorine the convergent series must have a vibrating molecule as its ground state, and calculation shows it to be the one quantum state.

For iodine, the maximum absorption is 400 Å. on the short wave-length side of the convergence point; for bromine, it is 900 Å., and for chlorine 1400 Å., the absorption at the convergence point being very weak. The convergence point represents the dissociation of the molecule into atoms with no kinetic energy, hence in the case of chlorine the maximum absorption produces atoms possessed of very considerable kinetic energy. This also explains the difficulty of obtaining fluorescence of bromine vapour and the fact that it has not been obtained at all for chlorine, the absorption in the discontinuous portion being too slight. The heats of dis-

sociation in kg.-cal. calculated from the convergence point are: iodine 35·2, bromine 45·2, chlorine 58·5. E. B. LUDLAM.

Absorption spectra of the palladium and platinum triads. W. F. MEGGERS and O. LAPORTE (Physical Rev., 1926, [ii], **28**, 642—664).—By means of the under-water spark, the absorption spectra of ruthenium (2090·81—4709·49 Å.), rhodium (2206·03—4374·80 Å.), palladium (2068·68—4212·96 Å.), osmium (2211·97—4420·47) Å., iridium (2127·43—3220·79 Å.), and platinum (2030·53—3408·14 Å.) were observed, and the wave-lengths, intensities in absorption and emission, vacuum wave-numbers, and term combinations are tabulated. Tables of low terms in the spectra are also given. The lowest energy is represented by a quintuplet-F term for ruthenium, a quadruplet-F term for rhodium, and a singlet-S term for palladium; probably the lowest level for iridium is a doublet D-term and for platinum a triplet-D term. A. A. ELDRIDGE.

Infra-red absorption spectrum of didymium in glass and in solutions. P. LUEG (Z. Physik, 1926, **39**, 391—401).—The absorption bands for didymium in different kinds of glass and of solutions of didymium, neodymium, and praseodymium chlorides were measured in the region 0·7—2 μ. The curves for neodymium and praseodymium showed marked differences; those for didymium in glass resembled the curves obtained from the solutions, although the intensities were not the same; this may be due to different proportions of the neodymium and praseodymium being present. E. B. LUDLAM.

Form of the absorption bands in solutions of the organic dyes, and a relation between absorption and fluorescence. E. MERRITT (Physical Rev., 1926, [ii], **28**, 684—694).—On the assumption that, for a given position relative to the solvent molecules, the potential energy of an excited molecule is different from that of the normal molecule, and that the change in this potential energy which occurs during excitation or re-emission is to be regarded as part of the energy change that determines the frequency, the relation $F=K'\nu e^{-h\nu/kT}$, where F is the intensity of fluorescence for the frequency ν, and K' is a function of T and probably of ν, is derived. If the active molecule acts as an electric doublet the moment of which changes from μ_1 (normal) to μ_2 (excited), the coefficient of absorption $\alpha=\alpha_0 e^{(\mu_1/\mu_1-\mu_2)h\nu/kT}$ on the red side of the absorption band. When μ_2 is small compared with μ_1, this relation is shown to hold for rhodamine-B and uranine. The electric moment of the active molecule is assumed to be 3×10^{-19} e.s.u. If the exciting light is of short wave-length, a considerable fraction of the absorbed energy is not re-emitted, but passes into thermal agitation; if, however, Stokes' law is violated, fluorescence is a cooling process. A. A. ELDRIDGE.

Absorption of ultra-violet light by organic compounds. IX. (MLLE.) E. KEPIANKA and L. MARCHLEVSKI (Bull. Soc. chim., 1926, [iv], **39**, 1368—1383).—See this vol., 775.

Dielectric constant of dilute aqueous solutions of electrolytes. H. HELLMANN and H. ZAHN (Physikal. Z., 1926, **27**, 636—640).—Recent work on the dielectric constant of electrolytes in water is marked by serious discrepancies between the results of different workers (cf. A., 1925, ii, 1117; Fürth, *ibid.*, 631; Walden, Ulich, and Werner, *ibid.*, 512, 774, 964). The magnitude of the depression of the dielectric constant for very dilute solutions is in reality so small that it can only be demonstrated crudely by the resonance method. The reported increase in the dielectric constant for concentrated solutions is confirmed. The experimental arrangement used by Walden is more trustworthy with loose coupling. R. A. MORTON.

Dielectric constants of some liquids and liquid mixtures. L. A. SAYCE and H. V. A. BRISCOE (J.C.S., 1926, 2623—2627).—Improvements have been made in the method of measurement of dielectric constants previously described (A., 1925, ii, 263; J. Sci. Instr., 1926, **3**, 116). The dielectric constants of seventeen organic liquids and of nine pairs of these liquids, mixed in several different proportions, have been determined. M. S. BURR.

[Dielectric constants of liquids.] P. WALDEN, H. ULICH, and O. WERNER (Z. physikal. Chem., 1926, **123**, 315).—The values of the dielectric constants of chlorobenzene and bromobenzene obtained by Williams and Krchma (this vol., 1000) agree with those previously obtained by the authors (A., 1925, ii, 773). L. F. GILBERT.

Temperature variation of dielectric constant in quartz, fluorspar, and gypsum. A. DIETERICH (Ann. Physik, 1926, [iv], **81**, 523—536).—The temperature coefficient of the dielectric constant $1/\varepsilon\times\Delta\varepsilon/\Delta\theta$, has been determined as follows: fluorspar $+2\cdot05\times10^{-4}$, gypsum $+3\cdot75\times10^{-4}$, glass $+1\cdot37\times10^{-4}$. For quartz, Hasenoerl found the large negative value -1×10^{-3}. In contradiction to this, the value is found to be very small, and of the same order (10^{-5}) as the experimental error. R. A. MORTON.

Volumes of uncombined halogen atoms or ions. F. EPHRAIM and O. SCHÜTZ (Helv. Chim. Acta, 1926, **9**, 914—919).—The volume of a halogen atom in a salt cannot be taken as half its molecular volume (cf. A., 1919, ii, 268; 1924, ii, 315). On the rule that the percentage contraction in the formation of salts of the same metal with different halogens is the same, free (?) atomic volumes for chlorine, bromine, and iodine are calculated as 74·4, 93·0, 124·8, respectively. When the percentage contractions in the formation of alkali halides are tabulated, it is seen that the above rule is an approximation only. With the dihalides of the alkaline-earth and iron groups, the deviation is greater, unless the free atomic volumes are separately calculated for these, in which case they attain the improbable values 306·3, 355·8, and 446·75, respectively. From the alkali fluorides, the atomic volume of fluorine is calculated as 29·0. E. W. WIGNALL.

Dependence of heat of formation of salts on the [atomic] volumes of their components. O. SCHÜTZ and F. EPHRAIM (Helv. Chim. Acta, 1926, **9**, 920—923).—The heats of formation of halides plotted against the atomic volumes of the halogens give straight lines for each metal, with deviations in

the cases of cæsium, thallium, and copper. For any metal, the heats of formation of the halides are in linear dependence on the molecular volumes, and also on the absolute contractions on formation.
E. W. WIGNALL.

Optical properties of some sugars. G. T. KEENAN (J. Washington Acad. Sci., 1926, **16**, 433—440).—The optical properties of a number of sugars have been determined by the oil immersion method in mixtures of mineral oil, $n=1\cdot49$, and monochloronaphthalene, $n=1\cdot64$, in such proportions as to give a difference in n of 0·005 or less between successive mixtures. M. S. BURR.

Action of magnetic fields on the refractive index of gaseous carbon dioxide. P. N. GHOSH and P. C. MAHANTI (Nature, 1926, **118**, 734).—A decided change has been observed in the refractive index of pure, dry, gaseous carbon dioxide when subjected to a constant magnetic field of 3600 gauss, acting transversely to the direction of propagation of light, and the pressure gradually increasing from 10 to 400 mm. A. A. ELDRIDGE.

Werner's co-ordination theory and the electrical structure of the atom. Relationship between valency and co-ordination. S. H. C. BRIGGS (Phil. Mag., 1926, [vii], **2**, 1026—1041).—A general discussion of the co-ordination theory showing its connexion with the electron theory of valency. It is pointed out that the formation of all types of chemical compounds is due to the co-ordination of electrons or electron orbits and that all valency phenomena are based therefore on co-ordination. A. E. MITCHELL.

Monatomic molecule of the noble gases. F. J. VON WISNIEWSKI (Z. Physik, 1926, **39**, 299—307).—The molecule is regarded as a univalent ion and an electron, like the hydrogen atom. The values calculated for atomic radius, excitation potential, and diamagnetic susceptibility are in good agreement with experiment, except for helium. On the assumption that the molecules of oxygen, carbon dioxide, and hydrogen sulphide have a structure similar to that of the halogens, the value of the Loschmidt number is calculated; for oxygen and hydrogen sulphide, the result is good; for carbon dioxide it is rather high. E. B. LUDLAM.

Born's dipole theory of anisotropic liquids. W. KAST (Z. Physik, 1926, **39**, 490; cf. Szivessy, this vol., 888).—Polemical. The author maintains his criticism of Szivessy's conclusions.
E. B. LUDLAM.

Electron displacement *versus* alternate polarity in aliphatic compounds. G. BERGER (Nature, 1926, **118**, 734).—The results of Henri and Schou (this vol., 774, 883) on interatomic distances are considered to support the alternate polarity theory. The conclusions, however, become doubtful if carbon monoxide contains a triple linking.
A. A. ELDRIDGE.

New *X*-ray lines in certain rare-earth samples. C. J. LAPP, R. A. ROGERS, and B. S. HOPKINS (Physical Rev., 1925, [ii], **25**, 882; cf. this vol., 1083).—The *X*-ray region from 1·240 to 2·800 Å. of the spectra of samples of neodymium and samarium previously examined (U.S. Bur. Standards, Sci. Paper 442, 1922, **18**, 201) reveals the following lines which cannot be assigned to any known elements: 1·6927, 1·5878, 1·5486, 1·4051, 1·3753, 1·3604, 1·3441, 1·2487 Å.
A. A. ELDRIDGE.

Limit of absorption of the *K*-series of element 75 [rhenium]. B. POLLAND (Compt. rend., 1926, **183**, 737—738; cf. this vol., 258).—The limit of absorption of the *K*-series of the 1% of element 75 in a brown precipitate prepared from potassium permanganate has been determined by a very sensitive ionisation spectrometer. Mean values of $0\cdot1735\pm0\cdot0007$ and 0·1686 Å. were obtained for this element and for osmium, respectively. J. GRANT.

Immersion of metals in homogeneous media opaque to *X*-rays. Improvement in radiographic methods. H. PILON and A. LABORDE (Compt. rend., 1926, **183**, 658—659).—It is suggested that to assist the *X*-ray examination of metals of complicated form, in which absorption varies considerably from one part of the object to another, the object to be tested should be immersed completely in a homogeneous salt solution which has almost the same absorption coefficient as the metal. If the solution penetrates all parts of the object, the whole of it is rendered visible. Suitable concentrations of salt solutions are calculated for various metals. For aluminium, iron, and copper objects, respectively, barium chloride (35 g. in 100 c.c. of solution), saturated lead chlorate, and barium iodide (150 g. in 100 c.c. of solution) are used. The barium iodide solution is also used with iron. J. GRANT.

Mathematical study of crystal symmetry. A. F. ROGERS (Proc. Amer. Acad. Arts Sci., 1926, **61**, 161—203).—An attempt to settle disputed matters regarding the true elements of symmetry in crystals, particularly the question of the centre of symmetry which Groth, Federov, and others have contended is not a true element. CHEMICAL ABSTRACTS.

Crystal structure of beryllium oxide. A. CLAASEN (Z. physikal. Chem., 1926, **124**, 139—143).—It is impossible, contrary to the statements of Zachariasen (this vol., 562), to distinguish between an atomic and an ionic lattice in a beryllium oxide crystal by *X*-ray methods. The scattering power of the oxygen atoms in such a crystal has been determined for different angles, and the value of the parameter is given as 0·39. S. BARRATT.

Structure of crystalline sodium hydrogen fluoride and the form of the HF_2-ion. C. C. ANDERSEN and O. HASSEL (Z. physikal. Chem., 1926, **123**, 151—159).—By application of the rotating crystal method, the structural element is shown to be a face-centred rhombohedron, with edges 6·15 Å. The distance between hydrogen and fluorine is 1·25 Å.
R. CUTHILL.

Atomic grouping in the tetragonal crystals of potassium metaperiodate, $K_2I_2O_8$. E. HYLLERAAS (Z. Physik, 1926, **39**, 308—321).—The crystal contains two face-centred *K*-lattices, two face-centred *J*-lattices each of which forms a diamond-like lattice, and eight face-centred *O*-lattices. The intensities

of the reflexion-lines indicate a tetragonal-bipyramidal structure and a space-group C_{4h}^{6}. The ionic radius, calculated from the distance between the atoms, indicates that the atoms have acquired the configuration of a noble gas, by gain or loss of an electron. E. B. LUDLAM.

Crystal structure of rolled iron, nickel, and molybdenum plates. S. T. KONOBEJEVSKI (Z. Physik, 1926, **39**, 415—426).—Strips of the metallic foil were placed on the axis of a half cylinder of photographic film and the *X*-rays from a rhodium anticathode directed on it either perpendicularly or at an angle. From the patterns obtained, it was calculated that the axis of orientation in iron is the (110) direction; for nickel the axis lay between the (111) and the (211) directions at an angle of 8° to the latter; for molybdenum, the direction was (110). In some cases, the patterns differ from the usual forms, suggesting either distortion of the lattice or an approach to an amorphous type. E. B. LUDLAM.

Structure of catalytically active copper. F. H. CONSTABLE (Nature, 1926, **118**, 730).—If A is the thickness of an oxide film, S the surface area, C the electrical conductivity of the mixture of oxide and metal, the suffix 1 denoting values for an activated or sintered catalyst at time t after the commencement of oxidation at constant temperature, and the suffix 2 representing the same variables either for the film before activation or for the fully activated film before annealing, then $(da/dt)_1S_1/(da/dt)_2S_2=(dC/dt)_1/(dC/dt)_2$. Thus a method is available for measuring the increase of area on activation and the decrease of area on sintering. Activation experiments seem to indicate that the increase in area of the supported copper films on successive reduction is not large, but the nature of the surface alters considerably. With sintering, the nature of the surface is changed, and there is marked increase in surface area. As the time is increased, the relative rate of increase of thickness of the oxide film considerably diminishes. A. A. ELDRIDGE.

Crystal structure of the *A* modification of the sesquioxides of lanthanum, cerium, praseodymium, and neodymium. W. ZACHARIASEN (Z. physikal. Chem., 1926, **123**, 134—150; cf. Goldschmidt, Ulrich, and Barth, this vol., 228).—The structure of the sesquioxides has been examined by both Laue's and by Debye and Scherrer's methods. The values in Å. of a and c, respectively, for the elementary cells of the various oxides are: lanthanum, 3·93, 6·12; cerium, 3·88, 6·06; praseodymium, 3·85, 6·00; neodymium, 3·84, 6·01. For ceria, $d_{calc.}$ is 6·86. If both the metal atoms and the oxygen atoms in the crystals are structurally equivalent, which appears to be the case, the crystal structure must be represented by the space-grouping, D_3^2.
R. CUTHILL.

Volume and atomic number. C. DEL FRESNO (Anal. Fís. Quím., 1926, **24**, 508—511; cf. this vol., 450).—Data given by Barth and Lunde (this vol., 664) for the lattice constants of elements of the eighth group confirm the relationship, deduced by the author, between atomic volume and atomic number. G. W. ROBINSON.

[Lattice constants of the platinum metals and of silver and gold.] T. BARTH and G. LUNDE (Z. physikal. Chem., 1926, **123**, 476; cf. this vol., 664).—A correction.

Crystalline structure of anhydrite. J. A. WASASTJERNA (Phil. Mag., 1926, [vii], **2**, 992—994).—Some points of the work of Dickson and Binks (this vol., 781) are discussed in conjunction with the work of the author (Soc. Scient. Fennica, 1925, **2**, 26) and the difficulty of deciding between the possible alternative structures of anhydrite is emphasised. A. E. MITCHELL.

Crystal structure of solid carbon disulphide. J. DE SMEDT (Natuurwetensch. Tijdschr., 1926, **8**, 13—14).—At −185°, the crystals are tetragonal; $c/a=0·46$, $a=8·12$, $c=3·77$, $p=1·25$ Å. A list of the pyramid faces (h, k, l) is given. The unit cell contains three molecules. S. I. LEVY.

Molecular orientation in solids. G. SHEARER (Trans. Faraday Soc., October, 1926, advance proof).—A *résumé* of recent *X*-ray work (cf. A., 1925, ii, 366, 938). R. CUTHILL.

***X*-Ray investigation of the normal saturated dicarboxylic acids and their ethyl esters.** A. R. NORMAND, J. D. M. ROSS, and E. HENDERSON (J.C.S., 1926, 2632—2637).—An examination of long-chain dicarboxylic acids, by the *X*-ray spectrometer, shows that the increase of d_1 (1·7—2·1 Å.), in passing from an odd to an even acid, is greater than that for the passage from an even to an odd acid (0·05—0·6 Å.). This is in agreement with Müller and Shearer's views on the direction of length of the fatty acid chains with respect to the long-spacing plane (J.C.S., 1923, **123**, 3156; Nature, 1925, **116**, 45). The even and odd members of the dicarboxylic acids thus belong to two distinct series. The diethyl esters, both odd and even, however, form only one series. This is in agreement with the results obtained by Fairweather for the m. p. of these substances (this vol., 668). The spacings observed for the monoethyl esters indicate that these contain two molecules between successive reflecting planes, whilst the acids and diethyl esters contain only one.
M. S. BURR.

Crystallographic study of certain aromatic nitro-derivatives. G. RESEGOTTI (Atti R. Accad. Lincei, 1926, [vi], **4**, 218—222).—α-Phenyl-β-2 : 4-dinitro-*m*-tolyl-α-methylhydrazine (cf. Giua, A., 1921, i, 198) crystallises in the prismatic class of the monoclinic system, $a:b:c=1·27507:1:1·37644$, $\beta=93°\ 30'\ 30''$; α-phenyl-β-4 : 6-dinitro-*m*-tolyl-α-methylhydrazine (*loc. cit.*) in the same class, $a:b:c=0·81915:1:0·96209$, $\beta=93°\ 37'$; and α-phenyl-β-5-chloro-2 : 4-dinitrophenyl-α-methylhydrazine (cf. Giua, A., 1924, i, 338) in the same class, $a:b:c=2·8747:1:1·4563$, $\beta=128°\ 3'$. T. H. POPE.

New types of mixed crystals. D. BALAREV (Z. anorg. Chem., 1926, **156**, 301—308; cf. A., 1922, ii, 864).—The red to dark violet particles of the composition $BaSO_4,KMnO_4$ or $BaSO_4,NaMnO_4$, which Grimm (A., 1924, ii, 828) regards as a new type of mixed crystal, possess none of the properties which usually characterise those systems. They are,

rather, particles of barium sulphate into the interstices of which potassium or sodium permanganate is adsorbed as part of the aqueous component. This is confirmed by the formation of barium sulphate particles coloured by substances of a type, *e.g.*, manganese dioxide, which could not form mixed crystals with it. M. CARLTON.

Electrometric study of the allotropic forms of mercuric sulphide. M. BOURGEAUD (Bull. Soc. chim., 1926, [iv], **39**, 1396—1405).—See this vol., 803.

Electric discharge in gases and the accompanying radiations. A. DAUVILLIER (Phil. Mag., 1926, [vii], **2**, 1046—1052).—See this vol., 330.

Analogy in behaviour and isomorphism between cerium and thorium. G. SCAGLIARINI (Atti R. Accad. Lincei, 1926, [vi], **4**, 204—210).—The mixed oxides of the rare earths undergo no change when introduced into fused potassium hydroxide. When obtained in presence of a large proportion of lime and magnesia or potassium hydroxide, ceric oxide is quite insoluble in nitric acid. Thorium oxide in presence of a large excess (90—99%) of an oxide of a tervalent rare-earth metal is soluble in dilute nitric acid, whereas zirconia is completely insoluble in nitric acid under such conditions. These results are incompatible with the hypothesis that in mixed oxides of rare-earth metals ceric oxide forms part of a saline oxide, and it is more probable that the ceria is present in a condition of amorphous solid solution and that its solubility in acids depends on its extreme subdivision. It is, however, possible that, when dissolved in other oxides, ceric oxide does not undergo that process of polymerisation which renders it insoluble when it is calcined either alone or in homogeneous mixture with other oxides. The same considerations hold for thorium dioxide.

In accordance with the positions of the two metals in the periodic system, thorium and cerium acetylacetonates are completely isomorphous.

T. H. POPE.

Iron single crystals. W. GERLACH (Z. Physik, 1926, **39**, 327—331).—Previous experimental results are discussed, together with those of Geiss and van Liempt (cf. B., 1926, 752). By cold-working, the specific resistance increases greatly, but its temperature coefficient diminishes; on heating, the iron becomes normal again. The change in conductivity is not due to change in the form of the lattice, but to slight changes in the parameters; it is not due to a ruckling of the crystal planes, but to a deformation of the outer electrons in the atom. Cold-working increases the strength of a single crystal, but not of a rod consisting of many fine crystals, yet both show great increase in "magnetic hardness." Heating produces magnetic restoration. It is not so much the number of the crystals which determines the magnetic properties as their quality. A single crystal was stretched and gave no Barkhausen effect (noise in a telephone); it was bent and produced loud noise. Steel gave no noise. In "magnetically pure iron" the elementary magnets are already present; the process of magnetisation consists in a reversible directing of them. E. B. LUDLAM.

Effect of heat treatment on the contact *P.D.* of nickel and copper. J. E. SCHRADER (Physical Rev., 1925, [ii], **25**, 249).—The *P.D.* before heat treatment was about +0·25 volt; simultaneous heat treatment in a high vacuum by induced high-frequency currents caused the *P.D.* to change to −0·15 volt. A. A. ELDRIDGE.

Thermo-electric properties of pure metals and alloys. A. E. CASWELL (Physical Rev., 1925, [ii], **26**, 286).—Except for aluminium, iron, and tin, the thermo-*E.M.F.* between a compressed metal and the same uncompressed metal is represented by an equation of the form $E=apt(1+bp)(1+ct)$. Aluminium appears to undergo a quasi-allotropic modification under pressures in excess of 6500 kg./cm.^{2}

A. A. ELDRIDGE.

Electrostriction in gases. W. KLIEFOTH (Z. Physik, 1926, **39**, 402—414).—If the attraction between the molecules of a gas is of electrical origin, this internal pressure will be increased by an external electric force in the case of gases possessing an electric moment. The contraction in volume on applying a powerful electric field across a condenser consisting of two concentric spheres was measured by observing the motion of particles of tobacco smoke in a capillary by means of a microscope. Carbon dioxide and sulphur dioxide showed the effect, also air, nitrogen, and oxygen. A finite value for the electric moment was obtained for carbon dioxide and sulphur dioxide, but for oxygen and nitrogen the value was practically zero. For voltages over 15,000 the results are not in agreement with the theories of Gans or of Debye and Frivold, possibly because the dielectric constant may vary with the electric field. E. B. LUDLAM.

Influence of adsorbed gas on the electrical resistance of a wire. II. T. SEXL (Z. Physik, 1926, **39**, 334—336; cf. A., 1925, ii, 642).—The increased resistance is calculated on Lorentz's theory of the collision of electrons with the atoms of the metal plus the atoms of dissolved gas, and the formula is in good agreement with the few existing measurements. A similar calculation for heat conductivity is made, but no experimental results are known. The Wiedemann–Franz ratio for the two conductivities should not be altered. E. B. LUDLAM.

Electrical resistivity of aluminium-calcium alloys. J. D. EDWARDS and C. S. TAYLOR.—See B., 1926, 883.

Magnetic properties of single crystals of nickel. W. SUCKSMITH and H. H. POTTER (Nature, 1926, **118**, 730—731).—A preliminary investigation of the variation of hysteresis loss with grain size.

A. A. ELDRIDGE.

Differentiation of the various types of ferric oxide and hydrated ferric oxide by their differing magnetic properties. I. E. WEDEKIND and W. ALBRECHT (Ber., 1926, **59**, [*B*], 1726—1730).—The hydroxides, $Mn(OH)_2$, $Co(OH)_2$, $Fe(OH)_3$, $Ni(OH)_2$, $MnO(OH)_2$, $Cr(OH)_3$, $Cu(OH)_2$, are more strongly magnetisable than the corresponding oxides, thus indicating that they are well-defined hydroxy-compounds of the metals. Ferric oxides, prepared under different conditions, differ markedly in mag-

netic properties. Ferric oxide hydrates are invariably more strongly magnetic than the corresponding oxides, those in which the water content varies between 22% and 43% exhibiting a susceptibility which decreases with increasing water content. The mode of preparation does not influence the susceptibility to such an extent as to lead to specific values for specimens prepared by unusual methods. Ferric oxide, containing 2—3% of water, prepared by heating the precipitated hydroxide in an autoclave with water or sodium hydroxide, is ferromagnetic.

H. WREN.

Magnetic susceptibilities of gases. G. W. HAMMAR (Proc. Nat. Acad. Sci., 1926, **12**, 594—596).—The susceptibilities of air, oxygen, nitrogen, carbon dioxide, and hydrogen at the ordinary temperature and under various pressures have been determined by measuring the force exerted on a cylinder of some diamagnetic substance suspended in a non-homogeneous magnetic field in the gas under examination. It is found that, contrary to Glaser's results (A., 1925, ii, 82), even at the lowest pressures the volume susceptibility is directly proportional to the pressure.

R. CUTHILL.

A possible explanation of the "Glaser effect." G. W. HAMMAR (Proc. Nat. Acad. Sci., 1926, **12**, 597—598).—Glaser's data for the magnetic susceptibilities of gases (A., 1925, ii, 82), which are in conflict with the results of recent determinations (cf. preceding abstract), seem to have been vitiated by the presence of moisture in the apparatus used.

R. CUTHILL.

Investigations on paramagnetism at low temperatures. II. L. C. JACKSON (Phil. Trans., 1926, **A**, **226**, 107—133; cf. A., 1923, ii, 609; 1924, ii, 90).—The principal susceptibilities χ_1, χ_2, χ_3, of crystals of cobalt ammonium sulphate and nickel sulphate follow Curie's law $\chi_n(T+\Delta_n)=C$, T being absolute temperature, $n=1$, 2, 3, Δ_n is a constant, and C is the Curie constant, which has the same value for each of the principal magnetic axes of the crystal. In the present work, a delicate apparatus has been constructed for measuring susceptibilities by Faraday's method; a section ground in a known direction from a crystal is suspended in a non-homogeneous magnetic field and the force on it is measured, using a quartz microbalance. The relation between $1/\chi$ and absolute temperature is linear for the range 170—290° Abs., and the values of $1/\chi$ for the principal susceptibilities of cobalt potassium sulphate lie on three approximately parallel lines. The constants in the expression $\chi_n(T+\Delta_n)=$const. are discussed for the crystals of cobalt ammonium sulphate and cobalt potassium sulphate.

The results indicate for cobalt potassium sulphate a Weiss magneton number equal to 26·1, calculated from the mean of the principal susceptibilities, as compared with 25·3 by direct measurement with the powdered substance. Finke's results (A., 1910, ii, 179) are too high.

The principal susceptibility of nickel ammonium sulphate follows Curie's law with $\Delta=-16$. The Weiss magneton number is 16·0 (powdered material 15·9). Preliminary results on manganese ammonium sulphate are recorded.

R. A. MORTON.

Specific heats of tungsten, boron, boron nitride, and beryllium oxide. A. MAGNUS and H. DANZ (Ann. Physik, 1926, [iv], **81**, 407—424).—Improved forms of the colorimetric methods of Magnus (*ibid.*, 1912, [iv], **48**, 193; A., 1923, ii, 374) and of Magnus and Hodler (this vol., 998) were employed. The mean specific heat between a temperature t and 0° has been determined over a wide range of values of t by extrapolating the values obtained experimentally between t and the ordinary temperature. By extrapolating from data referring to 99% tungsten containing varying amounts of tungsten oxide, the atomic heat of pure tungsten is given by $6{\cdot}7807+0{\cdot}0010475t$ over the range 400—900°. By a similar calculation, the value for 97% amorphous boron is given by $2{\cdot}3658+7{\cdot}9080\times10^{-3}t-4{\cdot}9023\times10^{-6}t^2$ over the range 100—900°. For pure boron nitride, the value is $2{\cdot}5153+6{\cdot}3096\times10^{-3}(t-22)-3{\cdot}2885\times10^{-6}(t-22)^2$ over the range 400—900°. The behaviour of pure beryllium oxide is abnormal, the curve consisting of two approximately straight lines intersecting at 400°. The atomic heat is represented approximately by $3{\cdot}0890+7{\cdot}4640\times10^{-3}t-4{\cdot}7859\times10^{-6}t^2$ over the range 100—900°. It is shown that there is an extraordinary discrepancy between the data now cited for tungsten and those calculated by means of Debye's formula from the low-temperature data of Lange (Z. physikal. Chem., 1924, **110**, 343), and that the data for boron and boron nitride are in agreement with the predictions of Debye's theory.

R. W. LUNT.

Calorimetric researches on sulphur and selenium. P. M. MONVAL (Bull. Soc. chim., 1926, [iv], **39**, 1349—1368).—The behaviour of liquid sulphur has been investigated in the neighbourhood of 160°. Heating and cooling curves show discontinuity at 162·8° and 157·7°, respectively, and the curve obtained by plotting the heat given out by 1 g. of sulphur on cooling from T to 15° against T consists of four parts corresponding with orthorhombic, monoclinic, liquid, and vitreous sulphur. From the curves, it is deduced that the heats of transformation of orthorhombic to monoclinic and of liquid to vitreous sulphur are 2·7 and 2·8 g.-cal., respectively, whilst the heat of fusion of monoclinic sulphur is 9·3 g.-cal. per g. The mean specific heats found for orthorhombic, liquid, and vitreous sulphur are 0·176, 0·220, and 0·290, respectively.

Similar curves have been obtained for selenium, and from these it is found that the heats of transformation of the metallic allotrope into red crystalline, vitreous, and liquid selenium are, respectively, 2·2, 13·5, and 16·4 g.-cal. per g. The mean specific heats for metallic selenium are 0·078 (15—75°) and 0·084 15—217°), whilst the values for red crystalline, vitreous, and liquid selenium are, respectively, 0·082 (15—75°), 0·106 (15—100°), and 0·118 (217—300°).

A. S. CORBET.

Thermal expansion of copper between +101° and −253°. W. H. KEESOM, F. P. G. A. J. VAN AGT, and (MISS) A. F. J. JANSEN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 786—791).—The

coefficients of linear expansion of copper over the temperature ranges −252·8° to −185·5°, −185·5° to −102·9°, −102·9° to 0°, and 0° to 100°, determined by the method of Agt and Onnes (this vol., 231), are 4·92, 12·10, 15·35, and $16·16\times10^{-6}$, respectively. To represent the results over the whole temperature range, an interpolation formula involving powers of t up to the fourth is necessary. A. B. MANNING.

Entropy of perfect gases and the heat of vaporisation at the absolute zero. N. DE KOLOSOVSKI (J. Chim. phys., 1926, **23**, 728—732).—A reply to the criticisms of Verschaffelt (this vol., 463). J. S. CARTER.

Falling drop method for determination of specific gravity. H. G. BARBOUR and W. F. HAMILTON (J. Biol. Chem., 1926, **69**, 625—640).—The authors' previous method (Amer. J. Physiol., 1924, **69**, 654) has been modified by comparing the time taken by a drop of the fluid under investigation to fall through a given length of a suitable mixture of xylene and bromobenzene with that taken under the same conditions by a similar drop of a solution of potassium sulphate of known density. The error of the method is 0·01%. C. R. HARINGTON.

Relation between orthobaric densities. J. HORIUCHI (Bull. Chem. Soc. Japan, 1926, **1**, 189—197).—Theoretical. The following relationship between V_l and V_g, the molecular volumes of a substance in the liquid and gaseous states, respectively, has been derived: $RT\log_e V_g/V_l=A\{1/(V_l-E)-1/(V_g-E)\}$, where A and E are quantities characteristic of the substance considered. This expression has been found to be applicable to a number of different substances, including both normal and abnormal (*i.e.*, associated) liquids, even alcohols, but not to water. A and E are related to the critical constants as follows: $E=0·17V_k$ and $A=32·3T_k^2/P_k$. By putting $T/T_k=0$ and $V/V_k=\varphi$, a reduced equation, in accordance with the theory of corresponding states, is obtained. An equation for vapour pressure at low temperatures has also been derived, viz., $\log_e P=\log_e RT/V_l-1/RT\times A/(V_l-E)$. M. S. BURR.

Vapour pressures and thermal properties of potassium and some alkali halides. E. F. FIOCK and W. H. RODEBUSH (J. Amer. Chem. Soc., 1926, **48**, 2522—2528).—The vapour pressures of potassium between 400° and 760°, and of sodium chloride, potassium chloride, potassium bromide, potassium iodide, and cæsium iodide between 900° and 1030°, measured by the method of Rodebush and Dixon (this vol., 117), are given, respectively, by the expressions: $\log_{10}p$(mm.)$=-4433/T+7·1830$; $\log_{10}p=-9419/T+8·3297$; $\log_{10}p=-9115/T+8·3526$; $\log_{10}p=-8780/T+8·2470$; $\log_{10}p=-8229/T+8·0957$; and $\log_{10}p=-8282/T+8·1772$. The calculated heats of vaporisation in g.-cal./mol. are: 20,260 (per g.-atom), 43,050, 41,660, 40,130, 37,610, and 37,854, respectively. The lattice energy of the salts is nearly equal to the heat of solution of the appropriate gaseous ions, which justifies Born's assumption that the energy relations of an ion depend only on its charge and its "effective atomic radius" (Z. Physik, 1920, **1**, 45). When a salt molecule evaporates from a lattice, the two ions appear to approach more closely and the molecule becomes less polar. The heat of dissociation of sodium chloride vapour into sodium and chlorine ions is approximately 128 g.-cal. S. K. TWEEDY.

Vapour pressure. II. Mononitrotoluenes. J. F. T. BERLINER and O. E. MAY (J. Amer. Chem. Soc., 1926, **48**, 2630—2634; cf. A., 1925, ii, 1045).—The vapour pressures of the isomeric nitrotoluenes have been determined from 50° to a few degrees above the b. p. The *o*-, *m*-, and *p*-isomerides have b. p. 220·38°, 231·87°, and 238·34°, respectively, at 760 mm. The vapour pressures agree closely with those calculated from the latent heat equations, and the entropies of vaporisation at a concentration of $0·00507M$ indicate that the molten isomerides are normal liquids. F. G. WILLSON.

Curve of ideal expansion. L. SCHAMES (Physikal. Z., 1926, **27**, 630—631; cf. this vol., 234).—In the deduction of an equation of state from specific heat, the curve of ideal expansion of a gas is important. From Amagat's measurements with hydrogen, this curve appears to be parabolic. When Bridgman's data are also considered and the curve $p/R\,.\,(\delta v/\delta T)_p$ is plotted, the curve of ideal expansion given by $p/R\,.\,(\delta v/\delta T)_p=1$ is hyperbolic. This result is discussed in its bearing on van der Waals' equation and the law of corresponding states. R. A. MORTON.

Measurement of the compressibility of the alkali halides. J. C. SLATER (Proc. Amer. Acad. Arts Sci., 1926, **61**, 135—150).—Bridgman's method was applied to large crystals of the alkali halides. CHEMICAL ABSTRACTS.

Simple kinetic theory of viscosity. J. S. DUNN (Trans. Faraday Soc., 1926, **22**, 401—405; cf. Satô, this vol., 234).—Viscosity is discussed from the point of view of the kinetic theory and, from certain assumptions, the expressions $1/\eta=Ae^{-Q/RT}$ and $d(1/\eta)/dT=-Q/RT^2$ (A and Q are constants) are deduced for the fluidity and temperature coefficient of fluidity, respectively. Approximately straight lines are obtained when logarithms of fluidity are plotted against reciprocals of absolute temperature for a number of ethers and other substances; it is found that the values of Q vary in a regular manner in a homologous series.

The relation between fluidity and vapour pressure is discussed. A. S. CORBET.

Dependence of viscosity on temperature in supercooled liquids. G. TAMMANN and W. HESSE (Z. anorg. Chem., 1926, **156**, 245—257).—The viscosity of substances having a low m. p. may be expressed by the formula $\log\eta=-A+B\times10^3/(T-T_\infty)$, where A, B, and T_∞ are constants and η is the coefficient of viscosity. For the interval (T_s-T_a), where T_s is the m. p. and T_a the temperature at which the viscosity has the value 10^{13}, the formula $T_s-T_a=cT_s/\sqrt[3]{M}$ holds, where M is the mol. wt. of the substance and c is a constant. The higher the m. p. the greater is the temperature interval in which the working of the viscous mass by blowing, drawing, etc. is possible. The viscosity of the liquids was determined by measuring the rate of fall of a small gold ball. Since only small quantities of liquid were

available, Ladenburg's modification of Stokes' formula was used; $\eta=2/9\times gR^2/a\times[(S-\sigma)/(1+2{\cdot}4R/\rho)](1+3{\cdot}3R/h)$, where η is the coefficient of viscosity, g the acceleration due to gravity, R the radius of the ball, ρ the radius of the tube, h the height of the column of liquid, a the rate of fall of the ball, S the density of the ball, and σ the density of the liquid. With viscosities between 10 and 10^3 g./cm./sec., the maximum error is about 3%, but with higher viscosities the error may be 10%. It was necessary to work with substances which could be kept supercooled for some hours without spontaneous crystallisation.

Rates of fall varying from 6 sec./cm. to 15,000 sec./cm. corresponding with viscosities of 10 to 10^4 were obtained. Results are tabulated and show that if a liquid be supercooled below its m. p., its viscosity increases, slowly at first, and then extraordinarily quickly, until finally, after the liquid has become hard and brittle at a temperature T_a, the viscosity again increases slowly with falling temperature. In the temperature interval (T_s-T_a), the viscosity changes from about 1 to 10^{13}. M. CARLTON.

Theory of "structural turbulence." M. REINER (Kolloid-Z., 1926, **39**, 314—315; cf. this vol., 678; Ostwald and Auerbach, *ibid.*, 470).—It is shown that Ostwald's explanation of structural turbulence (*loc. cit.*) can be tested experimentally by measuring the flow of liquids through capillary tubes of various diameters. From the expression $\tau=rp/2l$, where p is the driving pressure, r the distance from the tube axis, and l the tube length, an equation $V_{crit.}=R/4\eta\times T$ (where R is the tube radius and T the limiting value of $\tau_{max.}$), is derived for the critical velocity at which structural turbulence appears. This is compared with Reynold's formula $U_{crit.}=\eta K/R\rho$, where ρ is the density of the liquid and K is a constant, and it is shown that the two critical velocities have opposing characters, since $V_{crit.}$ increases with R and decreases with η, whilst $U_{crit.}$ decreases with R and increases with η. L. L. BIRCUMSHAW.

Ebullioscopic constant and Poisson's capillary constant. N. DE KOLOSOVSKI (Bull. Soc. chim., 1926, [iv], **39**, 1328—1329; cf. this vol., 791, 1008).—From expressions previously deduced it is found that M^2a^2/E and $M^2\sigma/Ed$ are constants and equal to $1{\cdot}23\times10^4$ and 6×10^4, respectively, where E is the molecular elevation of b. p. of a liquid of mol. wt. M, a^2 the capillary constant, σ the surface tension, and d the density at the b. p. These expressions are confirmed by the substitution of available data.

A. S. CORBET.

Effusion of gases. H. WEIDE and F. R. BICHOWSKY (J. Amer. Chem. Soc., 1926, **48**, 2529—2534).—An effusiometer is described in which the special conditions assumed in the derivation of the equation for the effusion of a gas through a fine orifice into a vacuum are realised as far as possible. The use of the apparatus in measuring the temperature, dissociation, and mol. wts. of gases is described. A preliminary investigation of the dissociation of iodine leads to a value of 3·7 for log k at 915°, k being the dissociation constant. The calculated value is 3·4.

S. K. TWEEDY.

Separation of helium from gas mixtures. F. PANETH and K. PETERS.—See B., 1926, 916.

Density of the system acetone–water at 20°. P. NAVILLE (Helv. Chim. Acta, 1926, **9**, 913).—The densities of acetone–water mixtures, determined at 19·2—23·0° and reduced to 20°, are at 10% intervals from 0 to 100% acetone: 0·998, 0·986, 0·974, 0·958, 0·942, 0·921, 0·900, 0·877, 0·852, 0·825, 0·795.

E. W. WIGNALL.

Molecular solution volumes and association. G. J. BURROWS and A. E. JAMES (J. Proc. Roy. Soc. N.S.W., 1925, **59**, 223—229; cf. A., 1924, ii, 453).—Observations have been extended to solutions in methyl alcohol, acetone, benzene, and toluene. In all cases, the molecular solution volume of a substance is greater when dissolved in benzene or toluene, which have a low dielectric constant, than when dissolved in the alcohols or acetone, which have high dielectric constants. The molecular solution volumes in toluene are in good agreement with the molecular volumes of the liquid substances, and for non-associated solutes such as chlorobenzene or toluene these values differ only slightly with the alcohols or acetone as solvents. For an associated solute such as aniline, the molecular solution volume in acetone or the alcohols is markedly lower than the value in the free state or that in solution in toluene.

G. M. BENNETT.

Binary azeotropes. II. M. LECAT (Rec. trav. chim., 1926, **45**, 620—627; cf. Ann. Soc. scient. Bruxelles, **45**, I, 169—177).—Of 117 binary mixtures of organic substances that have been examined, 84 give azeotropes of the first and 5 those of the second type (*i.e.*, constant-boiling mixtures more and less volatile, respectively, than each constituent), whilst the remaining 28 are euzotropic (*i.e.*, give no constant-boiling mixture). The composition of each azeotropic mixture is given. The temperature changes produced on mixing the constituents in azeotropic or other known proportions have also been obtained; and although no rigid rule can be deduced, the azeotropes of the first type usually show a fall and those of the second a rise in temperature, whilst of the euzotropic systems about half show a rise and the other half a fall. Where a rise of temperature occurs, one constituent is usually a polyhalogen compound.

S. J. GREGG.

Limiting states of [ferrous] alloys. L. GRENET (Compt. rend., 1926, **183**, 600—602).—The mechanism of the transformation of alloys from one crystalline state to another is discussed with special reference to alloys of iron with aluminium, silicon, and cobalt. The change may take place suddenly or through an intermediate state in which the properties of both phases are detectable. A theory is suggested in which the existence of limiting states in such alloys is assumed.

J. GRANT.

Ludwig–Soret effect in alloys. M. BALLAY (Compt. rend., 1926, **183**, 603—604).—The heterogeneity produced in solutions after they have been subjected to unequal heating (Ludwig–Soret effect) has been detected in liquid and solid alloys. Lead–tin and tin–cadmium liquid alloys in horizontal and

in vertical silica tubes were heated at one end at 900°. After 8—11 hrs. an excess of tin varying from 0·20 to 3·98% was found at the heated end, but the lead–tin eutectic mixture heated in a horizontal tube showed decreases of 0·26 and 0·48%. A solid bar of lead–thallium alloy was heated at 360° for 336 hrs., when the lead content had changed from 48·8% to 49·98% and 48·32% in the regions heated at 310° and 200°, respectively. J. GRANT.

Solubility relations of naphthalene. H. L. WARD (J. Physical Chem., 1926, **30**, 1316—1333; cf. Schröder, A., 1893, ii, 366; Étard, *ibid.*, 1894, ii, 8).—The solubility of naphthalene in hexane, benzene, toluene, chlorobenzene, nitrobenzene, aniline, carbon tetrachloride, acetone, acetic acid, and methyl and *n*-butyl alcohols has been determined between 0° and 80°. The curves obtained by plotting the logarithm of the mol. fraction against the reciprocal of the absolute temperature belong to the reversed S-form described by Mortimer (*ibid.*, 1923, ii, 299), which type is apparently due to the effect of at least two factors causing deviations from Raoult's law. At high concentrations, the low solubilities are due to differences in internal pressure of solvent and solute as postulated by Hildebrand (*ibid.*, 1921, ii, 23), whilst at lower concentrations a second factor partly neutralises this effect. The system naphthalene–chlorobenzene is nearly ideal. The results of Speyers (*ibid.*, 1903, ii, 64) are adversely criticised. L. S. THEOBALD.

Adhesion forces in solutions. VIII. Solubility and adsorption of electrolytes. N. SCHILOV and M. TSCHEPELEVETZKI (Z. physikal. Chem., 1926, **123**, 248—260; cf. this vol., 20, 238).—The adsorption, by charcoal, of alkali chlorides, bromides, and iodides from dilute solutions has been studied. The adsorption curves are similar in form, the iodides being adsorbed most and the chlorides least. Lithium exhibits a singular behaviour, recalling the apparently anomalous position of its salts in the m. p. series of the alkali halides, as in each series of halides the adsorption falls from the lithium to the sodium salt and thereafter rises as the atomic weights of the cations increase. The solubility data for a large number of inorganic salts suggest that solubility and adsorption depend on the mutual influences of anion and cation. L. F. GILBERT.

Adsorption of dissolved substances. II. (i) Separation of adsorbed substance from adsorbent. (ii) Reciprocal displacement of adsorbed substances. (iii) Catalytic activity of adsorbed substances. A. CHARRIOU (J. Chim. phys., 1926, **23**, 673—709).—A continuation of previous work (this vol., 899) primarily concerned with the elimination of errors introduced into analytical determinations by the adsorption of dissolved substances during precipitation.

(i). Very little of the adsorbed substance is removed by the washing of precipitates on the filter-paper. Even the use of the Lumière arrangement (B., 1922, 524A), whereby an extremely slow stream of water passes over the precipitate, fails to remove all the adsorbed substance. Prolonged boiling with water, however, is often efficacious. Agitation at the moment of precipitation reduces the degree of adsorption only in the case of crystalline precipitates of substances having a measurable though slight solubility (*e.g.*, barium sulphate, calcium oxalate). In the case of less soluble substances (*e.g.*, iron and aluminium hydroxides), agitation of the medium has no effect on the adsorption. Under the influence of an electric field, the whole of the adsorbed substance passes rapidly and completely into solution, the constituent ions collecting round the electrodes of opposite sign. This operation may be carried out in a few minutes using a Gooch crucible, one electrode being placed immediately below the crucible and the other in the liquid inside. If the adsorbed substance is not soluble in water, some appropriate electrolyte solution must be substituted (*e.g.*, a solution of ammonium chloride in the case of adsorbed cobalt oxide).

(ii). The possibility of replacing the original adsorbed substance by some other compound more readily removed has been investigated by treating precipitated aluminium hydroxide which had adsorbed chromic acid or sulphuric acid with solutions of various alkali and ammonium salts, and precipitated arsenious sulphide containing adsorbed barium hydroxide with solutions of various metallic chlorides. The results of such experiments lead to the following general rules: (1) an adsorbed substance may be replaced by one of higher valency or by one of the same valency provided that the latter is present in sufficiently concentrated solution (*e.g.*, chromic acid adsorbed on aluminium hydroxide is replaced by the corresponding acids on treatment of the precipitate with solutions of arsenates, phosphates, and moderately concentrated solutions of salts of dibasic acids); (2) under no conditions can an adsorbed substance be replaced by one of lower valency (*e.g.*, barium hydroxide is not removed from arsenious sulphide by treatment with solutions of alkali chlorides). Precipitates of aluminium, iron, and chromium hydroxides may be freed from adsorbed mono- and di-basic acids by washing them on the filter with a 5% solution of ammonium hydrogen carbonate. The mobilisation of potassium in soil is attributed to the displacement of potassium hydroxide adsorbed on humic acid by lime in presence of water charged with carbonic acid. As a technical application, the washing of photographic prints is considered.

(iii). Experiments in which the catalytic activities of specimens of alumina which had adsorbed varying quantities of various substances were investigated by measurements of their accelerating effect on the rate of decomposition of diethyl ether into water and ethylene show that, in general, the catalytic activity decreases with increasing concentration of the adsorbed substance. Specimens containing blue tungstic oxide (W_2O_5) are, however, more efficient. It would appear that as the concentration of adsorbed substance increases the activity of the specimen approaches that of the substance adsorbed. J. S. CARTER.

Adsorption of gases by glass walls. III. Sulphur dioxide. M. CRESPI and E. MOLES (Anal. Fís. Quím., 1926, **24**, 452—464; cf. this vol., 1002).—The adsorption of sulphur dioxide by the walls of a

glass vessel follows the Freundlich formula, $v = K \times 10^{-6} \times p^{1/2}$. Adsorption is expressed as a function of time of contact by an equation of the type $v = K(\log t + 1)^m$, where $m = 0{\cdot}25$. G. W. ROBINSON.

Adsorption by humic acid. K. KAWAMURA (J. Physical Chem., 1926, **30**, 1364—1388).—The adsorption isotherms of bases and acids by artificial humic acid, prepared from sucrose and hydrochloric acid, have been investigated. The behaviour of humic acid was compared with that of stearic acid towards barium and sodium hydroxides. The base was completely taken up when its initial concentration was 3·5 and 3·0 equivalent millimols. per 100 c.c. for stearic and humic acids, respectively. When the acid is treated with a stronger solution, the base taken up by the stearic acid remains practically constant and independent of concentration, but with humic acid it is a logarithmic function of the final concentration, indicating the formation of a humate which then adsorbs the base. Sodium hydroxide is adsorbed less than barium hydroxide owing to the greater solubility of sodium humate. The amounts of phosphoric, sulphuric, nitric, and hydrochloric acids absorbed are logarithmic functions of concentration and afford no evidence of compound formation. This adsorption of mineral acids by humic acid is low when compared with that of a base by its humate.

When stearic and humic acids were treated with barium hydroxide, the p_H value of the liquid remained constant, whilst the base was completely taken up by the acid. Beyond this point, the amount taken up by stearic acid remained constant, whilst the p_H value changed. With humic acid, however, the p_H value increased with the amount of base taken up, the latter being a logarithmic function of p_H value. Humic acid is considered to be a true acid. L. S. THEOBALD.

Adsorption of ions by metallic mercury. J. E. ROSENBURG and G. STEGEMAN (J. Physical Chem., 1926, **30**, 1306—1315).—The time factor in the adsorption of ions by a metallic surface has been investigated by measuring the potential of a flowing mercury electrode against a stationary one in 0·1*N*-potassium chloride or 0·1*N*-hydrochloric acid saturated with calomel. The greater the velocity of flow and the shorter the length of the stream, the more negative is the flowing mercury to that which is stationary. The maximum potential of the combination Hg(stationary)|0·1*N*-KCl|Hg_2Cl_2|Hg(flowing) is 0·53 volt. With a given time of contact, smaller differences in potential were observed between the flowing and stationary electrodes in solutions of higher mercury-ion concentration. It is inferred that an appreciable time is required for the adsorption of mercury ions at the surface of a mercury electrode to reach a maximum and the *P.D.* developed is due to this time requirement. Further, the single electrode potential of the mercury electrode depends on the concentration of mercury ions at its surface, and not directly on the concentration of the solution. Finally, adsorption of ions by a metallic surface may have an influence in producing over-voltage.

L. S. THEOBALD.

The hydrate problem. IV. Adsorption of electrolytes by parchment paper and electro-endosmosis. H. REMY and H. REISENER (Z. physikal. Chem., 1926, **124**, 41—48).—The adsorption of hydrochloric acid, barium chloride, potassium chloride, and *p*-toluidine hydrochloride on parchment paper was investigated by conductivity and potentiometric measurements of the solutions (0·001—0·1*N*) before and after shaking with the paper. The adsorption of the cation is very slight, decreasing from the hydrogen to the toluidine ion. Although the specific electroendosmosis of 0·001*N*-solutions decreases in the reverse order, the relative masses of water transported in stronger (*N*) solutions under an applied *P.D.* bear no relation to the above series. The theory previously advanced (this vol., 128) of water transport in the stronger solutions is therefore considered to be corroborated. L. F. GILBERT.

True and apparent adsorption. P. N. PAVLOV (Kolloid-Z., 1926, **40**, 116—120).—Apparent adsorption is given by the difference between the initial and final concentrations of the solution after exposure to the adsorbent. True adsorption is the amount of solute taken up by the swollen adsorbent. The relation between the two is discussed.

E. S. HEDGES.

Derivation of adsorption isotherms. B. TAMAMUSHI (Bull. Chem. Soc. Japan, 1926, **1**, 185—188).—Theoretical. On the basis of Volmer's characteristic equation for a surface containing an adsorbed substance (A., 1925, ii, 539), several different types of adsorption isotherm are deduced. M. S. BURR.

Rotatory and refractive dispersions of aqueous solutions of *d*-tartaric acid. M. L. PAGLIARULO (Atti R. Accad. Lincei, 1926, [vi], **4**, 199—203).—Although the curves of refractive dispersion for aqueous tartaric acid solutions are perfectly normal, the derived curves are similar to those used for the two optically isomeric asparagines (Nuovo Cimento, 1926) and exhibit a change of direction corresponding almost exactly with the maxima of the rotatory dispersion curves. T. H. POPE.

Rotatory dispersion of tartaric acid. E. VELLINGER (Compt. rend., 1926, **183**, 741—743; cf. A., 1925, 356, 964).—If the straight lines representing the dispersion of tartaric acid are plotted according to the method of Darmois, those obtained by the author for aqueous solutions of tartaric acid of different p_H values meet at the same point as those obtained for crystalline tartaric acid and for the acid dissolved in organic solvents or in salt solutions. The slopes of the lines decrease in the following order: (extreme dextro-) solutions of p_H 7·0, 3·9, 3·5, 2·4, zero, solutions in alcohol, alcohol–ether, alcohol–benzene, calcium chloride solution, and solid tartaric acid (extreme lævo-). Solutions of tartaric acid therefore exist in two forms, dextro- and lævo-, corresponding, respectively, with the structure of the tartarates and with that of the molecules in the solid tartaric acid crystal, the latter being as yet undetermined. Those solvents which lower the electrolytic dissociation most produce the strongest lævorotation. J. GRANT.

Influence of boric acid on the rotatory power of malic and tartaric acids. II. Boric–tartaric complexes. E. DARMOIS (J. Chim. phys., 1926, **23**,

649—672).—Using the same method as that employed in the examination of the boric-malic complexes (this vol., 337), evidence has been obtained of the existence of a dextrorotatory complex, $H_3BO_3,2C_4H_6O_6$, in mixed solutions of the two acids, and of the existence of the corresponding salt, $H_3BO_3,2C_4H_5O_6M$, in partly neutralised mixtures. Strongly alkaline solutions contain a lævorotatory complex. J. S. CARTER.

Influence of the solvent on the solubility and light absorption of true salts. A. HANTZSCH and H. CARLSOHN (Z. anorg. Chem., 1926, **156**, 199—209).—The potassium, rubidium, cæsium, tetramethylammonium, tetraethylammonium, and methylpyridinium salts of tetrathiocyanatodiamminechromic acid (Reinecke's acid) separate as anhydrous crystals from concentrated aqueous solutions, but the sodium, barium, strontium, and calcium salts contain 1, 2, 6, and 6 mols. of water of crystallisation, respectively. The hydrated salts are readily soluble in alcohol and ethyl acetate, but the anhydrous salts are insoluble unless water is added. The anhydrous salts are, however, readily extracted from aqueous solution by shaking with ethyl acetate, and the hydrated salts less readily. From such solutions in moist ethyl acetate the anhydrous salts are precipitated quantitatively by warming; the salts capable of forming hydrates are less readily precipitated as the stability of the hydrates increases. It is concluded that in such solutions mixed solvates are formed. The mol. extinctions of aqueous solutions of the hydrated and anhydrous salts are the same, and are unchanged by dilution and by the addition of large excesses of neutral salts. The hydrated salts also behave similarly in alcohol, ethyl acetate, and acetone. The anhydrous salts have higher mol. extinctions in acetone than the hydrated salts, and the values diminish with dilution. The mol. extinction depends slightly on the solvent, and is least in acetone, in which the anhydrous salts are soluble, and greatest in alcohol and ethyl acetate, which do not dissolve anhydrous salts. It is not parallel to the dielectric constant. The addition of non-ionising solvents to alcoholic solutions increases the mol. extinction. It is concluded that optical changes are not dependent on electrolytic dissociation, but on solvation, and that solubility, solvation, and light absorption are closely related. A. GEAKE.

Surface tension of charged surfaces. O. K. RICE (J. Physical Chem., 1926, **30**, 1348—1355).—Expressions are derived for the interfacial tension at a charged surface separating two immiscible liquids. In the first case, two solvents are each supposed to contain various ions. The ions cannot cross the boundary, but can be transferred from one solvent to another in such a way as to produce a *P.D.* between the solvents and a double layer at the surface. The second case is represented by the capillary electrometer, and in both cases the surface tension is given by the equation $\gamma_1=\gamma_0-\int_0^{\phi_1}Qd\phi$, where γ_0 is the surface tension of the surface when the potential ϕ is 0, γ_1 when $\phi=\phi_1$, and Q is the charge per unit surface. In the third case, ions are considered to be adsorbed at the boundary of two liquids forming a unimolecular layer, whilst one liquid contains dissolved ions. The expression for surface tension is then $\gamma_1=\gamma_0-\int_0^{\phi_1}Qd\phi-\int_0^{\phi_1}Q/e\,.\,d\mu/d\phi\,.\,d\phi$, where μ equals the chemical potential of the adsorbed ion and e its charge per unit mass. The last term of this expression is discussed in terms of the kinetics of the ions forming the unimolecular layer at the boundary. L. S. THEOBALD.

Influence of surface tension of colloidal solutions and suspensions on their stability. A. BOUTARIC and C. SEMELET (Rev. gén. Colloïd., 1926, **4**, 268—269).—To different preparations of colloidal arsenious sulphide, gum mastic, and gamboge were added equal volumes of (1) distilled water, (2) water saturated with camphor, (3) water saturated with menthol, (4) 20% ethyl alcohol, (5) water saturated with *iso*amyl alcohol. Measurements were made of the surface tension of the resulting mixtures, and of their stability towards precipitation by various electrolytes. The tabulated results show that no relation exists between surface tension and stability in these systems. E. S. HEDGES.

Theory of Liesegang rings. WO. OSTWALD (Kolloid-Z., 1926, **40**, 144—148).—Contrary to the views of Dhar and Chatterji (cf. A., 1925, ii, 865, 959), the gel plays only a secondary rôle in periodic precipitate formation, for many instances are cited of periodic precipitation in absence of a gel. Objections raised by Dhar and Chatterji to the author's "diffusion-wave theory" (*ibid.*, 530) are dealt with. E. S. HEDGES.

Formation of Liesegang rings and peptising effect of gels. A. C. CHATTERJI and N. R. DHAR (Kolloid-Z., 1926, **40**, 97—112).—A study is made of the formation of stratified precipitates in gels of gelatin, agar-agar, silicic acid, and starch, and of the peptising effect of these gels on a number of slightly soluble substances. A large number of substances were obtained for the first time in the form of periodic structures, and they fall into two groups: (*a*) layers of precipitate separated by the clear gel, (*b*) alternate layers of precipitate and peptised colloid. The gel employed has a specific influence, and the best results are obtained in a gel having a medium peptising effect on the precipitate. The precipitated substance forms a colloidal sol and not a supersaturated molecular solution. Light has the effect of increasing the number of rings, in consequence of the coagulating influence it exerts on the sol. Spiral formations can be observed both in the light and in the dark, especially with salts of heavy metals. E. S. HEDGES.

Principles of colloid chemistry. R. WINTGEN (Kolloid-Z., 1926, **40**, 141—142).—A reply to criticisms by McBain (cf. this vol., 1095), the author maintaining his position. E. S. HEDGES.

Production of stable metal sols in benzene. F. HAUROWITZ (Kolloid-Z., 1926, **40**, 139—141).—Colloidal sols of iron, nickel, aluminium, lead, tin, zinc, copper, and magnesium in benzene were prepared by an electro-dispersion method, using a high-frequency alternating current and a low voltage. An alloy (brass) was obtained in colloidal solution for the

first time. The sols are stabilised by the presence of caoutchouc, and will keep for months.

E. S. HEDGES.

Gel of metallic platinum. A. F. BENTON (J. Physical Chem., 1926, **30**, 1415—1416).—The formation of a stable, rigid gel of platinum as a shiny black substance, showing syneresis and containing approximately 40—50 mols. of water to 1 mol. of platinum, is reported. A boiling solution of sodium chloroplatinate containing 29 g. of platinum per litre was added to boiling sodium formate solution (5%), and the electrolytes were removed by washing by decantation, when the second washing, after keeping for 2 days, was partly transformed into a gel. No visible structure could be detected under the microscope, nor could the gel be duplicated.

L. S. THEOBALD.

General method for bringing fibroin, chitin, casein, etc. into a plastic state and into colloidal solution. P. P. VON WEIMARN (Kolloid-Z., 1926, **40**, 120—123).—Cellulose, fibroin, chitin, casein, fibrin, and keratin become plastic, and finally go into colloidal solution, when treated with concentrated aqueous solutions of very soluble, strongly hydrated inorganic salts. In order of influence these are: $LiSCN > LiI > LiBr > LiCl$; $NaSCN > NaI$; $Ca(SCN)_2 > CaI_2 > CaBr_2 > CaCl_2$. In some cases, it is necessary to heat the solution, but the rate of dispersion depends also on the purity, age, and previous history of the substance. The substances are reprecipitated by addition of alcohol.

E. S. HEDGES.

Condition of silver chromate in gelatin from electric conductivity and diffusion experiments. A. C. CHATTERJI and N. R. DHAR (Trans. Faraday Soc., October, 1926, advance proof).—Previous work by Sen and Dhar (A, 1924, ii, 730) has shown that ordinary solubility relations do not apply to the peptisation of silver chromate in gelatin. It is now shown that the electrical conductivity of silver chromate in solutions containing varying amounts of gelatin is less than that calculated on the assumption that the salt is completely ionised, and from diffusion experiments it is found that the chromate ion, and not silver chromate, diffuses through a gelatin gel. These results show that silver chromate exists in gelatin mainly in the colloidal condition. The presence of excess of chromate ions in gelatin containing potassium chromate and silver nitrate in equivalent amounts is explained by the preferential adsorption of silver ions by albuminous matter.

The production of rings by diffusion of silver nitrate or potassium chromate into a gelatin gel containing silver chromate is possible only when the concentration of this salt lies between definite limits and is due to the coagulation of this peptised substance.

A. S. CORBET.

Hydrogen-ion concentration and the viscosity of aluminium, chromic, and ferric hydrosols. J. H. YOE and E. B. FREYER (J. Physical Chem., 1926, **30**, 1389—1400).—The effect of hydrogen-ion concentration, over a range p_H 2·5 (approx.) to 9, on the viscosity (at 25°) of hydrosols of aluminium, chromic, and ferric oxides, containing, respectively, 0·06, 0·03, and 0·015% of oxide, has been determined. Practically no change in viscosity occurs until the p_H is 7, when a maximum is quickly reached (p_H 7—8 with the various sols), after which the viscosity decreases rapidly to an almost constant value, except in the case of the more dilute ferric oxide sols. The addition of small quantities of ammonium hydroxide to the more concentrated ferric oxide sols (0·85 and 0·12% oxide) results in a slight decrease in viscosity, followed by an increase which soon develops to a maximum. An explanation is advanced of this property which is considered to be a general one. The change in viscosity of the hydrosols is attributed partly to a change in the degree of hydration (cf. Dhar, this vol., 123). L. S. THEOBALD.

Parallelism between effect of neutral salts on electrical charge of hydrated manganese oxides and concentration of hydrogen ions liberated. B. GHOSH (J.C.S., 1926, 2605—2614).—The interaction of manganese oxides, prepared by mixing hot solutions of manganous sulphate and potassium permanganate containing a little sulphuric acid, with solutions of neutral salts of sodium, potassium, lithium, barium, strontium, and magnesium, has been studied and the results have been satisfactorily accounted for on the adsorption theory of Mukherjee. In agreement with this theory, the capacity of the different cations to liberate hydrogen is in the order $Ba^{\cdot\cdot} > Sr^{\cdot\cdot} > Mg^{\cdot\cdot} > K^{\cdot} > Na^{\cdot} > Li^{\cdot}$, *i.e.*, the same as that obtained from electro-osmotic experiments, and represents their capacity to neutralise the negative charge of the surface. This latter is reversed by bivalent cations, showing that the primarily adsorbed ions are univalent. The electrical adsorption of one bivalent cation therefore liberates one hydrogen ion, and, in addition, the replacement of hydrogen ions through the osmotic penetration of cations into the mobile sheet of the double layer probably occurs. The adsorption of acids and the primary adsorption of anions have been demonstrated. The adsorption of the acids studied is in the order $H_3PO_4 > H_2SO_4 > HNO_3$. N. H. HARTSHORNE.

Velocity of coagulation of colloids in presence of a peptising agent. C. K. JABŁCZYŃSKI and (MLLES.) G. KAWENOKI and J. KAWENOKI (Bull. Soc. chim., 1926, [iv], **39**, 1322—1327).—The presence of a peptising agent is necessary for the stability of colloids, but this may be changed or destroyed by addition of a salt, and coagulation will result. Using ferric chloride as peptising agent, the velocity of coagulation of ferric hydroxide by different salts has been determined by a method described previously (A., 1925, ii, 35). It is suggested that a state of equilibrium exists between the free peptising agent and that attached to the colloid and that the addition of a salt may cause a shift in the equilibrium by decomposition of the peptising agent or by formation of a double salt. Anions increase the velocity of coagulation in the order $Cl' > NO_3' > Br' > I'$. With alkali metal cations the mass and tendency to form double salts act in opposite directions and the velocity of coagulation shows a minimum in the series $Li^{\cdot} > Na^{\cdot} > K^{\cdot}$, $NH_4^{\cdot} < Rb^{\cdot} < Cs^{\cdot}$. The same phenomenon is shown more feebly in the series $Mg^{\cdot\cdot} > Ca^{\cdot\cdot} > Sr^{\cdot\cdot} < Ba^{\cdot\cdot}$. A. S. CORBET.

Effect of temperature on the rate of coagulation of gold sol. M. GARNER and W. C. M. LEWIS (J. Physical Chem., 1926, **30**, 1401—1409).—The influence of temperature on the rate of coagulation of gold sol by barium chloride has been determined colorimetrically at 25° and 80°, using the method of Hatschek. The values of β_0, the constant in the Smoluchowski equation (A., 1917, ii, 297), fall steadily. This is also shown by a closer examination of the results of Anderson. The increase in the velocity of coagulation with temperature is due to a change in the viscosity of the medium. The curves obtained by plotting time against the expression $(v_0/v_1)^1-1$, where v_0 and v_1 are the numbers of primary particles present initially and after a given time, respectively, indicate that the primary particles of the sol are unequally charged, the extrapolated curves cutting the time-axis at a negative value. L. S. THEOBALD.

Significance of the variation in the Smoluchowski coagulation coefficient (β). M. GARNER (J. Physical Chem., 1926, **30**, 1410—1414; cf. preceding abstract).—A theoretical paper in which the variation in β found in previous work is discussed. Assuming that the particles of a metallic sol are unequally charged, the behaviour of β during coagulation is predicted for the region in which the rate of coagulation varies with the concentration of the electrolyte, and is found to be in agreement with the experimental observations previously recorded. L. S. THEOBALD.

Flocculating power of organic anions. E. HERRMANN (Helv. Chim. Acta, 1926, **9**, 785—792).—Employing the method of Bach (A., 1920, ii, 360), the opacity numbers of organic anions towards ferric hydroxide and arsenic sulphide have been determined. Ions of the same valency vary greatly in coagulating power, *e.g.*, the *p*-bromobenzoate is 150 times as active as the trichloroacetate ion. Whilst no generalisation can be drawn connecting coagulating power with strength of the acid, or with other physico-chemical properties, it is found to be increased by the following replacements: $XH'<XCl'<XBr'<XCN'$; $XBr'<XI'$; $XH'<XMe'<XPh'$; $Ph[CH_2]_2\cdot CO_2'<CHPh{:}CH\cdot CO_2'$. The effect of hydroxyl varies; that of change of position of substituents may be considerable, and in this effect the *meta* is intermediate between the *ortho* and *para* substituted ions. Of these the former is more active, except when the substituent is the hydroxyl or amino-group. It seems that coagulating power is greater with less stable ions; contrary to experience with inorganic ions, protective power increases with coagulating power.

E. W. WIGNALL.

Anomalous flocculation of clay. H. B. OAKLEY (Nature, 1926, **118**, 661—662; cf. this vol., 576, 679).—Experiments with a 0·1% purified clay suspension show that calcium hydroxide tends to stabilise a suspension containing calcium chloride if the time of flocculation is longer than 12 min., whilst for a time of 6 min. or less calcium hydroxide flocculates more rapidly than the chloride. 0·9*N*-Sodium hydroxide is a better flocculant than sodium chloride. For a 0·1% suspension of amorphous silica, sodium and calcium hydroxides are much better flocculants than the corresponding chlorides. A. A. ELDRIDGE.

Kinetics of protein denaturation. Effect of variation in the hydrogen-ion concentration on the velocity of the heat denaturation of (I) oxyhæmoglobin. (II) Egg-albumin; critical increment of the process. (III) Influence of neutral salts on velocity of heat denaturation of oxyhæmoglobin. P. S. LEWIS (Biochem. J., 1926, **20**, 965—992).—(I). The velocity of heat denaturation of oxyhæmoglobin at 60·5° and 68° passes through a minimum at p_H 6·76 when [H]=[OH]. The critical increment of the process is 77,500 g.-cal.

(II). The velocity of heat denaturation of egg-albumin at 65° and 70·2° in unbuffered solutions was also found to pass through a minimum at p_H 6·76. The critical increment of the process in this case is 130,000 g.-cal.

(III). From experiments on the influence of varying concentrations of ammonium sulphate, sodium chloride, and sodium sulphate at constant hydrogen-ion concentration, it was found that the neutral salts have a dual effect. One predominates at lower, the other at higher concentrations of the salt. The first tends to charge the p_H value corresponding with minimum velocity, and the second tends to lower the velocity.

The results obtained in the above investigations support the hypothesis that denaturation of proteins is due to a localised hydrolysis of labile linkings in the heavily hydrated molecule. S. S. ZILVA.

Effect of colloidal and semi-colloidal ferric oxide on gelatin solutions. II. R. WINTGEN and E. MEYER (Kolloid-Z., 1926, **40**, 136—139; cf. A., 1925, ii, 524).—To a series of tubes containing equal amounts of colloidal ferric oxide were added progressively increasing quantities of 5% gelatin solution, each successive tube receiving 0·5 c.c. more than the preceding one. Mutual precipitation occurs, and determinations were made of the amount of dried precipitate and that of ferric oxide after ignition. The values attain a maximum, followed by a region of less complete precipitation, after which a second precipitation zone occurs. E. S. HEDGES.

Reciprocal protective effect of colloidal magnesium, calcium, strontium, and barium carbonates. G. STELLA (Kolloid-Z., 1926, **40**, 112—116).—The individual colloidal carbonates obtained by mixing solutions of the chlorides with sodium carbonate in dilute gelatin solution are stable for a few minutes only. When two or more colloidal carbonates are formed together in this way, mutual protection occurs, and the sol may be stable for many hours. If magnesium carbonate is one of a pair, the presence of excess of sodium carbonate confers additional stability. Increase in the ratio of the mixed carbonates has a progressive effect on the stability. It is considered that mixed crystals, and in some cases double salts, are formed. E. S. HEDGES.

Cataphoresis in colourless sols. I. Charge on rubber in benzene. R. H. HUMPHRY and R. S. JANE (Trans. Faraday Soc., 1926, **22**, 420—425).—For the observation of cataphoresis in colourless sols in a non-aqueous medium, a modification of a method previously described (Humphry, this vol., 577) is employed and use is made of the difference between

the refractive indices of the sol and dispersion medium by Toepler's "Schlieren" method (Annalen, 1867, 131, 33) to study cataphoresis of a rubber sol in benzene. Although an undried sol exhibits charges of both signs, no appreciable charges are present when thoroughly dried materials are employed. The charges are unaffected by the addition of small quantities of benzoic and dichloroacetic acids, but the change in viscosity thus produced cannot be attributed to an "electro-viscous" effect.

The bearing of the results on metal sols stabilised by rubber in non-aqueous media is discussed.

A. S. CORBET.

Principles of electro-dialysis, and a simple apparatus. L. REINER (Kolloid-Z., 1926, **40**, 123—128).—Previous methods of electro-dialysis are reviewed, and it is shown that the influence of the charge on the membranes has been over-estimated, and that a change in p_H must occur with ideal, uncharged membranes. By electro-dialysis of an indiffusible ampholyte, the final p_H is independent of the charge on the membranes and very nearly represents the iso-electric point. A new apparatus is described, involving two membranes of collodion (prepared by a special method), in which the electro-dialysis of serum diluted four times is complete in 2 or 3 hrs.

E. S. HEDGES.

Rate of filtration of protein solutions, particularly of mucin. S. AMBERG and F. SAWYER (J. Pharm. Exp. Ther., 1926, **29**, 339—354).—The rate of filtration of a solution of mucin (0·001% or greater) is much slower than that of distilled water, being least when the solution is neutral or weakly alkaline in reaction, and greater when slightly acid. This slow filtration cannot be accounted for by the viscosity or surface tension. W. O. KERMACK.

Applications of the equation of transfer in the kinetic theory of gases. J. HAAG (Ann. Physique, 1926, [x], **6**, 254—293).—A mathematical paper in which expressions are obtained for the coefficients of diffusion, viscosity, and thermal conductivity. It is assumed that all gases in a mixture obey Maxwell's distribution law. Whilst this is incompatible with the equations of Boltzmann, it is held to be true for a certain instant and in a particular region. It is claimed that these expressions are independent of the law of molecular forces if the correction factor in the expression for the law of distribution of velocities is assumed to be of the third degree. R. W. LUNT.

Gaseous explosions. I. Ionisation in hydrogen and oxygen explosions. W. E. GARNER and S. W. SAUNDERS (Trans. Faraday Soc., 1926, **22**, 342—337; cf. this vol., 654).—The ionisation produced in a gaseous explosion has been studied by measuring the maximum current passing between two platinum electrodes (1·6 cm. in diameter and 1·31 or 2·0 cm. apart) maintained at different potentials in a bomb in which a mixture of hydrogen and oxygen was exploded. The current, measured by an Einthoven string galvanometer, was recorded photographically. The current is independent of the distance between the electrodes, and for voltages above 1 is a linear function of the voltage, being given by: $C=10^{-4}(12+13V)$. The current decreases with rising initial temperature of the gas mixture, and increases with increasing initial pressure, being proportional to the concentration of the gas between the electrodes. With change of composition of the explosive mixture, the current is maximal for the composition $2H_2+O_2$. The form of the current–composition curve indicates that the ionisation is mainly thermal in character. The addition of water vapour up to about 2% has no effect, but the addition of nitrogen causes a decrease in the conductivity of the gas. The addition of small quantities of organic and organometallic substances affects the conductivity considerably, those which tend to prevent detonation in the internal-combustion engine reducing it, whereas the so-called knock inducers produce the opposite effect.

A. B. MANNING.

Reaction regions. XI. Explosion regions nitrous oxide–ether vapour–oxygen and nitrous oxide–ether vapour–air. W. P JORISSEN and B. L. ONGKIEHONG (Rec. trav. chim., 1926, **45**, 633—637; cf. this vol., 359).—Using the method described in the previous paper, gaseous mixtures of known composition have been sparked, and the upper and lower limits of composition of inflammable mixtures thus determined. Data are given and expressed graphically for the following systems: ether vapour–oxygen; ether vapour–nitrous oxide; ether vapour–oxygen–nitrous oxide; ether vapour–air–nitrous oxide; chloroform–oxygen; chloroform–nitrous oxide; chloroform–oxygen–nitrous oxide. S. J. GREGG.

Changes in ferric, chromic, and aluminium oxides on ignition. L. BLANC (Ann. Chim., 1926, [x], **6**, 182—243).—The thermal effects which appear when certain metallic oxides are heated have been observed with the aid of the Saladin–Le Chatelier recording galvanometer. Zinc oxide, although crystalline, evolves a considerable amount of heat at 450°, whereas amorphous alumina, zirconia, and silica manifest no thermal effects at any temperature within the range examined. It therefore appears likely that, in some instances at least, such effects are due to polymorphic changes, rather than to the occurrence of crystallisation, as Böhm has suggested (this vol., 113). The trihydrate of alumina, either in the form of hydrargyllite or as precipitated from aqueous solutions of aluminium salts in the cold, commences to lose water at 50°. The decomposition temperatures of the dihydrate obtained by precipitation from boiling solutions and of bauxite are 200° and 500°, respectively. Alumina obtained by the oxidation of aluminium amalgam in the air is anhydrous. If precipitated (α-)chromic oxide is heated at 230° for some time, black CrO_2 is obtained, and from this oxide, by hydrolysis, α-Cr_5O_9. If this latter is heated at above 350°, a mixture of β-chromic oxide and β-Cr_5O_9 is formed, this reaction evolving so much heat at 450° that it brings about the transformation of α-chromic oxide into the β variety, whereas in absence of oxygen this transformation occurs only at a much higher temperature. Guignet's green appears to be merely anhydrous chromic oxide in a finely-divided state, and not a hydrate, as Wöhler supposed (cf. A., 1911, ii, 401). The magnetic oxide of chromium is probably an

unstable variety of Cr_5O_9 intermediate between the α and β forms, and has a magnetic susceptibility between 0 and 200 gauss very nearly equal to that of magnetite. The susceptibility of β-ferric oxide is practically constant from the ordinary temperature up to 600°, at which temperature it falls suddenly, commencing to rise again in the neighbourhood of 700°. With chromic oxide, the first change is a sudden rise at 800°, followed by a gradual fall beyond 900°. Density measurements show that with both oxides these changes are accompanied by discontinuous changes in the state of aggregation. R. CUTHILL.

Influence of intensive drying on inner equilibria. II. A. SMITS (J.C.S., 1926, 2655—2657; cf. A., 1925, ii, 532).—Thermodynamic considerations suggest that if intensive drying has any influence on the stability of the pseudo-components the process will also in general result in a shifting of the inner equilibrium. The direction of this shift will, however, be quite fortuitous. It is to be expected that the influence of intensive drying on the velocity of inner transformations will vary in different cases, the final state depending on the properties of the substance, its state of aggregation, and the temperature.

N. H. HARTSHORNE.

Influence of intensive drying on inner equilibria. III. A. SMITS, W. DE LIEFDE, E. SWART, and A. CLAASSEN (J.C.S., 1926, 2657—2670).—To determine whether intensive drying results in a fixing of the inner equilibrium, or a displacement of the inner equilibrium followed by fixation, measurements of the vapour pressure of intensively dried nitrogen tetroxide and *n*-hexane have been made. Nitrogen tetroxide after intensive drying for 23 months at the ordinary temperature in an apparatus the glass of which was not freed from capillaries showed an increase in the vapour pressure of 1·9 cm. of mercury; a part of the liquid was then distilled off, and the increase fell to 0·4 cm., but after a further 11 days this had risen to 1·47 cm. In another apparatus made of capillary-free glass, a much more rapid drying effect was obtained, for after 16 months the vapour pressure had risen by 3·3 cm. On raising the temperature, the increase passed through a maximum, as had been anticipated on theoretical grounds. The changes of vapour pressure and of colour to a deeper brownish-red prove that the drying process had effected a displacement of the inner equilibrium in the direction $N_2O_4 \rightarrow 2NO_2$. The observation of Baker and Baker that the b. p. of the dried liquid rose more than 30° (*ibid.*, 1912, **101**, 2339) can be explained by the fact that a certain amount of the liquid had evaporated before the b. p. was reached.

With *n*-hexane, intensive drying at about 40° results in a decrease of vapour pressure. After only 14 weeks, this reached 0·9 cm., showing that, in contrast to nitrogen tetroxide, the inner equilibrium is here shifted towards the less volatile component. The decrease was augmented by raising the temperature, and after distilling off a portion of the liquid at the drying temperature, the vapour pressure tended to revert to its previous value, showing that the inner equilibrium had not been reached. The experiments are compared with those of Mali (this vol., 117), which show, in agreement with those of the authors, that intensive drying takes place more rapidly at about 40° than at the ordinary temperature.

N. H. HARTSHORNE.

Soret effect. J. CHIPMAN (J. Amer. Chem. Soc., 1926, **48**, 2577—2589).—The Soret effect, the concentration difference set up in a solution by a temperature gradient, is investigated for a series of acids, bases, and salts, the gradient being 10° and the concentration changes being followed by conductivity measurements. The experimental results with very dilute solutions (especially acids) are not reproducible. The Soret effect is believed to be independent of the dimensions of the cell used. The Soret coefficient ($=d \log_e M/dT$, where M is the molality) passes through a maximum at $1M$ for hydrochloric acid solutions; it is not an additive property of the ions.

S. K. TWEEDY.

Theory of electrolytes. E. SAERENS (Natuurwetensch. Tijdschr., 1926, **8**, 4—13).—A discussion of the thermodynamic solubility product of a sparingly soluble salt in dilute salt solutions. S. I. LEVY.

Dissociation constants of compounds of boric acid with salts of some organic hydroxy-acids. I. M. KOLTHOFF (Rec. trav. chim., 1926, **45**, 607—619).—The increased solubility in water of some organic hydroxy-acids brought about by adding boric acid shows that the complexes formed with the latter are often fairly stable. The dissociation constants of some of these complexes have been determined from the solubility of the sparingly soluble salts of the hydroxy-acids in boric acid solution, and from them the constitution of the complexes has been inferred. If AB_n represents the complex ion derived from the acid ion A and the boric acid molecule B, with the elimination of one or more mols. of water, then tartaric acid gives AB_2'', dissociation constant $K = 1·9 \times 10^{-3}$; salicylic AB', $K = 4·6 \times 10^{-2}$; meconic AB', $K = 4 \times 10^{-2}$; and citric AB_2''', $K = 1 \times 10^{-3}$. The f.-p. depression of a mixed solution of sodium potassium tartrate and boric acid in water is less than corresponds with the total number of molecules and ions nominally present, thus confirming the occurrence of combination. Since the formation of these complexes decreases the acidity of boric acid, the titration of polyhydric alcohols by boric acid in the presence of organic hydroxy-acids gives inaccurate results.

S. J. GREGG.

Organic acids and bases in non-aqueous solutions. I. F. HÖLZL (Monatsh., 1926, **47**, 119—149).—The behaviour of acetic acid towards the bases ammonia, ethylamine, diethylamine, *p*-toluidine, mono- and di-methylaniline, benzylamine, α- and β-naphthylamine, *o*-, *m*-, and *p*-phenylenediamine, carbamide, and acetamide, in absolute alcoholic solution of varying concentrations, has been investigated by conductivity measurements at 25°, with special reference to the formation of compounds. Although the conductivity of a solution of acetic acid in alcohol increases gradually with time (due partly to esterification, but also depending on the previous treatment of the acetic acid), this increase is small compared with the change in the conductivity when a compound is formed, and the error is removed by making the

measurements immediately the acid and base are mixed. With the stronger bases, ammonia and the alkylamines, only compounds of the type AB (A= 1 mol. of acetic acid, B=1 mol. of the base) are produced, but with the weaker aryl bases in the more concentrated solutions the strength of the base is insufficient to overcome completely the association and polarisation of the acetic acid, and compounds consisting of several molecular proportions of the acid with 1 mol. of the base are shown to be produced by the occurrence of distinct maxima on the conductivity curves. In such cases, dissociation of the acid is more complete in dilute solution, and only equimolecular compounds are then formed. The following summary shows the various compounds formed at different dilutions; ammonia 0·8N, ethylamine 0·68N, diethylamine 1·07N and 0·11N, and benzylamine 0·425N and 0·20N all form only equimolecular compounds of the type AB; aniline 3·4N, yields A_3B and A_3B_2; 0·5N, A_2B and AB; p-toluidine 4N, A_3B; 1·9N, A_7B_3; 0·5N, A_2B; 0·125N, AB; methylaniline 0·3 and 0·1N, A_3B_2 and AB_2; dimethylaniline 0·5, 0·2, and 0·1N, A_2B and AB; α-naphthylamine N, $A_{2-3}B$ and AB; 0·1N, AB and AB_2; β-naphthylamine 0·25N, A_2B and AB; o-phenylenediamine 0·255 and 0·125N, A_2B and AB; m-phenylenediamine 0·063N, A_2B and AB; o-phenylenediamine 0·25, 0·27, 0·125, and 0·063N, A_2B and AB. In the case of carbamide, compound formation is assumed when the value of $\Delta=\kappa-(\kappa_s+\kappa_\beta-\kappa_\alpha)$ is positive (these being, respectively, the conductivities of the mixture, acid, base, and alcohol), and the position of the maximum value of Δ indicates the composition of the compound, and thus the compound AB is shown to exist in 0·5 and 0·3N-solutions, whilst no compound is formed in 0·1N-solution. No evidence of the formation of a compound between acetic acid and acetamide was found. The hygroscopic power of absolute alcohol was investigated by changes in its conductivity, and was found to be considerable when the alcohol was allowed to drop slowly from a burette through air saturated with water vapour at 14°. J. W. Baker.

Solvate formation. (Mrs.) M. S. Burr (Proc. Leeds Phil. Lit. Soc. Sci. Sec., 1926, **1**, 74—80).—The solubility of 2 : 4-dinitrotoluene, and other aromatic nitro-compounds, in sulphuric acid–water mixtures of concentration varying from 84·5% to 95% of acid, may be represented by an equation of the form $S_c=\sigma e^{kc}$, where S_c is the solubility in g. per 100 g. of solvent of concentration c in "free" sulphuric acid, σ is a constant depending on the particular solute employed and on the temperature, and k a constant depending only on the solute. The amount of free sulphuric acid is determined by regarding the solvent as a mixture of sulphuric acid and sulphuric acid monohydrate, the concentration of the former thus varying from 0% to 67·78%. It is shown that the form of the equation may be explained by supposing that the solute forms, with the better solvent, a continuous series of solvates in equilibrium with a certain amount of free solute. The application of the equation to similar cases may be complicated by the formation of compounds between the two constituents of the solvent if these are not sharply defined, as is sulphuric acid monohydrate. Experiments on the solubility of anthraquinone in sulphuric acid–water mixtures suggest, on the other hand, that in this case one particular solvate is formed in overwhelmingly large proportion. M. S. Burr.

Ionic interaction. E. Güntelberg (Z. physikal. Chem., 1926, **123**, 199—247).—Electrometric measurements have been made of activity coefficients in 0·01—1·0M-hydrochloric acid solutions at 20°. The results are normal, agreeing with the Hückel theory, and giving the usual minimum at about 0·35M. Figures are also given for mixtures of hydrochloric acid with sodium, potassium, lithium, or cæsium chloride. Log f is shown to be a linear function of the ratio salt concentration : total concentration. The solubility of nitrothiocyanatotetraminocobaltic chloride in 0·1M-solutions of hydrochloric acid and the chlorides has also been determined. The theory which follows is restricted to mixtures of univalent ions. Bjerrum's theory of complete dissociation requires the activities of the ions in a solution to be additive, whence f_{HCl} in solutions of hydrochloric acid containing a chloride of a constant total concentration should be constant. The figures given show that this is not the case, in contradiction of the work of Ming Chow (A., 1920, ii, 281). Further, since f_{HCl} is not constant in the mixed solutions, the MacInnes–Harned–Lewis hypothesis, viz., that the activity of an ion is dependent only on the nature of the ion and on its total concentration, is untenable. Brönsted has also shown this hypothesis to be untenable on thermodynamic grounds, and a condensed version of his proof is given. With reference to Brönsted's views on the linear variation of log f and of osmotic coefficients and the same author's theory of specific interaction, it is shown that these are compatible with one another only in the case of mixtures of salts with a common ion.

The linear change of log f with the ratio salt concentration : total concentration is in agreement with both these theories, but Brönsted's solubility measurements for hetero-ionic solutions are not in agreement with the linear change in the osmotic coefficient required by the first theory. In homo-ionic mixtures, satisfactory agreement is obtained. Brönsted's theory of "specific interaction" is then given in detail, starting with the assumptions that ions of opposing sign influence one another differently, whilst ions of the same sign act equally upon one another, and that each ion has a specific influence on every other ion in the solution. Although Brönsted's theory of specific interaction is not in very good agreement with the observed facts in the case of mixtures of univalent ions, much more satisfactory agreement is claimed for mixtures of bivalent ions. The theory is correlated with Bjerrum's theory of complete dissociation and with the Debye–Hückel equations. Some of Hückel's later work on the relation between log f and concentration is described, and the incompatibility of Hückel's conclusions with the ionic interaction theory is discussed. H. F. Gillbe.

Freezing-point lowering at infinite dilution. M. Randall (J. Amer. Chem. Soc., 1926, **48**, 2512—2514).—The plot of $j/\sqrt{M}$ against $\sqrt{M}$, where $j=1-(\theta/1{\cdot}858\nu M)$, θ being the f.-p. lowering, ν the

number of ions formed per mol., and M the molality of a solution (cf. Lewis and Randall, A., 1921, ii, 427), is useful in the empirical extrapolation of f.-p. measurements, since it visualises the accuracy of the results. The theoretical limiting values of $j/\sqrt{M}$ for $M=0$ are tabulated for certain salt types at 0° and 25°. The graphs for strong electrolytes agree in dilute solutions with the results of the interionic attraction theory. S. K. TWEEDY.

Activity coefficient of electrolytes from the vapour pressure of the solvent. M. RANDALL and A. M. WHITE (J. Amer. Chem. Soc., 1926, **48**, 2514—2517).—The divergence function h of Lewis and Randall ("Thermodynamics," 1923, p. 273) is modified to apply to electrolyte solutions: $h=1+55{\cdot}5\log_e a/\nu M$, where a is the activity of the solvent, from which $\log_e\gamma=-h-2\int_0^M h/\sqrt{M}\times d\sqrt{M}$. This integral can be evaluated by plotting $h/\sqrt{M}$ against $\sqrt{M}$ (cf. preceding abstract); at 0°, this graph becomes identical at infinite dilution with the $j/\sqrt{M}$ curve, and very nearly so at other temperatures. Assuming the interionic attraction theory, these two curves for potassium chloride intersect in dilute solution, indicating a systematic error in the vapour-pressure measurements. The activity coefficients, γ, calculated from the latter agree with the values obtained by Scatchard below $0{\cdot}1M$ (cf. A., 1925, ii, 397). S. K. TWEEDY.

Activity coefficient of soap solutions. M. RANDALL, J. W. MCBAIN, and A. M. WHITE (J. Amer. Chem. Soc., 1926, **48**, 2517—2522).—By an application of the graphical methods previously outlined (cf. preceding abstracts), the activity coefficients of the various soaps are calculated, and are shown to offer evidence in favour of the micellar structure of these substances. S. K. TWEEDY.

Free energy of hydration of ions and the electrostriction of the solvent. T. J. WEBB (J. Amer. Chem. Soc., 1926, **48**, 2589—2603).—Theoretical. The energy of the electric field in the cavity of radius r_0 surrounding an ion of charge e is $e^2/2r_0$; the difference between this and the energy necessary for charging an ion in water and for compressing the solvent in its vicinity gives the free energy of hydration of the ion, F', which is tabulated for ions of various radii. The volume change produced by the addition of an infinitesimal quantity of the ions to an infinitely dilute solution of the ions is likewise calculated, as well as the electrostriction (the contraction of the solvent resulting from the attractions of the water dipoles by the ions). Both are obtained as $f(r_0)$. With the aid of these equations, F' and r_0 are calculated for a series of ions; the values of r_0 are 0·47 Å. greater than the corresponding values in the crystal state. Some calculations of electron affinities and lattice energies are also made. S. K. TWEEDY.

Freezing-point measurements for very dilute solutions of strong electrolytes in *cyclo*hexanol. E. SCHREINER and O. E. FRIVOLD (Z. physikal. Chem., 1926, **124**, 1—15).—The f. p. of dilute solutions of lithium chloride, bromide, and perchlorate, and guanidine nitrate in *cyclo*hexanol have been determined. Deviations are observed from the f. p. which would be expected from the classical theory, and are found to agree fairly closely with those calculated on the basis of the Debye–Hückel theory. This is indicative that the theory holds for solutions in which the solvent has a low dielectric constant. H. F. GILLBE.

Factors determining solubility. G. B. BONINO (Gazzetta, 1926, **56**, 573—588).—A theoretical paper in which the concepts of the Debye–Hückel theory of strong electrolytes (A., 1923, ii, 459, 724) are applied to calculate the change in solubility of one solute on the addition of a second solute. The expression obtained for the condition of thermodynamic equilibrium reduces to a classical form for ideal and dilute solutions. R. W. LUNT.

Thermal dissociation of fluosilicates. G. HANTKE (Z. angew. Chem., 1926, **39**, 1065—1070).—Sodium and barium fluosilicates begin to dissociate into metal fluoride and silicon fluoride at 600° Abs., whereas the potassium salt is stable up to 700° Abs. In each case, the metal fluoride formed goes into solid solution in the fluosilicate, remaining undecomposed up to a limit of 20 mol.-% for the sodium salts, and about 50 mol.-% for the barium salts. The limiting solid solution of sodium fluoride in sodium fluosilicate melts at 990° Abs. and has a heat of dissociation of 27,900 g.-cal.; the corresponding barium solid solution has a heat of dissociation of 31,800 g.-cal. These figures agree fairly closely with the results calculated from heats of formation after making due allowance for variations in specific heat. The heat of neutralisation of hydrofluosilicic acid with sodium hydroxide is 37,110 g.-cal., with potassium hydroxide 42,200 g.-cal., and with barium hydroxide 32,600 g.-cal. per g.-mol. From determinations of the dissociation pressures of sodium, barium, and potassium fluosilicates at different temperatures, the heats of formation of the fluoride–fluosilicate solid solutions have been calculated to be 18,000, 5000, and about 22,600 g.-cal., respectively. A. R. POWELL.

System naphthalene–*m*-dinitrobenzene. N. A. PUSCHIN (Z. physikal. Chem., 1926, **124**, 16—22).—This system has been investigated at atmospheric pressure by a thermal method, and shows only one eutectic point, viz., at 51° and 56% (molecular) of naphthalene, contrary to Kremann's results (A., 1905, ii, 77). The heats of combustion of equimolecular mixtures of the components, after fusion and resolidification, agree with those calculated from the law of mixtures. It is concluded that the compound $C_6H_4(NO_2)_2,C_{10}H_8$, reported by Hepps (A., 1882, 317) and Kremann, does not exist. A thermal investigation of the equimolecular mixture at high pressures (up to 2500 kg./cm.^{2}) gave results agreeing qualitatively with this conclusion. L. F. GILBERT.

Freezing-point curves of the systems benzene–ether and benzene–acetone. S. YAMAMURA (Bull. Chem. Soc. Japan, 1926, **1**, 183—184).—The f.-p. curves of mixtures of benzene and ether and of benzene and acetone show a simple eutectic point. The eutectic mixture in each case contains more than 90% of the second constituent, and the eutectic temperature is only a little below the m. p. of the latter. M. S. BURR.

Hydrates of manganous oxalate. N. H. CHAMBERLAIN, J. HUME, and B. TOPLEY (J.C.S., 1926, 2620—2623).—The solubility of manganous oxalate dihydrate between 0° and 36° and of the unstable trihydrate between 0° and 30° has been determined. The transition temperature for these two hydrates has been calculated from the Ramsay and Young equation and from an equation of the type $\log_{10}s = A - B/T - C\log_{10}T$, where A, B, and C are constants and T is the absolute temperature corresponding with the solubility s. The value found is approximately −41°. The density of the dihydrate is 2·2946, and of the trihydrate 1·9930, at 0°.

N. H. HARTSHORNE.

Solubility of thallous chloride in salt solutions at 0°, 25°, and 50°, and its heats of solution. J. A. V. BUTLER and E. S. HISCOCKS (J.C.S., 1926, 2554—2562).—A relation connecting the heat of solution with the temperature coefficient of solubility has been derived, which, although equivalent to that of Brönsted (A., 1922, ii, 354), can be more easily applied to experimental data. It has been tested by measurement of the solubility of thallous chloride in various salt solutions at 0°, 25°, and 50°. The activity coefficients in these solutions were obtained by an extrapolation method based on the equation of Debye and Hückel. Values of $1/c_s^{0\pm}$ (the reciprocal of the theoretical solubility in a solution of zero ionic strength) have led to values for ΔH_0, the heat of solution of thallous chloride in an infinitely dilute solution. The results show that the temperature variation of the activity coefficient of a salt cannot be obtained with certainty from solubility data.

N. H. HARTSHORNE.

Precipitated solids. I. Strontium sulphate. B. LAMBERT and W. HUME-ROTHERY (J.C.S., 1926, 2637—2648).—The influence of temperature, concentration, and the nature of the precipitating solutions on the form and nature of precipitated strontium sulphate has been studied. Generally in concentrated solutions the initial precipitate is a voluminous, flocculent mass of needle-shaped crystals of a new hydrated form to which it has not been possible to assign a formula. The needles change both in the mother-liquor and in air into rhombic crystals of anhydrous strontium sulphate (celestine), the velocity of the change increasing rapidly with rise of temperature. The form of the anhydrous crystals varies greatly with the temperature and concentration of the solutions: all forms are, however, modifications of the celestine lattice. In general, increase of temperature and decrease in concentration of the precipitating solutions cause an increase in the size of the precipitated particles, but at extreme dilutions a point is reached at which this effect is reversed. This limiting concentration moves towards increasing dilution as the temperature is raised.

The times taken for the precipitate to form under different conditions have been measured and are in agreement with the view that an intermediate positively charged colloidal form of strontium sulphate is formed. In N-solutions, the time appears to be determined chiefly by the protective or precipitative action of the ions in the mother-liquor on this colloidal form, whereas in more dilute solutions other factors such as diffusion and viscosity play an increasingly important part.

The size of the particles appears to be governed by two main factors, viz., velocity of precipitation, increase of which favours a small particle, and facilities for diffusion, which favours a large particle. At higher temperatures, these factors act in opposition, but the diffusion factor predominates and larger particles are formed.

N. H. HARTSHORNE.

Precipitated solids. II. Calcium sulphate. B. LAMBERT and R. J. SCHAFFER (J.C.S., 1926, 2648—2655).—For a given pair of precipitants, calcium sulphate is precipitated directly either as the dihydrate or the hemihydrate, the determining condition being temperature. For each pair of precipitants there is a fairly definite transition temperature above which the hemihydrate is stable. The normal form of the dihydrate obtained is (110) (010) (111), but the presence of acetate ion has a marked effect and gives rise to the forms (110) (010) (103) and (110) (010) (203), of which the latter has not hitherto been described. These forms crystallise in a variety of twins of a type determined by the concentration of the acetate ion. Direct evidence has been obtained that the faces $(\bar{1}11)$ $(\bar{1}1\bar{1})$—pyramidal faces on $(\bar{1}01)$—which are usually found rounded and water-worn in natural gypsum crystals, owe their appearance to solvent action. It has been shown that crystal growth does not always take place by deposition in parallel layers and that gypsum crystals grow in stages, with the development of a possible face at each stage. The velocity of precipitation of calcium sulphate is affected by the ions in the mother-liquor for the reasons holding in the case of strontium sulphate (see preceding abstract).

N. H. HARTSHORNE.

Equilibrium between zirconium oxide and carbon and their reaction products at incandescent temperatures. C. H. PRESCOTT, jun. (J. Amer. Chem. Soc., 1926, **48**, 2534—2550).—Apparatus and technique have been developed for the investigation of the equilibrium between oxides and carbon (involving only one gaseous component) at 1000—2200° Abs. and at equilibrium pressures from a few cm. of mercury to 3 atm. The rate of change of pressure with time is observed for a series of pressures at different temperatures, from which the equilibrium pressure at each temperature is estimated. X-Ray examination of the solid phase in the above system indicated the reaction to be: $ZrO_2+3C=ZrC+2CO$. The equilibrium pressures are given by $\log_{10}p$ (atm.) $= 8{\cdot}592-(16580/T)$, from which $\Delta F = 151800-78{\cdot}68T$ and $\Delta H = 151{,}800$ cal. At 1930° Abs., $p=1$ atm. and $\Delta F=0$.

S. K. TWEEDY.

Space diagram of the three-component system NaOH–NaCl–H_2O. W. ANTROPOFF and W. SOMMER (Z. physikal. Chem., 1926, **123**, 161—198).—The system NaOH–NaCl was investigated from 160° to 800°, with results in approximate agreement with, and supplementary to, those of Scarpa (A., 1915, ii, 633). An apparatus is described which is suitable for the examination at high temperatures of systems containing a volatile component and was applied to the

systems (i) $NaOH-H_2O$, for which the fusion curve was completed (cf. A., 1924, ii, 837) and the 1 atm. b.-p. curve determined between 150° and 400°; the latter does not agree with that of Gerlach (A., 1887, 1012). (ii) $NaCl-H_2O$, for which the "second b. p." was found to be 780±5°, with a water content of 0·2%±0·2%. (iii) $NaOH-NaCl-H_2O$, for which the fusion diagram between 150° and 800° and the 1 atm. isobars of various mixtures between 270° and 800° were established. The system is discussed in detail. L. F. GILBERT.

Systems nickel sulphate–potassium sulphate–water, zinc sulphate–potassium sulphate–water, and manganese sulphate–potassium sulphate–water at 25°. R. M. CAVEN and W. JOHNSTON (J.C.S., 1926, 2628—2632).—In continuation of previous work (A., 1924, ii, 683), the existence and limits of stability of the following double salts at 25° have been demonstrated by a study of the appropriate ternary systems: $NiSO_4,K_2SO_4,6H_2O$, from 0·031 to 3·8 mols. of $NiSO_4$ to 1 mol. of K_2SO_4 per 1000 g. of water; $ZnSO_4,K_2SO_4,6H_2O$, from 0·19 to 21·3 mols. of $ZnSO_4$ to 1 mol. of K_2SO_4 per 1000 g. of water; $MnSO_4,K_2SO_4,4H_2O$, from 1·5 to 10·4 mols. of $MnSO_4$ to 1 mol. of K_2SO_4 per 1000 g. of water. In each case, the addition of potassium sulphate causes an increase in the solubility of the other solid component. N. H. HARTSHORNE.

Equilibria in systems in which the phases are separated by a semi-permeable membrane. XVI. F. A. H. SCHREINEMAKERS (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 846—854; cf. this vol., 1102).—A further discussion of membrane equilibria. A. B. MANNING.

Thermal decomposition of calcium oxalate. II. Thermochemistry and kinetics of the reaction. E. MOLES and C. D. VILLAMIL (Anal. Fís. Quím., 1926, **24**, 465—494; cf. A., 1924, i, 831).—The thermal decomposition of calcium oxalate begins at 370°. It is catalysed by carbon and in the presence of a trace of lamp-black begins at 355°. On the other hand, in an atmosphere of carbon monoxide the initial temperature of decomposition is raised to 377°. The authors have determined the relationship between dissociation pressure and temperature between 648° and 695° Abs. The results can be expressed by the equation $\log p=-30{\cdot}1874+0{\cdot}04782T$. The heat of reaction is −20·900 g.-cal. Q/T is thus 32·6 and the reaction may be considered as reversible. It is also shown that the thermal decomposition of calcium oxalate follows the equation proposed by Moles and Crespi (A., 1925, ii, 877) for the decomposition of permanganates, viz., $dx/dt=(K_1+K_3x/a)(a-x)$, and is unimolecular and autocatalytic. G. W. ROBINSON.

Calorimetric researches. XIII. Heats of combustion of successive terms of homologous series: dimethyl esters of the oxalic acid series. Alternation phenomena. P. E. VERKADE, J. COOPS, and H. HARTMAN (Rec. trav. chim., 1926, **45**, 585—606; cf. this vol., 686).—In their previous paper, the authors show that the heats of combustion of the acids of the oxalic series exhibit alternation, the increment in the heat due to the introduction of a CH_2 group into an acid with an even number of carbon atoms being 158·3, whilst for one with an odd number it is 155·1 kg.-cal. They believe this phenomenon to be connected with a difference in crystalline form of the two classes of acid, and accordingly have determined the heats of combustion for the dimethyl esters of the first nine of these acids in the undercooled liquid state at 19·5°, the acids themselves being too difficult to obtain in this condition. The values they thus obtain for the molecular heat of combustion at constant pressure, Q_p, are: oxalate 405·8, malonate 554·0, succinate 707·1, glutarate 863·2, adipate 1019·6, pimelate 1176·0, suberate 1332·3, azelate 1488·3, sebacate 1644·7, and from the succinate onwards the increment due to each increase of CH_2 is constant at 156·3 kg.-cal. As with the corresponding acids, the heats of combustion of dimethyl oxalate and dimethyl malonate are abnormally high, indicating that constitutive influences are becoming appreciable. The molecular refractions show a constant increment for each CH_2 group, which agrees with those for other homologous series. The molecular volume shows a constant increment of 16·77 after dimethyl succinate, and the b. p. affords no evidence of alternation. The f. p., however, shows distinct alternation. The molecular refraction, m. p., and heats of combustion of the acids of this series in the solid state also show alternation, whereas the b. p. does not. It is probable, therefore, that alternation is a characteristic of the crystalline state. Since the phenomenon is probably due to a difference in crystalline form between the odd and even members, X-ray investigation is very desirable. S. J. GREGG.

Investigations in the critical region. I. Specific heats of carbon dioxide at the critical point. K. BENNEWITZ and E. SPLITTGERBER (Z. physikal. Chem., 1926, **124**, 49—65).—Definite amounts of carbon dioxide in steel cylinders were heated in steps of about 2° from 10° to 44°. The specific heats of the equilibrium gas–liquid mixtures below the critical point, and of the gas alone above the critical point, and the heats of vaporisation were determined calorimetrically. From these data, the specific heats at constant volume of liquid and of gas were calculated, and are in fair agreement with Dieterici's values. L. F. GILBERT.

Free energy of formation of zinc oxide. C. G. MAIER, G. S. PARKS, and C. T. ANDERSON (J. Amer. Chem. Soc., 1926, **48**, 2564—2576).—The values for the free energy of formation, ΔF, of zinc oxide from its elements are calculated from *E.M.F.* measurements on cells of the type $H_2(g)|dil.Ba(OH)_2|ZnO(s)+Zn(s)$, from the specific heats of the oxide, which were determined at 90—290° Abs. with the aid of Nernst's theorem, and from solubility data (de Wijs, A., 1925, ii, 889), and are compared with the value obtained from high-temperature equilibrium experiments (Maier and Ralston, this vol., 358). The most probable figures are $\Delta F_{298}=-75{,}930\pm150$ g.-cal./mol. and $\Delta S_{298}=10{\cdot}2\pm0{\cdot}2$ g.-cal./1°, S being the entropy. The preliminary value of −132,220 g.-cal./mol. is found for the free energy of formation of zinc hydroxide from its elements. Solid solutions of zinc in zinc oxide and allotropic modifications of the latter appear not to exist. S. K. TWEEDY.

Connexion between energy of formation, contraction, and polymerisation in chemical reactions. G. Beck (Z. anorg. Chem., 1926, **156**, 288—300).—In analogy to the gas equation $Q=RT(\log_e V_a - \log_e V_c)$ . . . (i), the formula $kQ=RT(\log V_a - \log V_c)$ . . . (i*a*) is applied to solid phases, where Q is the heat of reaction in kg.-cal., V_a the volume of the reacting components, V_c the volume of the compound formed, R is 2, and T is 273. Values of k are tabulated for halides, oxides, sulphides, and hydrides of the alkali and alkaline-earth metals and for some oxygen salts of these metals considered as compounds of the metal oxides with acid anhydrides. For halides, with the exception of the fluorides and cerium halides, k is 1·31. The deviations of the fluorides may be due to their formula being of the type M_2F_2. For compounds of the oxides with acid anhydrides, k is 0·33. Thus in the formation of salts from acid anhydride and base, the heat evolution is four times that in the formation of halides from the metal and a halogen. This is explained by assuming that, in the latter case, one positive and one negative elementary charge per mol. take part and so the energy is proportional to $1e\times 1e=1e^2$; whilst in the former case, one bivalent and two univalent ions take part and so the energy is proportional to $2e\times 2e=4e^2$.

This change in the constant by definite quanta is unmistakable. The values of k for the substances investigated are multiples of 0·334; moreover, the constancy of k in the alkali halides indicates that the valency electrons possess equal velocity. A second formula is introduced, $k'Q=(V_a-V_c)N/V_c^{2/3}M$ . . . (ii), containing the constant k', where V_a and V_c are as before, N is the sum of the atomic numbers, and M the sum of the atomic or mol. wts. of the reacting substances. By combining (i*a*) and (ii), an equation $(V_a-V_c)N/(\log V_a-\log V_c)MV_c^{2/3}=k''$ . . . (iii) is obtained, where k'' varies between 4 and 4·7 for reactions with small heat evolution, rises to 5 for strongly exothermic reactions, and in cases of polymerisation rises to 7 and above. Tables are given, and the calculated results are in good agreement with those obtained physico-chemically.

Three types of reaction are discussed in relation to equation (iii). (1) A+B=AB, (2) nA+nB=nAB, (3) nA+nB=(AB)$_n$. Application of (iii) to (1) is clear. For (2) k is independent of the number of mols. reacting, but for (3) $k=(V_a-V_c)N/(\log V_a-\log V_c)MnV_c^{2/3}$ . . . (iii*a*). From this formula the degree of polymerisation is calculated and agrees well with those values obtained physico-chemically; for complexes k has the value 7—8 or higher; this does not necessarily indicate polymerisation, but may mean that compounds with neutral parts in a second sphere round a primary molecule are being considered. There is support for this assumption in that it gives complex compounds of still higher order in which a third zone of neutral parts exists round the second, *e.g.*, $\{[Co(NH_3)_6](NH_3)_{10}\}I_3$.

Since $(\log V_a-\log V_c)$ is approximately equal to V_a/V_c-1, formula (iii) may be simplified to $M/N=cV_c^{1/3}$ . . . (iv), *i.e.*, the quotient of the mol. wt. and the sum of the atomic numbers is equal to the product of a constant into the radius of the molecule. Values of c are tabulated, and the maximum values belong to substances of highest density and m. p., *e.g.*, osmium, iridium, platinum, tungsten, etc.

M. Carlton.

Thermodynamical equations determining the distribution of the constituents of a mixture between its phases. R. D. Kleeman (Physical Rev., 1925, [ii], **25**, 250—251).—If a mixture involves n constituents and exists in m phases, it will satisfy n equations involving the equality of the total mass of each constituent and the sum of the masses in the phases, $m-1$ involving equality of the pressures of the phases, one involving equality of the volume of the mixture and the sum of the volumes of the phases, and $(m-1)n$ of the type $\int(\partial p_1/\partial M_{1a})_{r1}\,.\,\partial v_1 - RT\log M_{1a}=\int(\partial p_2/\partial M_{2a})_{r2}\times\partial v_2 - RT\log M_{2a}$, where M_1, v_1, and p denote mass, volume, and pressure, respectively, the suffix a refers to the constituent a, and the suffixes 1 and 2 refer to two different phases.

A. A. Eldridge.

Photophoresis. H. S. Patterson and R. Whytlaw Gray (Proc. Leeds Phil. Lit. Soc. Sci. Sec., 1926, **1**, 70—73).—An apparatus is described for observing the movements, under the influence of an intense beam of light, of minute particles in gases at low pressure (cf. Ehrenhaft, Ann. Physik, 1918, [iv], **56**, 81). A large number of different substances have been examined and both positive and negative photophoresis obtained, far more light positive than light negative particles always being present. The change of sign which a few particles undergo may be conveniently observed by means of a cross beam of light.

M. S. Burr.

Conductivity of an electrolyte containing dielectric spheres. A. Slawinski (J. Chim. phys., 1926, **23**, 710—727).—A physico-mathematical paper in which formulæ for the conductivities of solutions of electrolytes containing non-conducting spheres are derived. In cases where the spheres are all in perfect contact, the expression is $k=1-w/(1+0{\cdot}3219w)^2$, where k is the ratio of the conductivity of the system to the conductivity when the electrolyte solution alone occupies the same volume and w is the ratio of the total volume of the spheres to that of the whole system. This formula has been verified experimentally. In cases where the spheres are uniformly dispersed throughout the system, the formula becomes $k=1/[1+w/p\times\{(1+0{\cdot}3219p)^2/(1-p)-1\}]$, where $p=xw^{2/3}$. For $w<0{\cdot}15$, $0{\cdot}15<w<0{\cdot}60$, and $w>0{\cdot}60$, the values of x are 0·806, $0{\cdot}806+0{\cdot}1333w$, and 0·9047, respectively. The formula has been verified experimentally by measurements of the conductivities of emulsions of castor oil in solutions of gum arabic containing a little potassium chloride.

J. S. Carter.

Conductivities of some organic salts of beryllium. N. V. Sidgwick and N. B. Lewis (J.C.S., 1926, 2538—2541).—The molecular conductivity of beryllium acetate solutions is normal, falling continuously as the concentration increases, whilst that of beryllium malonate resembles that of the oxalate (cf. this vol., 787) in remaining constant over a large range. This constancy is explained by the assumption that a complex ion $[BeOx_2]''$ (Ox=C_2O_4 or

$CH_2{:}C_2O_4$) is formed, leading to the equation $2BeOx \rightleftharpoons Be^{\cdot\cdot} + [BeOx_2]''$. Since the number of molecules on each side is the same, the equilibrium (and hence the molecular conductivity) will be independent of dilution. The assumption receives support from measurements of van 't Hoff's factor *i*.

N. H. HARTSHORNE.

Electrochemistry of non-aqueous solutions. VII. Conductivity of dilute solutions of silver nitrate in twelve organic solvents and determination of the limiting value of the molecular conductivity. R. MULLER, F. GRIENGL, and J. MOLLANG (Monatsh., 1926, **47**, 83—108; cf. Walden and Ulich, A., 1925, ii, 209).—Measurements of the conductivity of dilute solutions of silver nitrate in methyl, ethyl, *iso*amyl, and allyl alcohols, acetone, epichlorohydrin, α-phenylethyl alcohol, aniline, *m*-cresol, benzonitrile, pyridine, and quinoline at 25° have been made, a modification of the method of Ulich (*ibid.*, 671) being employed. In all cases, at high dilutions, the square root law is obeyed, the results being in good agreement with Debye and Hückel's theory (A., 1923, ii, 724). On successive increase in the dilution, a region is ultimately reached in which the experimental values show rapidly increasing divergences from the linear relationship, and it is assumed that here the limit of accuracy of the measurements has been reached. The mean values of Λ_∞ obtained from the values of Λ_v in the region in which the square root law is valid are confirmed by graphical extrapolation of the Λ_v/v curve to the Λ_v axis ($c=0$). The following results were obtained, the figures given referring, respectively, to the dielectric capacity of the solvent (from recorded data), the range of the measurements, the lowest value of v at which the square root law is valid, and the value of Λ_∞: methyl alcohol, 32·5, 100—1400, 500, 107; ethyl alcohol, 22, 1000—60,000, 2000, 64; *iso*amyl alcohol, 5·4 or 15·9, 1500—16,000, 2500, 7·5; allyl alcohol, 20·6, 500—8000, 500—8000 (silver nitrate is too sparingly soluble in this solvent for measurements on a solution stronger than 0·002*N* to be made), 50·5; acetone, 20·7, 1000—80,000, 14,000, 317; epichlorohydrin, 22·6, 8000—50,000, 16,000, 18; α-phenylethyl alcohol, —, 2000—26,000, 2500, 0·95; aniline, 7·14 or 7·32, 2000—50,000, 2000, 5·3; *m*-cresol, 10·3, 3000—48,000, 8000, 5·3; benzonitrile, 26·0, 50—405,600, 800, 41; pyridine, 12·4, 80—24,000, 1800, 75·9 [a minimum value for Λ_v was found at about $v=20$ in agreement with Sachanov (Diss., Odessa, 1916), who found a minimum at $v=15{\cdot}7$]; quinoline, 89, 200—204,800, 3200, 12·2.

J. W. BAKER.

Electronic theory of the anodic behaviour of metals, in particular those showing passivity. III. Influence of anions. U. SBORGI (Gazzetta, 1926, **56**, 532—539; cf. A., 1925, ii, 550).

Absolute electrolytic solution tension. I. Determination by the scraping method. K. BENNEWITZ and J. SCHULZ (Z. physikal. Chem., 1926, **124**, 115—138).—A method of determining the absolute zero potential is described which depends on the scraping of a rotating silver electrode in solutions of various concentrations of silver nitrate. The immediate liquid film is thereby continuously removed, with a consequent disturbance of the double layer equilibrium, the liberated charges thus causing a deflexion of a galvanometer connecting the first with a second and stationary electrode in the same solution. The concentration of silver nitrate which conditions no deflexion of the galvanometer is noted and the potential of a silver electrode in such a solution is taken to be the absolute zero. This value is $\pm 0{\cdot}475 \pm 0{\cdot}005$ volt. No current is observed under any concentration conditions unless the rotating electrode is scraped. About the same value was obtained, although not with so great an accuracy, by a modification of the method in which silver was replaced by mercury. Gold and platinum are unsuitable for the determination on account of their tendency to form complexes. The more electronegative metals copper, lead, and zinc are also unsuitable on account of their very low normal potentials; quantitative data were obtained, however, for the charges of the double layers of these metals in contact with various concentrations of their salts. It is shown that both electrodes of the cell act as polarisation capacities during the scraping experiments. From a knowledge of the polarisation capacity and the charge of the double layer, the absolute zero potential can be calculated. The necessary measurements and calculations were made in the case of silver and of copper, the same value as the above being obtained with both metals. Other considerations also point to the correctness of this value.

L. F. GILBERT.

Electrochemistry of beryllium [and magnesium]. S. BODFORSS (Z. physikal. Chem., 1926, **124**, 66—82).—Determinations of the potentials of the cell elements $Be|0{\cdot}1N\text{-}Be(ClO_4)_2, BeSO_4$ or $HClO_4$ have been made. Difficulty was experienced in obtaining reproducible results. The changes of potential caused by adding alkali halides to these cells, by diluting the beryllium perchlorate cell, and by adding beryllium salts to chlorine-ion concentration cells are all in accordance with the reactions: $Be \rightleftharpoons Be^{\cdot}$; $Be^{\cdot} + H^{\cdot} \rightleftharpoons Be^{\cdot\cdot} + H$. Experiments on the polarisation of beryllium electrodes in solutions of beryllium salts give results which also can be explained by these reactions. A similar mechanism for the ionisation of magnesium is advanced and is supported by data obtained during the electrolysis, with magnesium electrodes, of magnesium sulphate in the presence of various concentrations of sulphuric acid. Beryllous halides are considered to be much more complex than the corresponding beryllic salts; the influence of various concentrations of potassium chloride on the potentials of the $Be|Be(ClO_4)_2$ cell elements is in agreement with this view. Experimental evidence, including the results of conductivity measurements in solutions of ammonium beryllium fluoride and beryllium fluoride, is adduced that beryllic fluoride is a complex substance. Beryllium does not amalgamate with mercury; it is rendered passive by concentrated sulphuric acid.

L. F. GILBERT.

Extent to which electrometric determination of the hydrogen-ion concentration of hydrogen carbonate solutions is interfered with by pro-

duction of formic acid at the electrode. C. J. MARTIN and E. H. LEPPER (Biochem. J., 1926, **20**, 1077—1081).—The production of an acid at the hydrogen electrode in hydrogen carbonate solutions can be demonstrated when the concentration of hydrogen carbonate is small by adding an indicator to the solution. An acid zone is seen immediately surrounding the electrode, enveloped by a wider alkaline zone due to adsorption of carbon dioxide by the platinum-black. This production of acid does not, however, appreciably affect the determination of the p_H of hydrogen carbonate solutions until the molecular concentration is less than $0{\cdot}005M$. S. S. ZILVA.

Method of measuring [instantaneous values of single potential and current] in alternating current electrolysis. A. FÜRTH (Z. Elektrochem., 1926, **32**, 467—470).—A device is described which, when attached to the armature shaft of an alternating current generator, permits the measurement of instantaneous values of the single potential of an electrode in an electrolytic cell through which current from the generator is passing. The potential is measured against a comparison electrode, using a Dolezalek electrometer. By a simple adjustment, such measurements can be made at any instant in the alternating current cycle and instantaneous values of the current passing can also be determined. Preliminary measurements have been made on the cell: $Ag|0{\cdot}1N\text{-}AgNO_3|Ag$, the variations of current and single potential during a complete cycle being recorded. The solution bridge between the working electrode and the reference electrode, which is a silver wire in the same solution, is of special construction to minimise errors due to the potential gradient in the solution. H. J. T. ELLINGHAM.

Significance of hydration and adsorption in the mechanism of the production of *E.M.F.* P. PFEIFFER (Z. Elektrochem., 1926, **32**, 512).—The author claims priority for certain aspects of Isgarischev's theory (this vol., 802).

H. J. T. ELLINGHAM.

Periodic phenomena at anodes of magnesium, zinc, cadmium, mercury, tin, and lead, and at an unattackable anode. E. S. HEDGES (J.C.S., 1926, 2580—2594).—The periodic changes in potential and current strength with anodes of copper and silver (this vol., 807) have been observed in the electrolysis of the following systems, a platinum cathode being used throughout: zinc anode with sodium hydroxide, sulphuric acid; amalgamated zinc anode with sulphuric acid; cadmium anode with sulphuric acid, potassium cyanide; mercury anode with potassium cyanide, sodium hydrosulphide, nitric acid; magnesium anode with sulphuric acid; tin anode with sulphuric acid, nitric acid; lead anode with sodium hydroxide; platinum anode with silver potassium cyanide, alkaline chromium sulphate, and with ammoniacal solutions of silver nitrate, cupric chloride, cupric sulphate, and cobalt sulphate. With each attackable anode the influence of concentration of the solution and current density was examined with reference to the nature of the periodicity. The conditions necessary to secure periodic effects are: (i) a film must form over the anode; (ii) this film must be soluble in the electrolyte when the current is broken; (iii) the current density must be such that the film has approximately equal chances of forming or dissolving. These conclusions are verified by the experiments with the platinum anode.

N. H. HARTSHORNE.

Apparatus for measuring the velocity of very rapid chemical reactions. II. H. HARTRIDGE and F. J. W. ROUGHTON (Proc. Camb. Phil. Soc., 1926, **23**, 450—460).—A continuation of previous work (A., 1925, ii, 47). With modified forms of apparatus, reaction velocities of reactions half completed in 1/2000 sec. and from 1 sec. to 3 min. can be measured, and an apparatus devised for use with very dilute solutions has been employed for observations on $M/6\times10^6$ hæmoglobin solutions. The measurement of reaction velocity with small quantities of fluid has been achieved by simultaneously photographing the position of the absorption bands at several points along the observation tube. Methods have also been devised for studying reactions following one another in rapid succession, for the detection of short-lived transient compounds, and for the detection of concentration gradients in heterogeneous reactions. A. S. CORBET.

Velocity of gas-reactions. J. A. CHRISTIANSEN (Proc. Camb. Phil. Soc., 1926, **23**, 438—449).—Theoretical and mathematical. In their discussion on the theory of reaction rate, Lewis and Smith (A., 1925, ii, 799) have overlooked some important points. It is shown that the heat of activation is the heat required to bring an average molecule to the average "state of activation," and not that required to raise a molecule from zero internal energy to the condition of activation, as stated by Lewis and Smith. The equation deduced by the latter authors connecting the number of encounters between molecules and the quanta of light necessary for activation is criticised, and it is shown that the radiation theory cannot be upheld without additional assumptions to remove certain difficulties. A. S. CORBET.

Active nitrogen. E. J. B. WILLEY (Nature, 1926, **118**, 735).—Admission of various gases to the afterglow results in the formation of definite compounds only when the critical increment of the gas introduced does not exceed 45,000—50,000 g.-cal./g.-mol. Catalytic decay of active nitrogen takes place at fine metallic filaments, the efficiencies of the metals depending on the stability of their nitrides. Again, the energy of active nitrogen is computed at about 45,000 g.-cal./g.-mol. The decay of the afterglow is probably termolecular, but bimolecular with respect to the active nitrogen. The origin of the line 2154 Å. is discussed. A. A. ELDRIDGE.

Explosion-wave in cyanogen mixtures, and specific heats of nitrogen. C. CAMPBELL and H. B. DIXON (Trans. Faraday Soc., 1926, **22**, 307—313),—The rates of propagation of the explosion wave in mixtures containing equal volumes of cyanogen and oxygen and varying amounts of nitrogen or argon have been determined. The gas was contained in a long tube of 19 mm. internal diameter, and the time of passage of the wave automatically recorded. The rate in the undiluted mix-

ture was 2700 metres per sec.; addition of nitrogen in the proportion 1·5 : 1 reduced the rate to 2405 metres per sec., addition of argon (0·5 : 1) to 2502 metres per sec. Further dilution with either gas gave somewhat discordant results. The formulæ of Jouguet and of Crussard have been used to calculate the mean mol. specific heats of the products of the explosion. Combination of these with the values obtained from the velocity of sound in nitrogen between 0° and 1000° gave the following formula for the mol. specific heat of nitrogen over the temperature range 0—6000° : $C_t=4{\cdot}89+0{\cdot}083\times10^{-3}t+0{\cdot}073\times10^{-6}t^2$. A. B. MANNING.

Mechanism of the substitution reaction of *trans*-dichlorodiethylenediaminecobaltic chloride in aqueous solution. K. MATSUNO (Bull. Chem. Soc. Japan, 1926, **1**, 133—139).—Since the reactions $[CoCl(1)Cl(6)en_2]Cl \longrightarrow [CoCl(1)H_2O(6)en_2]Cl_2 \longrightarrow [CoH_2O(1)H_2O(2)en_2]Cl_3$ (cf. A., 1921, ii, 644) involve a change in the valency of the complex cation, their course may be followed by the increase in the power of the solution to coagulate an arsenious sulphide sol. Using the equation previously deduced (*ibid.*, 637), the change is shown to consist of two successive unimolecular reactions with velocity coefficients at 25° of 0·011 and 0·0031, respectively. H. E. F. NOTTON.

Stability of benzenediazonium chloride solutions. I. Reaction of benzenediazonium chloride with water. H. A. H. PRAY (J. Physical Chem., 1926, **30**, 1417—1426).—The velocity of decomposition of benzenediazonium chloride by water in the presence of many substances, chiefly inorganic chlorides, has been studied by measuring the volume of nitrogen evolved. At 40°, with water only, the reaction appears to be unimolecular and the value obtained for the temperature coefficient agrees well with that found by Lamplough (A., 1909, ii, 30). Of the substances examined, few have any effect on the value of k, but sodium phosphate, succinate, and citrate give increased values of k by causing "coupling reactions" to take place. Ammonium molybdate greatly retards the velocity of decomposition, presumably by the formation of a benzenediazonium molybdate which is more stable than the chloride. Concentrated solutions of calcium and magnesium chlorides, used to increase the viscosity of the reaction medium, reduced the values of k, but viscosity is not the only factor involved, and there is, apparently, no quantitative relationship between viscosity and velocity of decomposition. Gelatin, dextrin, starch, agar, and egg-albumin affect neither the velocity of the reaction nor the rate at which nitrogen is evolved (cf. Findlay and Thomas, A., 1924, ii, 539). L. S. THEOBALD.

Combination of nitrogen with lithium and the mechanism of this reaction. W. FRANKENBURGER (Z. Elektrochem., 1926, **32**, 481—491).—The rate of formation of lithium nitride from lithium, purified by sublimation in a vacuum, and nitrogen has been measured by observing the variation of nitrogen pressure in the reaction vessel. This pressure is kept within a certain range by adding nitrogen to the vessel at frequent intervals. At a constant temperature within the range 0—50°, the rate of formation has an extremely small initial value, but increases with time to a maximum value, from which it falls off only very slowly. From the form of the rate of formation–time curve and from microscopical observations, it is concluded that, in the protective film of lithium nitride which is first formed, crystalline aggregates of this substance develop from a few centres, and, as the conversion of lithium into the nitride involves a notable contraction, these aggregates are porous and permit access of nitrogen to the underlying metal. At these temperatures, diffusion of nitrogen through the pores of the lithium nitride is slower than the chemical reaction between lithium and nitrogen, so that the observed rate of formation is determined by this rate of diffusion, and reaches a maximum when the metal surface is completely covered by a porous crust of the crystalline nitride. A calculation based on this view gives a value for the rate of formation under specified conditions which is comparable with the observed value.

At low temperatures, however, the chemical reaction becomes slower than the diffusion process, and hence controls the rate of formation of the nitride, the temperature coefficient of which thus becomes relatively large. At temperatures between −55° and −30°, the velocity coefficient, k, is given by $k=CT^{\frac{1}{2}}e^{-Q/RT}$, where the mean value of Q, the heat of activation, is 16·4 g.-cal. and $e^{-Q/RT}$ should represent the fraction of the total number of impacts per sec., $CT^{\frac{1}{2}}$, of nitrogen molecules on the lithium surface which are effective in causing combination. Since the value of the constant, C, obtained from the observed values of k is about 2×10^7 times the value calculated from the kinetic theory, it is concluded that each effective impact initiates a "reaction chain," the energy corresponding with the heat of reaction ($6Li+N_2=2Li_3N+74{\cdot}6$ g.-cal.) serving to increase the vibrational energy of neighbouring lithium atoms, and thus rendering effective a much larger proportion of the impacts between them and nitrogen molecules. If chemical combination between a nitrogen molecule and six lithium atoms occurred when each of these particles possessed one quantum of vibrational energy, the heat of activation would be 16·2 g.-cal. (observed, 16·4 g.-cal.). The breaking of the reaction chain after about 2×10^7 mols. of nitride have been formed is due to the contraction of the lithium lattice when nitrogen is introduced, causing crystals of about this size to separate from the underlying metal. *X*-Ray examination of the nitride crust confirms this view.

The above conclusions are discussed with reference to the mechanism of the reaction between lithium and oxygen and to that of the catalytic formation of ammonia. H. J. T. ELLINGHAM.

Corrosion and rusting of steel and iron. R. GIRARD.—See B., 1926, 881.

Rate of carbon elimination in the Martin [open-hearth steel] furnace. E. DE LOISY.—See B., 1926, 880.

Reaction mechanism of the catalytic oxidation of ammonia. S. UCHIDA (J. Physical Chem., 1926, **30**, 1297—1305).—The yield of nitric oxide given by varying times of contact of reaction mixture

with platinum gauze and the mixed oxides of bismuth and iron as separate catalysts has been found. With these catalysts the whole reaction is considered to be the result of the following consecutive reactions: (1) $4NH_3+5O_2=4NO+6H_2O$ and (2) $2NO=O_2+N_2$, which mechanism explains the maximum which occurs in the curve, yield of nitric oxide/time of contact. The maximum yield of nitric oxide is dependent on the ratio of the velocity coefficients k_1 and k_2 of the above reactions, which are assumed to be unimolecular. Reaction (1) is very rapid and k_1 is 180 times as large as k_2. The platinum of the catalyst evaporates slowly even at 580° (cf. Landis, Trans. Amer. Electrochem. Soc., 1919, **35**, 483), and the loss is not due to scaling of the activated surface.

L. S. THEOBALD.

Oxidising action of iodic acid and its restriction. F. G. FISCHER and C. WAGNER (Ber., 1926, 59, [*B*], 2384—2388; cf. Toda, this vol., 806; Wieland and Fischer, *ibid.*, 806).—The initial velocity of reaction of iodic and oxalic acids is little reproducible, since the change depends on the presence of iodine (cf. Lemoine, A., 1921, ii, 100, 500, 540); addition of iodine increases the initial velocity. Ferric salts do not exert a restrictive action, whereas ferrous salts exert this effect to an extent corresponding with the liberated iodine. Hydrocyanic acid in 0·001*M*-solution is almost completely inhibitive, and this effect is not counteracted by ferric salts. If, however, the hydrocyanic acid is treated with an equivalent quantity of iodine, reaction again proceeds normally. The inhibitive effect of hydrocyanic acid is therefore attributable to the conversion of iodine into cyanogen iodide. The same result follows the addition of molecular silver or silver nitrate. The uncatalysed reaction depends on the hydrolysis of iodine to hypoiodous acid (which oxidises the oxalic acid) and hydriodic acid (which reduces the iodic acid). Iron plays no part in the change.

H. WREN.

Autoxidation and antioxygenic action. Catalytic action of hydrocyanic acid and various cyanogen compounds. C. MOUREU, C. DUFRAISSE, and M. BADOCHE (Compt. rend., 1926, **183**, 685—689; cf. this vol., 1031).—Hydrocyanic acid has definite antioxygenic action towards substances from which all traces of iron have been carefully excluded. Its anticatalytic action cannot therefore be due to its action in removing the positive catalytic effects of iron. The complex cyanides such as the ferrocyanides and Prussian-blue have, moreover, their own catalytic effects, which may be either anti- or pro-oxygenic. Free hydrocyanic acid has a definite pro-oxygenic action in some cases. With styrene in particular, after a short period of inactivity the positive catalysis is very pronounced.

G. M. BENNETT.

Relationship of the catalytic and peroxydatic action of iron to its mode of combination. R. KUHN and L. BRAUN (Ber., 1926, 59, [*B*], 2370—2384).—Oxydase action with hydriodic acid as acceptor could not be observed with oxyhæmoglobin and a series of well-defined transformation and degradation products of blood pigment. Maximum acceleration of the separation of iodine from hydrogen peroxide and potassium iodide by oxyhæmoglobin from horse blood is observed at p_H 5·0—5·5; at the isoelectric point, p_H 6·8, only 50% of the maximal action is unfolded. The action of oxyhæmoglobin is peroxydatic, but not catalytic towards hydrogen peroxide. With hæmin, the peroxydatic action, with respect to the same amount of iron, is reduced without considerable displacement of the p_H curve. In this compound, however, the catalytic activity of iron is evident, and is characterised by slight dependence on hydrogen-ion concentration and very small temperature coefficient even in comparison with the true catalases. It is little influenced by hydrocyanic acid unless present in very great excess. The action of hæmin towards hydrogen peroxide is the result of catalase activity, catalytic decomposition of hydrogen peroxide by the iodine ion, non-catalytic separation of iodine from hydrogen peroxide and iodide, and the peroxydase action. In contrast to the first action, the second change is remarkably dependent on the hydrogen-ion concentration. Similarly, the third action is strongly influenced by the acidity of the solution, whereas the fourth change is independent of this factor within wide limits. Mesohæmin does not accelerate the action of hydrogen peroxide on hydriodic acid, but the peroxydatic action in comparison with that of hæmin is merely markedly displaced with respect to the hydrogen-ion concentration. Esterification of the carboxy-groups of hæmin has more effect than the saturation of the double linking. In monomethylchlorohæmin, the catalytic and peroxydatic properties are almost extinguished, as also in hæmato- and meso-porphyrin. The presence of iron appears a necessary although not completely sufficient condition of peroxydatic and catalytic activity. The iron must, however, be in complex union, since mixtures of the porphyrins with ferrous and ferric salts are completely inactive. The iron in tri-2 : 2′-dipyridylferrous bromide is inactive towards hæmin within the limits investigated. Sodium ferropentacyanide has no catalytic activity; peroxydatic properties are observed with benzidine or *p*-phenylenediamine as acceptor, but the acceleration of the action between hydrogen peroxide and hydriodic acid at 0° and p_H 6·8 is immeasurably small, as is also the case with sodium nitroprusside. The complex compound from ferrous salts and barbituric acid or *iso*nitrosodimethyldihydroresorcinol (cf. Haas, J.C.S., 1907, **91**, 1433) does not decompose hydrogen peroxide catalytically, and appears to be inactive with hydriodic acid as acceptor. Iron, as ferrous salt, does not appreciably accelerate the reaction between hydrogen peroxide and hydriodic acid even when present in relatively great concentration. In the first moments of the change, a definite amount of the halogen is liberated, but the difference between this amount and that of a blank experiment does not thereafter increase. Iron behaves as a stoicheiometric partner in the change, not as catalyst. If hydriodic acid is replaced by other oxygen acceptors such as benzidine or *p*-phenylenediamine, great acceleration of the formation of dye is observed. Ferrous and ferric salts catalytically decompose hydrogen peroxide, but to an extent less than that of

an equal amount of iron in hæmin. The catalytic oxidation of hydriodic acid in the presence of hæmin or, more particularly, of the true peroxydases does not appear explicable by the dehydrogenation theory. H. WREN.

Structure of catalytically active copper. F. H. CONSTABLE.—See this vol., 1195.

Stability of copper catalysts produced by thermal decomposition. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1926, **23**, 432—437).—The view that catalytic activity is due to frozen groups of atoms with strong specific external fields (this vol., 250) is further tested. Copper salts of monobasic fatty acids were heated in a current of alcohol vapour, and the birth and magnitude of the activity of the copper surface produced were measured by the rate of evolution of hydrogen. Catalysis commenced when metallic copper became visible and the activity attained persisted for hours. Heating and cooling measurements confirmed this stability. Subsequent oxidation and reduction produced only a slight increase in the activity of the copper.

Below 280°, the behaviour of the catalysts was very similar, and it is suggested that the active structure is formed by the sudden liberation of copper atoms and that the mixed crystallisation and freezing in the amorphous state of such atoms is the factor deciding the nature of the final surface, the original spacing of the copper atoms in the compound having only a secondary influence. A. S. CORBET.

Catalytic action of Japanese acid earth. III. Action on primary aliphatic alcohols. H. INOUE (Bull. Chem. Soc. Japan, 1926, **1**, 197—202).—Japanese acid earth at 150—500° acts like alumina as a dehydrating catalyst, dibutyl ether and di*iso*butylene being formed from *iso*butyl alcohol, and amylenes, diamylenes, and diamyl ethers from *iso*amyl alcohol. In addition, some oxidation to aldehyde occurs with methyl and ethyl alcohols, the latter also yielding ethyl acetate. B. W. ANDERSON.

Catalysts from plasmophile materials. H. HAEHN (Z. angew. Chem., 1926, **39**, 1148—1151).—A discussion of the recent results of the author and others on the hydrolysis of soluble starch by the system neutral salts–amino-acids–peptone, and of the reproduction of the Schardinger reaction with the system glycine–primary and secondary potassium phosphates (cf. A., 1925, i, 858). S. I. LEVY.

Preparation of sulphuryl chloride. T. H. DURRANS.—See B., 1926, 914.

Protection of aluminium and its alloys against corrosion by anodic oxidation. G. D. BENGOUGH and H. SUTTON.—See B., 1926, 882.

Results of modern photochemical research. B. K. MUKERJI and N. R. DHAR (Z. Elektrochem., 1926, **32**, 501—511).—A review of some recent work.

Dissociation of heteropolar molecules by absorption of light. V. KONDRATJEV (Z. Physik, 1926, **39**, 191—194).—Terenin's work (this vol., 776) is confirmed and extended. The vapour of sodium iodide, even at very low pressure, gives the *D*-line when illuminated with light of wave-length shorter than 2500 Å., but this excitation is not due to collisions, as supposed by Terenin. If this were so, the excited light should increase as the square of the pressure (both the light absorbed and also the number of collisions would increase with increasing pressure); the experiment proved that the increase was proportional to the pressure and not to its second power, hence the effect is not due to collisions, but is the primary result of the absorption of light, producing an excited sodium atom and an iodine atom. For cæsium iodide, a similar result was obtained, but the first member of the principal series lies in the infra-red and the second member 4555 was observed. The dissociation of cæsium iodide requires energy represented by 3·82 volts; the energy required to excite the above line is 2·71 volts; the sum 6·53 is less than that of the aluminium lines 1854 and 1862 Å., which produced the effect, but greater than that of the nickel lines about 2300 Å., which were ineffective. The energy relations thus support the explanation given. E. B. LUDLAM.

[Cupric-ammine compounds.] W. LANGE (Ber., 1926, **59**, [*B*], 2432; cf. this vol., 1112).—A correction. H. WREN.

Displacement of metals [from solutions of their salts]. J. BARLOT (Ann. Chim., 1926, [x], **6**, 87—181).—The above process has been examined by placing a sheet of filter-paper moistened with the solution under investigation on the upper surface of a glass plate, and a fragment of a suitable metal on the paper. Under these conditions, a metallic deposit is normally formed between the glass and the paper. It is suggested that the occurrence of such reactions depends on a difference in the affinities of the metals concerned for their electrons rather than on a difference in solution tensions. Thus the tendency of the electrons of zinc to escape is greater than that of the electrons of copper, so that when zinc is brought into contact with a solution of a copper salt it forms ions by loss of electrons, and the latter neutralise the charges on the ions of the copper, which is therefore deposited. Experimental evidence in favour of this hypothesis is adduced, and its application to rhythmic reactions discussed, these being considered to depend on differences in the rate of diffusion of the ions involved. It appears that the crystalline form of tin displaced from solution by zinc is influenced by the experimental conditions, two modifications being possible. R. CUTHILL.

Action of mixtures of oxygen and nitrogen on a few elements. C. MONTEMARTINI and L. LOSANA (Notiz. chim.-ind., 1926, **1**, 237—240).—Elements were heated in mixtures of oxygen and nitrogen, dry, or saturated with water vapour at 26°. At 800°, the percentage of magnesium oxide present in the oxide–nitride mixture increases with the increase in the percentage of oxygen, and tends also to increase with the velocity of the current of gas. With a mixture containing more than 75—80% of oxygen, no nitride is formed. In the gas containing water vapour the proportion of oxide formed was greater, owing to decomposition of the nitride, which, however, like calcium and aluminium nitrides, is stable at 800° in dry nitrogen. No nitride was formed

when the mixture contained more than 70% of oxygen. With dry and wet gas, respectively, containing 5% of oxygen, 15·12% or 12·20% of aluminium forms nitride at 800°; none is formed if the nitrogen concentration is below 50%. Below 45% of nitrogen, calcium at 800° forms only oxide; in 99% dry nitrogen, 51·5% of the calcium forms nitride, compared with 45·6% in wet nitrogen. At 1050°, titanium (94·86% pure) formed no nitride in dry mixtures containing less than 70% of nitrogen, but 98·2% of the titanium formed the nitride Ti_2N_2 in a dry mixture containing 99·4% of nitrogen. At 1050°, boron (96·75% pure) formed no nitride in dry mixtures containing less than 70% of nitrogen, but 95·2% of it so reacted in a dry mixture containing 99·4% of nitrogen. CHEMICAL ABSTRACTS.

Calcium sulphate. I. Action of water. L. CHASSEVENT (Ann. Chim., 1926, [x], **6**, 244—294).—The concentration of the solution obtained by shaking calcium sulphate completely dehydrated at 140—150° with water at, say, 30° has been shown by conductivity measurements to rise rapidly at first to a maximum, at which it remains for some time, then crystallisation sets in, and the concentration slowly falls to a value corresponding with the solubility of gypsum. Using the hemihydrate prepared at 145° instead of the anhydrous sulphate, very nearly the same maximum is reached, but the concentration begins to fall again immediately. These facts are considered to indicate that in contact with water anhydrous calcium sulphate is transformed into the hemihydrate, which then dissolves to saturation, the resulting solution being capable of existence for a short time before gypsum commences to crystallise out. The hemihydrate as normally prepared apparently contains nuclei of the dihydrate already, so that crystallisation commences before the solution becomes saturated with respect to the hemihydrate. This view is supported by measurements of the heat effects during the process. It has thus been possible to determine the solubility of the hemihydrate between 0° and 97°. When calcium sulphate is dehydrated below 300° it behaves in the same way as that prepared at 150°. At 300—313°, however, some change appears to occur in calcium sulphate, the rate of formation of the solid hemihydrate from the anhydrous salt prepared at higher temperatures being very slow, and becoming still slower as the temperature of dehydration is further increased. In all cases, crystallisation now commences before a saturated solution of the hemihydrate can be formed. Nevertheless, so long as solutions supersaturated with respect to gypsum are formed, the mass should set sooner or later, provided that the water is kept in contact with the solid. If, however, the temperature of dehydration is above about 600°, the rate of crystallisation, which depends on the rate of formation of solid hemihydrate, is so slow that the water has, under ordinary conditions, either evaporated or settled out before the mass has set completely. With sulphate prepared by dehydration of gypsum above about 300°, the rate of rehydration is influenced to some extent by the physical state of the gypsum used (cf. Farnsworth, B., 1925, 804). R. CUTHILL.

Dehydration of gypsum. D. BALAREV (Z. anorg. Chem., 1926, **156**, 258—260; cf. A., 1924, ii, 758).—The experiments of Linck and Jung on the process of dehydration of gypsum are discussed and compared with those of the author, who concludes that Linck and Jung's results do not confirm the zeolitic nature of the hemihydrate. The author's experiments show that the hemihydrate passes suddenly, not in a zeolitic manner, into soluble anhydrite when heated, the change taking place at 97±2° with a water vapour pressure of 23 mm.

M. CARLTON.

Boron hydrides. VIII. B_2H_6 and B_5H_{11}. B_2H_5I. IX. $B_3N_3H_6$. X. B_2H_5I. Synthesis of B_4H_{10}. A. STOCK and E. POHLAND (Ber., 1926, **59**, [*B*], 2210—2215, 2215—2223, 2223—2226; cf. A., 1924, ii, 405).—VIII. Diborane, after repeated fractionation to remove monosilane, has d^{-112} 0·447 (liquid), d^{-183} 0·577 (solid). Diborane is very slowly decomposed when exposed to light at the atmospheric temperature, yielding the pentaboron hydride, B_5H_{11}, b. p. 0°/57 mm., m. p. −129·1° to −128·3° for different fractions. The latter substance is converted by an excess of gaseous ammonia at the atmospheric temperature into hydrogen and a compound, $B_5H_9(NH_3)_4$, closely resembling the ammine obtained directly from the hydride B_5H_9 and, like it, converted by hydrogen chloride into hydrogen and the compound $B_5H_5Cl_4(NH_3)_4$. When heated, the ammine affords the compound $B_3N_3H_6$. In addition to the hydrides B_5H_{11} and $B_{10}H_{14}$, the compound B_4H_{10} is also formed when diborane is preserved. In contrast with the higher hydrides, diborane is not affected by air or oxygen at the atmospheric temperature. Excess of water causes hydrolysis to boric acid and hydrogen; partly oxidised hydrides are not obtained when water in deficiency is employed. Alkali metals react only superficially with diborane, whereas the liquid amalgams give compounds analogous to those described by Krause (A., 1924, i, 436; this vol., 628). Diborane and ammonia give the additive compound, $B_2H_6(NH_3)_2$, which in alkaline solution behaves like an alkaline solution of diborane, thus showing that the hydride has not suffered pronounced change; when heated in a sealed tube, the ammine gives the compound $B_3N_3H_6$. The main reaction between the diammine and hydrogen chloride follows the course: $B_2H_6(NH_3)_2+2HCl=B_2H_4Cl_2(NH_3)_2+2H_2$.

IX. The action of ammonia on diborane at about 200° leads to the replacement of the hydrogen atoms by amino- or imino-groups, so that when excess of ammonia is used, the ultimate product is boroimide, $B_2(NH)_3$. If the ammine, $B_2H_6(NH_3)_2$, is similarly heated, an analogous action occurs, but the amount of ammonia available is insufficient for complete replacement of the hydrogen atoms, and the main and only volatile product is the *compound* $B_3N_3H_6$ mixed with non-volatile condensed substances of composition between $(BNH_2)_x$ and $(BNH)_x$. The compound $B_3N_3H_6$ has b. p. 0°/84·8 mm., m. p. −58·0°, d^{-65} 1·00 (solid), d^{-57} −0·898 (liquid), d^{0} 0·824 (liquid). It is also prepared from the ammines derived from the hydride B_5H_{11}. The compound $B_3N_3H_6$ is distinguished by unusual stability. At a

high temperature, it decomposes into the compound $(BNH)_x$ and hydrogen. It is indifferent to oxygen. In cold water, it dissolves to an initially neutral solution, which gradually becomes alkaline; warm water causes quantitative hydrolysis to boric acid, ammonia, and hydrogen. Ice-cold water yields the *hydrate* $B_3N_3H_6(H_2O)_3$, converted by anhydrous hydrogen chloride into the *compound* $B_3N_3H_3Cl_3(H_2O)_3$ and hydrogen. The substance $B_3N_3H_6$ and hydrogen chloride slowly yield the non-volatile *compound* $B_3N_3H_6(HCl)_3$. Ammonia is absorbed by the compound $B_3N_3H_6$, but the reaction appears complex. The behaviour of the compound is best expressed by the constitution $BH<^{NH\cdot BH}_{NH\cdot BH}>NH$.

X. The action of iodine on diborane affords mainly boron tri-iodide and oily products. Diborane is readily converted by hydrogen iodide in the absence of a catalyst at 50° into the unstable *iodo*-derivative, B_2H_5I, m. p. −110°, b. p. 0°/78 mm., d^{-112} 2·0 (solid), d^{-108} 1·8 (liquid). Even at low temperatures, it decomposes moderately rapidly into diborane and boron tri-iodide. It is rapidly and quantitatively hydrolysed by water to boric acid, hydrogen iodide, and hydrogen. It is converted by sodium amalgam at −35° into the hydride B_4H_{10}, for which the constitution $BH_3\cdot BH_2\cdot BH_2\cdot BH_3$ is rendered probable if the "ethane" structure for diborane be accepted.

Boron tri-iodide has m. p. 48·1°. H. WREN.

Boron hydrides. XI. Constitutional formulæ of boron hydrides. A. STOCK (Ber., 1926, 59, [*B*], 2226—2229).—*X*-Ray analysis (Mark and Pohland, this vol., 227) and observation of the ultra-red absorption spectrum (Laski, unpublished work) show that diborane is more closely related than disilane to ethane. There is therefore no reason to doubt the constitution $BH_3\cdot BH_3$ for the simplest boron hydride. The structure $BH_3\cdot BH_2\cdot BH_2\cdot BH_3$ follows for C_4H_{10}. The boron atom is not invariably quadrivalent, and the following constitutions are suggested on the basis of its ter- and quadrivalency: $B_5H_9=BH_3\cdot[BH]_3\cdot BH_3$; $B_5H_{11}=BH_3\cdot BH_2\cdot BH\cdot BH_2\cdot BH_3$; $B_6H_{10}=BH_3\cdot[BH]_4\cdot BH_3$; $B_{10}H_{14}=BH_3\cdot[BH]_8\cdot BH_3$.

A modified nomenclature for the boron hydrides is suggested (cf. A., 1916, ii, 319), according to which the term borane is restricted to the "limit hydrides" containing tervalent boron, *e.g.*, B_2H_4=diborane, B_3H_5=triborane, $B_{10}H_{12}$=decaborane. The hydrides richer in hydrogen (the only hydrides already isolated) are termed "hydroboranes," thus B_2H_6, dihydrodiborane; B_5H_9, dihydropentaborane; B_5H_{11}, tetrahydropentaborane. H. WREN.

Combination of light metals and their carbides with nitrogen and sulphur in molten potassium thiocyanate. E. BIESALSKI and H. VAN ECK (Z. anorg. Chem., 1926, **156**, 226—236).—When aluminium is heated with potassium thiocyanate, the nitride and sulphide are formed. The maximum proportion of nitride, 63·6%, is obtained when equal molecular amounts are heated at 600°; with an excess of potassium thiocyanate or at a higher temperature, more sulphide is obtained. With calcium, the maximum of 25% of nitride is obtained by heating equal molecular amounts at 450—500°; no formation of calcium cyanamide was observed. Only 3% of magnesium nitride and 97% of sulphide were obtained. The reaction with aluminium may be represented $4Al+5KCNS=2AlN+Al_2S_3+2K_2S+KCN+4C+N_2$. When the light metal carbides are heated with potassium thiocyanate, complete reaction is not obtained. With magnesium and calcium carbides, comparatively little nitride is formed. With aluminium carbide, the removal of sulphur from the thiocyanate and the formation of sulphide is probably the first action, even when large amounts of nitride are obtained. A. GEAKE.

Compounds of gadolinium. P. B. SARKAR (Bull. Soc. chim., 1926, [iv], **39**, 1390—1396).—The following salts of gadolinium have been prepared: *formate*, $Gd(CO_2H)_3$; *tartrates*, $GdH(C_4H_4O_6)_2,2H_2O$ and $Gd_2(C_4H_4O_6)_3,5H_2O$; *citrates*, $Gd(C_6H_5O_7)$,4 and $5H_2O$; *acetylacetonate*, $Gd(C_5H_7O_2)_3,3H_2O$, m. p. 143·5—145°; *basic nitrate*, $3Gd_2O_3,4N_2O_5,20H_2O$; *bromate*, $Gd(BrO_3)_3,9H_2O$, m. p. 80°; *thiocyanate*, $Gd(SCN)_3,7H_2O$; *phosphate*, $GdPO_4,5{\cdot}5H_2O$; *iodate*, $Gd(IO_3)_3,5{\cdot}5H_2O$; *perchlorate*, $Gd(ClO_4)_3,8H_2O$; *periodate*, $GdIO_5,4H_2O$; *ferrocyanide*, $KGdFe(CN)_6,5H_2O$; *ferricyanide*, $GdFe(CN)_6,4{\cdot}5H_2O$; *sulphites*, $Gd_2(SO_3)_3,11$ and $12H_2O$; and the *double salts*, $Gd(SCN)_3,3Hg(CN)_2,12H_2O$; $KGd(C_2O_4)_2,4H_2O$; $K_2CO_3,Gd_2(CO_3)_3,12H_2O$; $Na_2CO_3,Gd_2(CO_3)_3,13H_2O$; $(NH_4)_2CO_3,Gd_2(CO_3)_3,4H_2O$; $K_2CrO_4,Gd_2(CrO_4)_3,7H_2O$; and $5K_2CrO_4,2Gd_2(CrO_4)_3,10H_2O$. The nitrates, $Gd(NO_3)_3,5$ and $6H_2O$ have m. p. 92° and 91°, respectively. A *dithionate* and *thiosulphate* were too unstable to permit of analysis. A. S. CORBET.

Constitution of the so-called pervanadic acid. J. MEYER and A. PAWLETTA (Z. angew. Chem., 1926, **39**, 1284—1286).—Examination of the colour changes obtained on addition of varying proportions of hydrogen peroxide to solutions containing vanadium pentoxide and varying concentrations of sulphuric acid indicates that an equilibrium $[VO_2]_2(SO_4)_3$ (reddish-brown) $+6H_2O \underset{H_2SO_4}{\overset{H_2O_2}{\rightleftharpoons}} 2VO_2(OH)_3$ (bright yellow) $+3H_2SO_4$ is attained. In agreement with this interpretation, it is found that the vanadium radical travels to the cathode on electrolysis. S. I. LEVY.

Pyrosulphuryl chloride. II. V. GRIGNARD and P. MURET (Compt. rend., 1926, **183**, 713—716; cf. this vol., 1113).—Sulphuryl chloride is hydrolysed quickly by the action of a large excess of water, and conductivity measurements indicate the equation $S_2O_5Cl_2+3H_2O=2H_2SO_4+2HCl$. The action is slow at first until the chloride has dissolved, but is increased by the presence of impurities produced during the preparation. With less water, two reactions occur, $S_2O_5Cl_2+H_2O=2HClO+2SO_2$, and $SO_2+2HClO=H_2SO_4+Cl_2$. In the presence of 1—3 mols. of water per mol. of chloride, the solution has oxidising properties. Measurements of the diamagnetism and molecular refraction of pyrosulphuryl chloride and of its related compounds have proved the existence of a sexavalent sulphur in sulphuric acid, and by a process of elimination the following formula is suggested: $S(:O)(OCl)\cdot O\cdot S(:O)(OCl)$. This accounts for the above chemical and physical properties. J. GRANT.

Thionyl bromide and Besson's supposed thionyl chlorobromide. H. A. MAYES and J. R. PARTINGTON (J.C.S., 1926, 2594—2605).—Thionyl bromide, best prepared by the prolonged action of hydrogen bromide on thionyl chloride, has b. p. 45°/22 mm. and 138°/773 mm. (decomp.), f. p. −52°, d_4^{15} 2·697. The mol. wt. (234—246), surface tension (43·71 dynes/cm. at 17°), and the Trouton coefficient (25·2) indicate association in the liquid. It decomposes slowly at the ordinary temperature, and rapidly at 100°: $4SOBr_2=2SO_2+S_2Br_2+3Br_2$. It is readily hydrolysed by water. With organic acids, it forms the acid bromides. No compound intermediate between thionyl chloride and thionyl bromide could be obtained from the product of bromination of the former (cf. Besson, A., 1896, ii, 358). The b. p., density, surface tension, and viscosity of the brominated product were the same as those of a mixture of the chloride and bromide. The b. p. of mixtures of the chloride and the bromide rose evenly from that of the former to that of the latter. The f.-p. curve of mixtures is a smooth mixed crystal curve, giving no indication of the existence of an intermediate compound. Thionyl chloride has f. p. −104·5°. W. THOMAS.

Reduction of chromium compounds by hydrogen at high temperatures and pressures. V. N. IPATIEV and B. A. MOUROMTSEV (Bull. Soc. chim., 1926, [iv], 39, 1384—1385).—See this vol., 1114.

Molybdic acid and molybdates. A. TRAVERS and MALAPRADE (Bull. Soc. chim., 1926, [iv], 39, 1408—1420).—See this vol., 925, 1114.

Deterioration of concentrated sodium hypochlorite solutions. R. L. WELLS.—See B., 1926, 874.

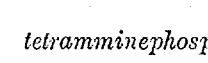
Metalammines and hydrazinates of the bivalent heavy metal chlorates and perchlorates as primary explosives. W. F. FRIEDERICH and P. VERVOORST.—See B., 1926, 933.

Nitroso-compounds of metals. Compound of manganese with nitric oxide. W. MANCHOT and H. SCHMID (Ber., 1926, 59, [*B*], 2360—2363).—The *salt*, $K_3Mn(CN)_5NO$, is prepared by treating an aqueous-alcoholic solution of manganous and potassium acetate with potassium cyanide in an atmosphere of nitric oxide. It is moderately stable when protected from light and gives a dark violet-red solution in water. It affords characteristic *precipitates* with manganous, zinc, ferric, ferrous, bismuth, and silver salts. H. WREN.

Action of steam and hydrogen on iron sulphide. F. FISCHER and H. TROPSCH.—See B., 1926, 874.

Influence of nitrogen on the solubility of ferrous materials in hydrochloric acid. H. H. GRAY.—See B., 1926, 919.

Phosphoric acid as bridge in complex cobalt compounds. R. KLEMENT (Z. anorg. Chem., 1926, 156, 237—244).—When dichlorodiaquodiamminecobaltic chloride or dichloroaquotriamminecobaltic chloride is warmed with aqueous disodium hydrogen phosphate, a green powder is obtained which consists of a mixture of cobaltous phosphate with a complex compound. The latter dissolves in ethylenediamine, forming *cis*-hydroxoaquodiethylenediamminecobaltic phosphate, $[(OH)(H_2O)Co\ en_2]HPO_4,3H_2O$. The molecular conductivity of the complex compound is $\mu=37$ at $v=1000$. It dissolves in concentrated hydrochloric acid, yielding *cis*- and a little *trans*-dichlorotetramminecobaltic chloride, and in oxalic acid to form *cis*-diaquotetramminecobaltic oxalate. It is concluded that the complex compound is



tetramminephosphato-cobalt, $[(NH_3)_4Co]\cdot O\cdot P{:}O,nH_2O$,

where $n=2$ and 3. The mother-liquor from its preparation yields *aquopentamminecobaltic phosphate*, $[(H_2O)(NH_3)_5Co]PO_4,2H_2O$. A. GEAKE.

Ruthenium. H. REMY (Z. angew. Chem., 1926, 39, 1061—1065).—For the detection of traces of ruthenium in a solution, sodium hydroxide is added to alkaline reaction, the solution is saturated with chlorine at 20° and then heated at 80° while a current of the same gas is bubbled through. The issuing gases are passed through an absorption flask containing 1 c.c. of a mixture of 1 part of hydrochloric acid, 1 part of alcohol, and 4 parts of water. A brown coloration in this solution indicates ruthenium, which may be further tested for by the thiocarbanilide method (Wöhler and Metz, A., 1924, ii, 874). By this procedure, 0·02 mg. of ruthenium may be detected in 200 c.c. of solution. Aqueous solutions of ruthenium tetroxide rapidly decompose on keeping unless a small quantity of free chlorine is present. The solubility of the tetroxide in water containing chlorine increases rapidly from 17·12 to 21·62 g. per litre with rise in temperature from 0° to 25°, falls to 20·81 g. at 34°, then slowly rises to 22·29 g. per litre at 75°. The saturated solution at 20° has d 1·0126. Ruthenium powder is much more rapidly converted into trichloride by heating in a mixture of carbon monoxide and chlorine than by heating in chlorine alone, probably owing to the intermediate formation of a carbonyl compound and to the more efficient removal of oxygen. A. R. POWELL.

Nitroso-compounds of metals. Compound of palladium with nitric oxide. W. MANCHOT and A. WALDMÜLLER (Ber., 1926, 59, [*B*], 2363—2366).—The *salt* $PdCl_2,2NO_2$ is obtained by passing nitric oxide saturated with the vapour of methyl alcohol at 50° over anhydrous palladous chloride. Palladous sulphate and dry nitric oxide yield the *salt* $PdSO_4,2NO$. Palladium nitrate readily adds nitric oxide, which is immediately oxidised by the nitrate radical, so that ultimately *palladium nitrite* appears to be produced. H. WREN.

Displacement of platinum by hydrogen at high pressures. V. IPATIEV and A. ANDREEVSKI (Bull. Soc. chim., 1926, [iv], 39, 1405—1408).—See this vol., 921.

Quinhydrone electrode. M. KÖHN (Z. angew. Chem., 1926, 39, 1073—1074).—The electrode consists of two parallel glass tubes passed through two holes in a rubber stopper. One tube is narrow and has thick walls carrying a platinum wire terminating at its lower end in a stout platinum plate. The other tube is 10 mm. in diameter and carries inside a somewhat similar electrode with a smaller platinum sheet

bent into a spiral; its lower end is closed with a glass cap, leaving a narrow annular gap between cap and tube to be filled with saturated potassium chloride solution. The tube itself is filled with the usual standard acetate solution containing quinhydrone. For use, the whole apparatus is immersed in the solution to be tested so that the top of the glass cap is just covered; it can be used continuously throughout the day without replacing the contents of the electrode with fresh solution. A. R. POWELL.

Buffer solutions with p_H value between 2·2 and 6·0. I. M. KOLTHOFF and J. J. VLEESCHHOUWER (Chem. Weekblad, 1926, **23**, 510).—Buffer mixtures prepared from primary potassium citrate with hydrochloric acid or sodium hydroxide have the advantage that the p_H value scarcely alters with change of temperature. For rapid preparation, citric acid and borax may be used in place of hydrochloric acid and sodium hydroxide, since then all the materials may be weighed. S. I. LEVY.

Potentiometric determination of hydrogen-ion concentration at higher temperatures. I. M. KOLTHOFF and F. TEKELENBURG (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 766—775).—The calomel electrode is unsuitable for measurements of p_H at varying temperatures owing to the time required to re-establish equilibrium. For such measurements, the quinhydrone electrode is to be preferred, although, if used for temperatures above 40°, frequent renewal of the solution is necessary. The temperature coefficients of the *N*-calomel electrode, the quinhydrone electrode in contact with a solution containing 0·01*N*-hydrochloric acid and 0·09*N*-potassium chloride (cf. Veibel, J.C.S., 1923, **123**, 2203), and the hydrogen electrode in contact with the same solution, have been determined over the range 0—60°, using the *N*-calomel or the quinhydrone electrode at 0° as a comparison electrode. The values were +0·00059, −0·00031, and +0·00046, respectively. An independent determination of the temperature coefficient of the combination quinhydrone electrode–hydrogen electrode gave the value −0·00076 (cf. Biilmann and Krarup, A., 1924, ii, 742). A. B. MANNING.

Reaction course of physiological buffer mixtures, examined by direct registration of the p_H changes. F. J. J. BUYTENDIJK and R. BRINKMAN (Proc. K. Akad. Wetensch. Amsterdam, 1926, **29**, 816—822).—The variation of the hydrogen-ion concentration in a solution of sodium hydrogen carbonate or sodium hydrogen phosphate during the period immediately following the addition of a small amount of dilute hydrochloric acid has been studied by using a modification of Goodc's electro-titration apparatus (A., 1922, ii, 307). A quinhydrone electrode was used in the buffer solution, which was stirred vigorously during the determination. The variation of the compensated plate current in the triode valve was recorded automatically by a string galvanometer, sensitive to changes of less than 0·02 in the p_H. With the phosphate solutions, the equilibrium p_H was reached immediately after addition of the acid. A lag of some tenths of a second, however, was observed with hydrogen carbonate solutions over the range of p_H 8·3—7·7; from p_H 7·7 to 7·5 the rise was more rapid, whilst from p_H 7·4 to 7·3 the increase in hydrogen-ion concentration passed through a sharp maximum, falling again and reaching the equilibrium value after 1—2 sec. This is attributed to the existence of carbonic acid during that period. The biological significance of the phenomenon is briefly discussed. A. B. MANNING.

Stability of constant b.-p. hydrochloric acid. J. A. SHAW (Ind. Eng. Chem., 1926, **18**, 1065—1066).—Constant-boiling hydrochloric acid remains unaltered in strength with respect to accuracy obtainable in ordinary volumetric work over a considerable period. D. G. HEWER.

Analysis of mixtures of compounds of bromine, oxygen, and hydrogen. F. POLLAK (Z. anorg. Chem., 1926, **156**, 179—198).—Hypobromite is determined by titration with arsenite. Bromide is determined by oxidising with bromic acid and titrating the excess of bromic acid with thiosulphate after removing the hypobromous acid with phenol or with a current of air. In a third portion of the solution, the total oxidising power is determined by adding it to potassium iodide solution acidified with a known amount of hydrochloric acid, and titrating with thiosulphate after 24 hrs. Excess of potassium iodate is then added, and by determining the additional iodine liberated the acid content of the solution may be calculated. The method of Pontius is not applicable to bromine compounds, neither can free bromine be removed with a current of air without loss of hypobromous acid. A. GEAKE.

Microscopical detection of bromides, hypobromites, and bromates by means of *m*-phenylenediamine. C. W. MASON and E. M. CHAMOT (Mikrochem., 1924, **4**, 145—148).—Bromine may readily be detected in concentrations as low as 0·5 μg. per c.c. by the characteristic crystalline precipitate it produces in a solution of *m*-phenylenediamine in 5% sulphuric acid. The test is carried out by liberating the bromine from the bromide, hypobromite, or bromate solution in any suitable manner and exposing a drop of the reagent on a watch-glass to the action of the vapours; chlorides and iodides do not interfere, so long as no large quantity of solid iodine is deposited on the test drop. To avoid this, the bromide solution containing iodide is heated with sulphuric acid and the oxidising agent added slowly so as to expel the iodine first, drop tests being made for bromine from time to time. Bromates are best reduced by hydrazine sulphate; for the liberation of bromine from hypobromites, acidification only is necessary. A. R. POWELL.

Determination of minute quantities of iodine. G. LUNDE (Mikrochem., 1926, **4**, 172—176).—A review of the latest methods of determination of very minute quantities of iodine such as occur in drinking water with especial reference to Fellenberg's method (Biochem. Z., 1923, **139**, 392; A., 1925, i, 329; cf. Steffens, B., 1926, 902). A. R. POWELL.

Volumetric determination of iodine. F. L. HAHN and H. WOLF (Chem.-Ztg., 1926, **50**, 674).—The iodide solution is acidified with sulphuric or

phosphoric acid, 3—5 c.c. of ethyl acetate are added, and the liquid is titrated with permanganate with vigorous shaking after each addition. The liberated iodine dissolves in the acetate layer and the usual pink permanganate end-point is therefore easily discerned in the aqueous layer. In the presence of chlorides or bromides, 3 c.c. of phosphoric acid (*d* 1·9) and 3—5 c.c. of saturated manganese sulphate solution are added to every 5 c.c. of iodide solution.

A. R. Powell.

Modification of Jellinek's method for determining sulphate. A. A. Briwul (Z. anorg. Chem., 1926, **156**, 210—212).—Sulphates may be determined by adding excess of barium chloride and titrating with standard potassium chromate until the solution becomes alkaline to methyl-red. A comparison solution is used which contains barium sulphate and chromate in suspension, and a correction which must be determined in a preliminary experiment is applied. A. Geake.

High values for potassium dichromate in determinations of thiosulphate. K. Böttger and W. Böttger (Z. anal. Chem., 1926, **69**, 145—165).—The high values obtained by others when titrating with thiosulphate solution the iodine set free by potassium dichromate in acid solution are confirmed. If the reaction solutions be previously boiled, and the liberation of iodine effected in an atmosphere of carbon dioxide, normal values are obtained. No loss of chlorine occurs on boiling the dichromate with hydrochloric acid if the amount of the latter does not exceed 9 c.c. (*d* 1·19) per 100 c.c. of solution. Exposure of a solution of potassium iodide and hydrochloric acid containing small quantities of chromic salts to air causes separation of iodine; in absence of air, no separation occurs. A long series of parallel experiments proved that the high values obtained with dichromate are due to liberation of iodine by atmospheric oxygen in presence of chromic salts.

S. I. Levy.

Use of sodium borate solution in the volumetric determination of weak bases. H. B. Rasmussen and C. E. Christensen (Dansk Tidsskr. Farm., 1926, **1**, 65—85).—Weak bases such as the alkaloids and ammonia can be accurately determined by solution in standard hydrochloric acid and titration of the excess with 0·1*N*-sodium borate solution. A micro-burette reading to 0·01 c.c. is employed; the end-point may be found either by using a drop of methyl-red as indicator (if the original liquid is coloured it is recommended to add also a drop of methylene-blue solution) or electrometrically with a quinol electrode. In the former case, the titration is stopped when the solution has become yellow with a slight red tinge, this tint corresponding with a p_H value of 5·5. A weaker (0·0143*N*) sodium borate solution can also be employed in place of sodium hydroxide to determine the small amounts of ammonia obtained in Pregl's micro-determination of nitrogen. A series of comparative tables is given of the results obtained in the determination of atropine, morphine, brucine, strychnine, and ammonia, using sodium borate and sodium hydroxide solutions, respectively. Sodium borate has the advantage over sodium hydroxide in giving a stable solution which is comparatively unaffected by carbon dioxide; this property is of especial value where only occasional determinations are required. H. F. Harwood.

Detection and determination of small quantities of arsenic in gases. G. Lockemann (Z. angew. Chem., 1926, **39**, 1125—1127).—Charcoal, freed from all traces of arsenic by heating with arsenic-free sodium hydroxide solution, filtering, warming with dilute sulphuric acid, and subsequent washing and drying, is a good adsorbent for arsine and may be employed to remove this impurity in the preparation of pure hydrogen. It is not, however, a satisfactory adsorbent in the determination of the amount of arsine in illuminating gas, since, probably owing to the poisoning action of the heavy hydrocarbons present, only 7% of the arsine present is adsorbed. Fuming nitric acid removes only 40% of the total quantity; the best adsorbent is arsenic-free bromine (cf. Z. anal. Chem., 1908, **47**, 132). After passage of the gas (about 350 litres) at the rate of 8—12 litres per hr., the bromine is evaporated on the water-bath, the residue treated dropwise with a mixture of fuming nitric and concentrated sulphuric acids (9 : 1, 15 c.c.), evaporated to dryness with sodium and potassium nitrate solution (23%, 20 c.c.), fused, and the arsenic determined as previously described (A., 1909, ii, 267). J. W. Baker.

So-called soluble silicic acid in silica rocks and in silicified rocks and its detection. R. Grengg (Mikrochem., 1926, **4**, 129—144).—The silica in rocks occurs either as quartz (or chalcedony) or as opal, the latter being more or less soluble in sodium hydroxide and sodium carbonate solution. There is no really sharp line of demarcation between the two varieties, as the solubility depends to some extent on the degree of subdivision of the material. The most satisfactory test for soluble silica consists in boiling the powdered mineral for 1 hr. with 10% sodium carbonate solution in a nickel dish, filtering off the insoluble residue, and adding hydrochloric acid until the solution just reddens a few drops of litmus solution which are added. Ammonium hydroxide is slowly dropped in until the solution becomes blue again; after vigorous shaking and keeping for 24 hrs., a blue, flocculent precipitate settles out if soluble silica is present. If the mineral mixture contains much soluble lime, it must first be treated with dilute hydrochloric acid. The behaviour of many rocks in this test is described and characteristic microstructures of rock sections after etching with dilute hydrochloric acid are illustrated.

A. R. Powell.

Determination of carbonic acid in small quantities of sea-water and other fluids by means of Krogh's micro-respiration apparatus. T. Gaarder (Physiol. Papers dedicated to August Krogh, 1926, 47—79).—By means of a strong acid, carbon dioxide is liberated from the sample in a closed, air-filled container, and is distributed between the fluid and the air by agitation, the increase in pressure being determined by a sensitive manometer; Krogh's micro-respiration apparatus is suitable.

Chemical Abstracts.

Utilisation of catalysis in microcrystalline analysis [for the detection of hydrocyanic acid]. G. DENIGÈS (Mikrochem., 1926, **4**, 149—154).—Hydrocyanic acid may be detected by taking advantage of its catalytic action in promoting the reaction between ammonia and alloxan with the formation of characteristic crystals of oxaluramide. One drop of a 1 : 5 ammonia solution is placed on a microscope slide and this is inverted over the tube containing the solution to be tested together with a few drops of sulphuric acid. After a few minutes, the slide is removed and placed under the microscope; on the addition of 1 drop of the alloxan solution, crystals of oxaluramide begin to form in a few minutes if the test solution contained a cyanide. Substitution of pyridine for ammonia renders the reaction far more delicate, so that a few drops of a solution containing 0·01 g. of hydrocyanic acid per litre give a positive result. The alloxan solution is made by boiling 0·1 g. of uric acid with 0·2 c.c. of nitric acid and 0·2 c.c. of water and diluting to 5 c.c. A. R. POWELL.

Determination of carbon monoxide in the air of workshops. F. SCHOOFS.—See B., 1926, 934.

Determination of organic matter in water by means of potassium dichromate and sulphuric acid. W. E. ADENEY and (MISS) B. B. DAWSON.—See B., 1926, 934.

Microchemical determination of silver. F. FEIGL and I. POLLAK (Mikrochem., 1926, **4**, 185—187).—The neutral nitrate solution (3—4 c.c.) is treated with 2—3 drops of 1 : 10 nitric acid and an excess of a hot rhodanin solution (saturated when cold). The yellowish-white, crystalline precipitate of silver rhodanin is collected in a Pregl filter tube, washed with cold 1% nitric acid, then with alcohol, dried at a gentle heat in a current of dry air, and weighed; it contains 44·943% of Ag. Mercury is the only common element that interferes. As the precipitate is appreciably less soluble than silver chloride, the method gives more accurate results for microchemical work.
A. R. POWELL.

Microchemical determination of strontium. R. STREBINGER and J. MANDL (Mikrochem., 1926, **4**, 168—171).—The chloride solution (5 c.c.), containing no free hydrochloric acid, is heated at 50—60° and treated with 1 c.c. of dilute sulphuric acid and 6 c.c. of 96% alcohol. After keeping for 1 hr. at 60° in a water-bath, the solution is filtered in a Pregl filter-tube and the precipitate washed with 50% alcohol, dried at 170—180°, and weighed as $SrSO_4$.
A. R. POWELL.

Detection and determination of strontium in sea-water. A. DESGREZ and J. MEUNIER (Compt. rend., 1926, **183**, 689—691).—The calcium sulphate in sea-water (2·105 g. per litre), isolated by evaporation and addition of ethyl alcohol, is found by observations of the intensities of the spectral lines due to strontium in mixtures of the salt with various proportions of ferric oxide to be associated with 0·0135 g. of strontium per litre of the water.
G. M. BENNETT.

Detection of cadmium and arsenic in glass. W. GEILMANN.—See B., 1926, 877.

Determination of very small quantities of iron. H. L. SMITH and J. H. COOKE (Analyst, 1926, **51**, 503—510).—Glass-stoppered tubes of the same diameter and with a mark at 30 c.c. are used; the solution is diluted to 30 c.c., and then 5 c.c. of nitric acid, 15 c.c. of a 5% solution of ammonium thiocyanate, and 5 c.c. of amyl alcohol and ether mixture are added. A blank colorimetric determination is performed. In the presence of silica, the control must contain silica. With bismuth, dissolution should be effected in hydrochloric acid and nitric acid avoided. Relatively large quantities of zinc interfere and must be removed and a preliminary separation of iron and zinc is necessary, preferably by extraction of ferric chloride with ether. D. G. HEWER.

Volumetric determination of chromium. E. MÜLLER and W. MESSE (Z. anal. Chem., 1926, **69**, 165—167).—Chromium salts are completely oxidised to chromic acid in alkaline solution by lead dioxide, the excess of which is readily removed by filtration. The solution should contain at least 80 g. of sodium hydroxide per litre; 10 min. boiling is sufficient. The chromate is determined in the filtrate by liberation of iodine and titration with thiosulphate in the usual manner. S. I. LEVY.

Determination of tin in cassiterite. A. PIRLOT.—See B., 1926, 921.

Drop reactions for the detection of titanium, zirconium, and thorium. F. PAVELKA (Mikrochem., 1926, **4**, 199—201).—When a drop of a solution of a salt of thorium, zirconium, or titanium is placed on an alizarin test paper (filter-paper soaked in alcoholic alizarin and dried) and the paper is held over a solution of ammonia, the spot is coloured violet, raspberry-red, and reddish-violet, respectively. In all cases, the reaction will detect 1 part of the metal in more than 100,000 parts of solution. Tartaric acid and other substances which prevent the precipitation of the hydroxides by ammonia interfere with the test. A. R. POWELL.

Behaviour of niobium and tantalum pentoxides towards carbon tetrachloride, and the determination of niobium and tantalum. O. RUFF and F. THOMAS (Z. anorg. Chem., 1926, **156**, 213—225).—Niobium pentoxide can be purified by heating in a bomb-tube with carbon tetrachloride, and fractionally subliming the chlorides formed. Tantalum pentoxide is best purified by conversion into potassium fluotantalate or sodium tantalate, and treating repeatedly with concentrated sulphuric acid. Niobium pentoxide is converted into the pentachloride when heated with carbon tetrachloride at 200—225°, whereas tantalum pentoxide is unaffected. The metals cannot, however, be separated by this treatment, because at this temperature niobium pentachloride reacts with tantalum pentoxide, forming niobium oxychloride and tantalum pentachloride. Niobium can be determined in the presence of tantalum by reducing with hydrogen to the tetroxide, and determining the increase in weight on ignition; tantalum pentoxide is not reduced. The black colour of the tetroxide is a sensitive qualitative test for niobium. A. GEAKE.

Potentiometric determination of the platinum metals. F. MÜLLER (Z. anal. Chem., 1926, **69**,

167—173).—The reduction of compounds of the platinum metals to the metals by means of titanium trichloride in acid solution may be followed potentiometrically. The titrations are carried out at 60° in oxygen-free atmospheres. With palladium and platinum, very sharp end-points are obtained; with ruthenium, rhodium, and iridium the change is less sharp. S. I. LEVY.

Detection of the products of atomic disintegration in the transmutation of elements. H. PETTERSSON (Mikrochem., 1926, **4**, 177—184).—Speculative. The author discusses the possibility of detecting both spectroscopically and microchemically new elements formed by the bombardment of certain elements with α-particles from radium emanation. A. R. POWELL.

***X*-Ray tube with detachable electrodes suitable for crystal analysis.** E. A. OWEN and G. D. PRESTON (J. Sci. Instr., 1926, **4**, 1—3).—A modification of the Shearer *X*-ray tube is described in which sealing-wax joints are replaced by rubber washers pressed against a flanged porcelain tube and the internal construction is modified. The tube is easily cleaned. R. A. MORTON.

Vacuum technique. (FRL.) M. A SCHIRMANN (Physikal. Z., 1926, **27**, 659—680).—The ordinary method of sealing off an evacuated vessel results finally in a vacuum poorer than at the commencement of the process owing to liberation of gas from the fused glass. Such gas tends to flow into the vessel rather than into the pump if the sealing-off occurs near the end of the vessel, whereas if advantage is taken of the Knudsen laws of molecular streaming, the reverse tendency is favoured by choosing a point nearer the pump. The new device consists essentially of gradual constriction of a fairly wide tube during the evacuation process and a quick sealing-off at some distance from the vessel itself. Another device is a tap or ground joint (*e.g.*, quartz to glass) employing neither greasy lubricant nor liquid (oil or mercury) seals. Advantage has been taken of the Johnsen–Rahbek phenomenon of electrostatic relay causing the electrical attraction of contacting surfaces to function as an electrostatic "luting" for the tap or joint. A full account is given of the theory and practical application of the new devices. R. A. MORTON.

Graduated gauge for the measurement of small volumes of gases. H. FIGOUR (Bull. Soc. chim., 1926, [iv], **39**, 1492—1496).—By means of apparatus described, consisting of graduated capillary tubes in the form of inverted U-tubes, it is possible to measure volumes of gases less than 0·20 and 0·04 c.c., respectively. A. S. CORBET.

Chlorine gas filters in relation to reaction velocity. W. TAYLOR (Nature, 1926, **118**, 697).—A very small pressure of chlorine in a light filter greatly reduces the actinic value of the light, but increases in the pressure of the chlorine produce less and less effect. The curve obtained on plotting the actinic power against the density of the filtering medium approximates to a rectangular hyperbola, tending for high densities to a definite "residual" value for the actinic power. A. A. ELDRIDGE.

All-glass circulating pump for gases. F. PORTER, D. C. BARDWELL, and S. C. LIND (Ind. Eng. Chem., 1926, **18**, 1086—1087).—The pump consists of a glass piston with a soft iron rod fixed by lead glass to the inside near the top, and operated by a solenoid surrounding the water jacket. The piston and tube are provided with glass ball and socket valves at their lower ends. The current is made to oscillate so that the piston never falls to the bottom of the tube. D. G. HEWER.

"Bubbler" laboratory fractionating column. H. T. CLARKE and E. J. RAHRS (Ind. Eng. Chem., 1926, **18**, 1092).—The distillation column resembles the Le Bel–Henninger in type, but the wash liquid is retained in traps which consist of elbows formed by downwardly inclined vapour-inlet tubes entering the vertical bubbling chambers. The reflux tubes enter the bubbling chamber at a point below that at which the vapour enters and leave at a point such that the vapour is forced through a layer of condensed liquid 3—6 mm. deep, the excess liquid passing downwards through the reflux tube to the trap below. D. G. HEWER.

Vacuum extractor for biochemical use. N. B. GUERRANT (Ind. Eng. Chem., 1926, **18**, 1090).—A pyrex balloon flask for the solvent has a capacity 10% greater than that of the extraction chamber; it is connected by a siphon arrangement with the lower part of the extraction chamber, and with the condenser above the chamber. The extraction chamber consists of a side-necked bell jar containing a perforated desiccator plate and covered with a well-fitting desiccator top through which the condenser is fixed. The exhaust tube is kept as far as possible from the path of the condensed vapour. A valve, manometer, and thermometer are essential for accurate control. D. G. HEWER.

Comparison of adsorption carbons. P. HONIG. —See B., 1926, 859.

Danger of mercury vapour. K. HOFER (Z. angew. Chem., 1926, **38**, 1123—1124).—A confirmation of Stock's views (this vol., 707, cf. Schmidt, *ibid.*, 815). J. W. BAKER.

S. Cannizzaro's contribution to the development of the concept of valency. R. NASINI (Gazzetta, 1926, **56**, 503—511).

Mineralogical Chemistry.

Lavas of Etna. H. S. WASHINGTON, M. AUROUSSEAU, and (MISS) M. G. KEYES (Amer. J. Sci., 1926, [v], **12**, 371—408).—The average of eighteen new analyses of lavas belonging to different periods is: SiO_2 51·91, TiO_2 1·61, Al_2O_3 18·16, Fe_2O_3 3·09, FeO 5·37, MnO 0·13, MgO 3·90, CaO 8·36, Na_2O 4·85,

K_2O 2·00, P_2O_5 0·62%. The silica percentage ranges from 46·26 in an andesine-andesite to 58·12 in an oligoclase-andesite. L. J. SPENCER.

Physico-chemical study of natural gold and its origin. S. F. SHEMTSCHUSHNI (Z. anorg. Chem., 1926, **156**, 153—178).—When aqueous solutions containing gold and silver are reduced by mercury, the proportion of gold in the precipitate is greater than that in the solution, and it is concluded that this would also be the case when an aqueous solution of these metals was reduced by organic substances during passage through the earth. The hardness of several gold nuggets examined was abnormally high, but was reduced to normal values by tempering. It is concluded that the nuggets had been deformed by movements of the earth's crust or similar causes. The nuggets were probably formed by crystallisation from aqueous solution, and not in the molten state. Two of the nuggets were permeated with fine cracks, amounting to 2·5 and 7·3% of their volumes, respectively. A. GEAKE.

Organic Chemistry.

Δ^{α}- and Δ^{β}-Hexenes. H. VAN RISSEGHEM (Bull. Soc. chim. Belg., 1926, **35**, 328—364).—When pure *n*-hexan-β-ol is heated with *p*-toluenesulphonic acid, an 80% yield of *n*-Δ^{β}-hexene is obtained of which about 50% has b. p. 68·0—68·2° (all b. p. corr. to 760 mm.), f. p. −148·7°, d_4^0 0·7000, $n_{H\alpha}^{15}$ 1·3956. The second stereoisomeride does not appear to be present, and attempts to obtain it by treating the stable form with hydrochloric acid or iodine in solar or ultra-violet light were unsuccessful. The same compound is again formed, together with *n*-hexane, on half reduction of Δ^{β}-hexinene with hydrogen and colloidal palladium. Dehydration of hexan-β-ol at 360° in presence of alumina affords 90% of alkylenes, principally Δ^{β}-hexene, but containing about 10% of a second hydrocarbon. The latter is identical with the Δ^{α}-hexene, b. p. 63·3—63·4°, f. p. −139°, d_4^0 0·6925, $n_{H\alpha}^{14\cdot9}$ 1·3885, prepared by the method of Brooks and Humphrey (A., 1918, i, 286), these authors' material having been insufficiently purified. The following compounds have been examined in a high state of purity: βγ-dibromohexane, b. p. 82·4—82·6°/18·5 mm., d_4^0 1·61505, $n_{H\alpha}^{14\cdot8}$ 1·5030, obtained with a little bromohexane, b. p. 139—142°, and *tribromohexane*, b. p. 121—123°/15 mm., by acting on Δ^{β}-hexene with bromine in sunlight; αβ-dibromohexane, b. p. 86·8—87·2°, d_4^0 1·6079, $n_{H\alpha}^{15}$ 1·5016; Δ^{β}-hexinene, b. p. 83·7—84·0°, f. p. −92°, d_4^0 0·7493, $n_{H\alpha}^{15}$ 1·4140; Δ^{α}-hexinene, b. p. 71·35—71·40°, f. p. −124°, d_4^0 0·7336, $n_{H\alpha}^{15}$ 1·3994. H. E. F. NOTTON.

Catalytic dehydration of α-unsaturated alcohols. C. PRÉVOST (Compt. rend., 1926, **183**, 743—745).—Catalytic dehydration of Δ^{β}-hexen-δ-ol gives a mixture of hydrocarbons, C_6H_{10}, mostly *cis*- and *trans*-$\Delta^{\beta\delta}$-hexadiene, b. p. 76—81°, together with a small amount of $\Delta^{\alpha\gamma}$-hexadiene (cf. this vol., 496). L. F. HEWITT.

Formation of chloroalkylsulphoxide from crude acetylene and chlorine. E. MÜLLER and H. METZGER (J. pr. Chem., 1926, [ii], **114**, 123—136).—The oil obtained by removing sulphur from crude acetylene by means of chlorine water contains 20% of organic matter, from which *αβα'β'-tetrachlorodiethylsulphoxide*, $C_4H_6OCl_4S$, m. p. 121°, was isolated. Oxidation with permanganate affords *ββ'-dichlorodiethylenesulphone*, b. p. 60—63°/0·35 mm., potassium αβ-dichloroethanesulphonate, and carbon dioxide, whilst phosphorus pentachloride causes reduction to *tetrachlorodiethyl sulphide*, b. p. 98—105°/11 mm. with partial decomp. Dehalogenation by sodium carbonate produces (probably) *ββ'-dichlorodiethylenesulphoxide*, b. p. 62°/0·2 mm., which is reduced to the corresponding *sulphide*, b. p. 65—75°/14 mm. A small yield of tetrachlorodiethylsulphoxide is obtained by the action of sodium hypochlorite on ββ'-dichlorodiethyl sulphide. J. M. GULLAND.

[Bromination and iodination of organic compounds.] J. DODONOW (Ber., 1926, **59**, [*B*], 2208—2209; cf. Zmaczynski, this vol., 604).—A question of priority. H. WREN.

Action of magnesium on methylene iodide. G. EMSCHWILLER (Compt. rend., 1926, **183**, 665—667).—Magnesium reacts with methylene iodide in anhydrous ethereal solution, yielding ethylene and magnesium methylene iodide, $CH_2(MgI)_2$, which is decomposed by water, giving methane. Magnesium reacts with methylene bromide in a similar manner. Magnesium methylene bromide is attacked by water, giving methane, and by iodine, giving methylene iodide. L. F. HEWITT.

Reaction between aluminium, iodine, ethyl alcohol, and water. Preparation of ethyl iodide. A. O. JONES and G. M. GREEN (J.C.S., 1926, 2760).—Aluminium can advantageously be used in place of phosphorus in the preparation of ethyl iodide. W. THOMAS.

Effect of structure of organic halides on their rate of reaction with inorganic halides. I. Effect of the hydroxy-, phenoxy-, and benzoyloxy-groups. W. R. KIRNER (J. Amer. Chem. Soc., 1926, **48**, 2745—2753; cf. A., 1925, i, 494).—The reactivity of substituted alkyl halides of the type A·$[CH_2]_n$Cl, where A=·OH, ·OPh, and ·OBz, has been examined by the method previously described (cf. Conant and Kirner, A., 1924, i, 273). An alternating effect in the reactivity of the halogen atom is observed as the chain is lengthened by the insertion of each successive methylene group. All the activating groups so far examined (*loc. cit.*) may be arranged in the following order of their decreasing activating influence: Bz>CO_2Et>Ac>OH>Ph>PhCO$_2$>OPh>Me, but this arrangement may be inverted, on account of the above alternation effect, when halogen and activating group are widely separated. *γ-Chloropropyl benzoate*, b. p. 133—134°/2 mm., is obtained by heating trimethylene chlorohydrin with

benzoyl chloride. β-Phenoxyethyl chloride and γ-phenoxypropyl chloride are conveniently prepared by treating the corresponding phenoxy-alcohols with thionyl chloride and pyridine (cf. Darzens, A., 1911, i, 513). F. G. WILLSON.

[3 : 5-Dinitrobenzoyl chloride and anthraquinone-β-carboxyl chloride in] qualitative organic analysis. T. REICHSTEIN (Helv. Chim. Acta, 1926, **9**, 799—803, 803—806).—3 : 5-Dinitrobenzoyl chloride is particularly suitable as a reagent for alcohols, using a mixture of benzene and pyridine as solvent, since all substances other than the esters required can be removed by washing with acid and with alkali. The following 3 : 5-dinitrobenzoates were prepared; the m. p. of each is given, followed in parentheses by that of its molecular compound with α-naphthylamine. Methyl, m. p. 110—110·5° (*α-naphthylamine* compound, 121—122°); ethyl, 93—94° (*α-naphthylamine* compound, 120—121°); n-*propyl*, 74—75° (103—104°); iso*propyl*, 121—122° (143—144°); *allyl*, 49—50° (120—121°); n-*butyl*, 61—63° (92·5—93°); iso-*butyl*, 87—88° (105·5—106·5°); tert.-*butyl*, 141·5—142·5° (143—144°); iso*amyl*, 61—62° (104—105°); β-*methylbutyl*, 70—70·5° (100—101°); tert.-*amyl*, 117—118° (123—124·5°); n-*hexyl*, 60—61° (103—104°); cyclo*hexyl*, 112—113° (125—126°); *furfuryl*, 80—81° (149—150°); n-*heptyl*, 47—48·5° (57—58·5°); n-*octyl*, 61—62° (48—49·5°); sec.-*octyl*, about 32° (66—67°); n-*decyl*, 56—57° (48—51°); *geranyl*, 62—63° (68—70°); *α-terpinyl*, 78—79° (92—94°). 3 : 5-*Dinitrobenzoic anhydride*, m. p. 219—221°; benzidine *compound* of furfuryl dinitrobenzoate, m. p. 88—89°; 3 : 5-*dinitrobenzoyl*isobutylamide, m. p. 162°.

Anthraquinone-β-carboxyl chloride gives the following anthraquinone-β-carboxylates: *methyl*, m. p. 167—168°; n-*propyl*, 115—116°; iso*propyl*, 140—141°; n-*butyl*, 122—123°; iso*butyl*, 121—122°; iso*amyl*, 88—89°; β-*methylbutyl*, 99—100°; tert.-*amyl*, 98—99°; n-*hexyl*, 88—89°; cyclo*hexyl*, 117—118°; n-*heptyl*, 76—77°; n-*octyl*, 86—87°; sec.-*octyl*, 50—52°; n-*decyl*, 91—92°; *geranyl*, 68—70°; *citronellyl*, oily; *farnesyl*, 160—161°; *allyl*, 158—160°. E. W. WIGNALL.

δ-Methyl derivatives of α-ethoxybutan-δ-ol. A. DEWAEL (Bull. Soc. chim. Belg., 1926, **35**, 301—305).—Ethyl γ-ethoxybutyrate is reduced by sodium and alcohol to *α-ethoxybutan-δ-ol*, (*a*), b. p. 180—181°/756 mm., d_4^{20} 0·9019, n_D^{20} 1·4253 (*acetate*, b. p. 192—193°/756 mm., d_4^{20} 0·9405, n_D^{20} 1·4161; *benzoate*, m. p. 118°). *α-Ethoxypentan-δ-ol*, (*b*), b. p. 181—182°/763 mm., d_4^{20} 0·8915, n_D^{20} 1·4201, is prepared from magnesium γ-ethoxypropyl iodide and acetaldehyde. When the corresponding chloride is used, only a small yield is obtained. Magnesium methyl bromide and ethyl γ-ethoxybutyrate yield *α-ethoxy-δ-methylpentan-δ-ol*, (*c*), b. p. 181—182°/757 mm., d_4^{20} 0·8879, n_D^{20} 1·4162. Ethyl γ-ethoxypropyl ketone, prepared in small yield from magnesium ethyl bromide and γ-ethoxybutyronitrile, is reduced by sodium and alcohol to *α-ethoxyhexan-δ-ol*, b. p. 190—191°/756 mm., d_4^{20} 0·8881, n_D^{20} 1·4265. Comparison of substances (*a*), (*b*), and (*c*) shows that introduction of δ-methyl groups into α-ethoxybutan-δ-ol does not alter the b. p., but causes the density to decrease. H. E. F. NOTTON.

Synthesis and hydrolysis of a glycerophosphoric di-ester, αβ-diglyceromonophosphoric acid: constitution of orthophosphoric acid. O. BAILLY and J. GAUMÉ (Bull. Soc. chim., 1926, [iv], **39**, 1420—1428).—The action of epichlorohydrin on sodium β-glycerophosphate in aqueous solution yields a mixed glycido-β-glyceromonophosphate, $(CH_2{\cdot}OH)_2CH{\cdot}O{\cdot}PO(ONa){\cdot}O{\cdot}CH_2{\cdot}\overset{\diagup O \diagdown}{CH}{\cdot}CH_2$, readily hydrolysed to *sodium αβ-diglyceromonophosphate*, $(CH_2{\cdot}OH)_2CH{\cdot}O{\cdot}PO(ONa){\cdot}O{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH$. On hydrolysis with 1 mol. of dilute sodium hydroxide it is converted quantitatively into a mixture of α- and β-glycerolmonophosphoric acids. This synthesis and hydrolysis of αβ-diglycerolmonophosphoric acid affords presumptive evidence of the equivalence of the three hydrogen atoms in orthophosphoric acid. Attempts to achieve the synthesis from glycerol α-monochlorohydrin and β-glycerolmonophosphate gave poor yields. R. BRIGHTMAN.

Organic phosphoric acid compounds. V. F. ZETZSCHE and F. AESCHLIMANN (Helv. Chim. Acta, 1926, **9**, 708—714).—Glycide reacts with syrupy phosphoric acid to yield only glycerol-α-phosphoric acid (yield 40—45%), no β-acid being formed, since no sparingly soluble double salt with barium nitrate (cf. Karrer and Salomon, this vol., 384) could be obtained, but with epichlorohydrin it yields α-chloropropane-βγ-diolphosphoric acid (76%), isolated both as a readily soluble and a sparingly soluble barium salt. With benzoyl chloride, stearyl chloride, and aniline, the ethylene oxide ring of glycide remains intact, the products being *benzoylglycide* (50%), b. p. 148—150°/12 mm.; *stearylglycide* (65%), m. p. 45°; and *γ-anilinopropylene-αβ-oxide* (glycide anilide), a brittle resin. With sulphuric acid, epichlorohydrin forms α-chloropropane-βγ-diolsulphuric acid (50%), isolated as its *barium* salt, which readily decomposes when moist or in solution. Phenylphosphoryl dichloride reacts with phenols in pyridine or quinoline solution to yield phenyl*cyclo*phosphates (cf. Zetzsche and Zurbrügg, this vol., 497), which could not be obtained in a crystalline condition. *Tetrabromopyrocatechol phenyl*cyclo*phosphate* softens at 80° and melts indefinitely at 110°. J. W. BAKER.

Oxidation of mercaptans and mercapto-acids to corresponding sulphonic acids. P. A. LEVENE and L. A. MIKESKA (J. Biol. Chem., 1926, **70**, 365—380).—The conclusion previously reached (this vol., 46) that secondary alcohols and their corresponding configuratively related halogen derivatives rotate polarised light in opposite directions, has been extended to the arylalkylcarbinols by the observation that oxidation of α-phenylpropyl mercaptan to the corresponding sulphonic acid involves a change in optical rotation; similar experiments and arguments indicate that configurative relationship exists between *d*-lactic acid, *d*-alanine, and *d*-α-chloropropionic acid, between *l*-malic, *d*-chlorosuecinic, and *d*-aspartic acids, and between *d*-β-hydroxy-, *l*-β-amino-, and *l*-β-chloro-butyric acids. l-β-*Thiolbutyric acid*, $[\alpha]_D^{20}$ −37·81°, gave l-β-*sulphobutyric acid*, $[\alpha]_D^{20}$ −6·46°; d-β-*thiolbutyric acid* gave d-β-*sulphobutyric acid*, *barium* salt, $[\alpha]_D^{20}$ +6·54°. *Thiolsuccinamide* had

$[\alpha]_D^{20}$ +60·0°, with 1 equivalent of sodium hydroxide $[\alpha]_D^{20}$ +31·59°, with 2 equivalents $[\alpha]_D^{20}$ +21·89°; *sulphosuccinamide* had $[\alpha]_D^{20}$ +23·78°, with 1 equivalent of barium hydroxide $[\alpha]_D^{20}$ +16·92°, with 2 equivalents $[\alpha]_D^{20}$ +0·66°. d-α-*Phenylpropyl mercaptan*, $[\alpha]_D^{20}$ +42·63°, gave l-α-*phenylpropanesulphonic acid*, $[\alpha]_D^{20}$ −1·50°. l-α-*Phenylpropyl mercaptan*, $[\alpha]_D^{20}$ −8·13°, d-α-*phenylpropyl mercaptan*, $[\alpha]_D^{20}$ +40·19°, d-α-*phenyl*-β-*methylpropyl mercaptan*, $[\alpha]_D^{20}$ +15·16°, d-α-*phenylamyl mercaptan*, $[\alpha]_D^{20}$ +17·94°, were all racemised completely on oxidation to the corresponding sulphonic acids. C. R. HARINGTON.

Configurative relationships of dialkylacetic acids. P. A. LEVENE and L. W. BASS (J. Biol. Chem., 1926, **70**, 211—217).—The following optically active dialkylacetic acids have been prepared, in the first three instances by fractional crystallisation of the quinine salts, and in the last instance of the brucine salt, from acetone: *l*-α-methylvaleric acid, $[\alpha]_D^{22}$ −13·2°; *l*-αβ-dimethyl-*n*-butyric acid, $[\alpha]_D^{22}$ −13·9°; *d*-α-methylhexoic acid, $[\alpha]_D^{22}$ +19·6°; *d*-αγ-dimethylvaleric acid, $[\alpha]_D^{22}$ +19·4°. C. R. HARINGTON.

Clupanodonic acid and certain derivatives. M. TSUJIMOTO and K. KIMURA (Chem. Umschau, 1926, **33**, 252—254).—Clupanodonic acid, prepared from Japanese sardine oil, is shown to have a definite action on a photographic plate, this property being shared with Takahashi's vitamin-*A*, "liver resin" (see A., 1924, i, 239), squalene, and to a much smaller extent with oleic acid. A table is given showing the solubilities of a series of viscous metallic salts of clupanodonic acid in organic solvents. Esterification of clupanodonic acid with glycerol in a sealed tube in the presence of carbon dioxide results in the formation of a mixture of *diclupanodonin* and *triclupanodonin*. The mixture, d_4^{15} 0·9755, yields ether-soluble bromides which blacken without melting at 200°. The glycerides are shown to have greater drying properties than the free acid, but the resulting films in each case are unstable to moisture. *Clupanodonyl alcohol*, $C_{21}H_{33}\cdot CH_2\cdot OH$, gives *decabromoclupanodonyl alcohol*, $C_{22}H_{36}OBr_{10}$, decomp. 220—250°. E. HOLMES.

Congocopalic acid. K. H. BAUER and K. GONSER (Chem. Umschau, 1926, **33**, 250—252).—The ether-soluble portion of Congo copal yields to 1% sodium hydroxide a crystalline acid, m. p. 115—118°, iodine value 93·3 (cf. Engel, A., 1908, i, 559). Methylation with diazomethane gives the ester as a viscid, yellow oil. Treatment with nitric acid yields *pentanitrocongocopalic acid*, $C_{38}H_{55}O_4(NO_2)_5$, decomp. 160° after softening at 140°, whereas bromine gives *pentabromocongocopalic acid*, $C_{38}H_{55}O_4Br_5$, decomp. 140°. On the basis of these results, congocopalic acid is a dicarboxylic acid, $C_{36}H_{58}(CO_2H)_2$. Destructive distillation from zinc dust, sulphur, or slaked lime gives no well-defined decomposition products, although there is evidence in the last case of the formation of terpenoid hydrocarbons, $(C_5H_8)_3$ or $(C_5H_8)_4$. E. HOLMES.

Denigès' reaction for citric acid. M. WAGENAAR (Pharm. Weekblad, 1926, **63**, 1293—1299).—The results obtained by addition of Denigès' reagent, mercuric oxide dissolved in sulphuric acid, and subsequent oxidation with permanganate, are greatly influenced by the presence of chlorides, the acetonedicarboxylic acid formed being further oxidised by the chlorine liberated, and yielding no or only a small precipitate of the mercury salt. If chlorides are first removed by means of silver nitrate, very much more uniform results are obtained. S. I. LEVY.

Constitution of aldehyde and ketone hydrogen sulphites. G. SCHROETER (Ber., 1926, **59**, [*B*], 2341—2343).—The transformation of phenyl propane-ββ-disulphonate by aqueous-alcoholic sodium or barium hydroxide into sulphite and β-hydroxypropane-β-sulphonate is confirmed (cf. A., 1919, i, 518). Since the sulphonate differs completely from "acetone sodium bisulphite," the structure assigned to the latter by Raschig (this vol., 598) cannot be accepted. H. WREN.

Action of paracetaldehyde as potassium iodide. R. HANSSEN (Z. angew. Chem., 1926, **39**, 1291—1292).—Paracetaldehyde prepared in the usual way liberates small quantities of iodine from potassium iodide. If this iodine be removed by means of thiosulphate, and the paracetaldehyde separated, dried, and distilled, it has no further action on the iodide. The action occurs in presence of traces of acetaldehyde, but is not directly proportional to the amount present, and is ascribed to presence of peracetic acid. S. I. LEVY.

Carbohydrate oxidation. VI. Action of potassium hydroxide on *dl*-glyceraldehyde. W. L. EVANS and H. B. HASS (J. Amer. Chem. Soc., 1926, **48**, 2703—2714; cf. following abstract, also this vol., 1228).—Detail improvements in the method of preparing glyceraldehyde (cf. Witzemann, A., 1914, i, 1050, 1124, 1165) are described. The action of aqueous potassium hydroxide on this aldehyde, at various concentrations and at 25° and 50°, has been studied. The products are formic, acetic, and lactic acids. The production of formic acid at 50° is an increasing logarithmic function of the potassium hydroxide concentration, until the latter reaches 0·7*N*, after which it becomes a decreasing logarithmic function of the alkali concentration. Formic acid is probably derived from the decomposition of pyruvaldehyde and of the triose enediol. The production of acetic acid also increases with the alkali concentration until the latter is 0·6*N*, after which it decreases. More acetic acid is produced as the temperature is raised. It is probably formed as the result of fission of pyruvaldehyde. Acetic acid may be determined in presence of formic acid and other non-acid reducing agents by determining the total acidity and then determining the residual acidity after boiling a sample of the original acid mixture with an excess of mercuric oxide, which oxidises the formic to carbonic acid. The production of lactic acid increases with increase in alkali concentration, but soon approaches a constant value. When the alkali concentration is below 3·0*N*, the production of lactic acid is increased with rise in temperature, but above this concentration, more lactic acid is produced at lower temperatures, on account of the formation of tars. When the alkali treatment is carried out in presence of alcoholic phenylhydrazine, the osazone

of pyruvaldehyde is precipitated. At 25°, the production of the latter increases until the alkali concentration is 1·0*N*, and then decreases, whilst at 50° the maximum is reached with an alkali concentration of 0·5*N*, probably on account of the more rapid formation of lactic acid. The following scheme is suggested as the mechanism of the formation of pyruvaldehyde and lactic acid from glyceraldehyde:

$$OH\cdot CH_2\cdot CH(OH)\cdot CHO \rightarrow OH\cdot CH_2\cdot C(OH){:}CH\cdot OH \xrightarrow{+H_2O} CHO\cdot CO\cdot CH_3 \xrightarrow{+H_2O} CH_3\cdot CH(OH)\cdot CO_2H.$$

The results obtained are thus in theoretical accord with those noted (*loc. cit.*) for the action of alkalis on dextrose and *d*-galactose. F. G. WILLSON.

Carbohydrate oxidation. V. Oxidation of dihydroxyacetone to hydroxypyruvaldehyde. W. L. EVANS and C. E. WARING (J. Amer. Chem. Soc., 1926, **48**, 2678—2681; cf. preceding abstract).—At the ordinary temperature, dihydroxyacetone is oxidised by saturated aqueous copper acetate to hydroxypyruvaldehyde, whilst at 65° mesoxalic acid is obtained. At 80°, aqueous copper sulphate oxidises dihydroxyacetone to hydroxypyruvic acid. Hydroxypyruvaldehyde exists in the solid state as a *trimeride*, m. p. 99°. This depolymerises slowly in cold, and rapidly in hot, water. F. G. WILLSON.

Some derivatives of Δγ-hexen-β-one and ζ-methyl-Δγ-hepten-β-one. J. PASTUREAU and (MLLE.) ZAMENHOF (Bull. Soc. chim., 1926, [iv], **39**, 1430—1439; cf. this vol., 272).—On treatment with magnesium methyl or ethyl bromide, the intermediate ketonic alcohols recently described (*loc. cit.*) afford the corresponding glycols. Thus δ-hydroxyhexan-β-one gives β-*methylhexane*-βδ-*diol*, b. p. 121°/30 mm., d^{18} 0·9321, n_D^{18} 1·4407, and γ-*methylheptane*-γε-*diol*, b. p. 121°/23 mm., d^{18} 0·9299, n_D^{18} 1·4467. δ-Hydroxy-β-methylheptan-ζ-one gives βζ-*dimethylheptane*-βδ-*diol*, b. p. 97°/7 mm., d^{18} 0·9020, n_D^{13} 1·4370, and γη-*dimethyloctane*-γε-*diol*, b. p. 130°/21 mm., d^{12} 0·9118, n_D^{12} 1·4453. The following tertiary alcohols were similarly obtained from Δγ-hexan-β-one and ζ-methyl-Δγ-hepten-β-one: β-*methyl*-Δγ-*hexen*-β-*ol*, b. p. 49°/11 mm., d^{18} 0·8536, n_D^{18} 1·443; γ-*methyl*-Δδ-*hexen*-γ-*ol*, b. p. 103°/75 mm., d^{20} 0·8571, n_D^{20} 1·4465; βζ-*dimethyl*-Δγ-*hepten*-β-*ol*, b. p. 48°/5 mm., d^{16} 0·8308, n_D^{16} 1·4373 (affording on hydrogenation in the presence of platinum-black βζ-dimethylheptan-β-ol, b. p. 48°/7 mm., d^{20} 0·8186, n_D^{20} 1·4242), and γη-*dimethyl*-Δδ-*octen*-γ-*ol*, b. p. 70°/11 mm., d^{18} 0·8374, n_D^{18} 1·4397. On dehydration with anhydrous oxalic acid at 130°, these tertiary alcohols are converted into the corresponding diolefines, whilst with hypochlorous acid or hypobromous acid they afford the halogenohydrin of the trisubstituted glycerols, R·CH(OH)·CHX·CR'Me·OH. These halogenohydrins are unstable and could not be converted into the corresponding substituted glycerol. βζ-Dimethyl-Δαγ-heptadiene, b. p. 31°/7 mm., d^{22} 0·7923, n_D^{22} 1·4606, absorbs 2 atoms of bromine in chloroform solution. βη-*Dimethyl*-Δβδ-*octadiene* has b. p. 58°/12 mm., d^{20} 0·7933, n_D^{20} 1·456. γ-*Chloro*-β-*methylhexane*-βδ-*diol*, an unstable oil, is obtained from β-methyl-Δγ-hexen-β-ol or from the chlorohydrin of Δγ-hexen-β-one and magnesium methyl bromide. γ-*Chloro*-βζ-*dimethylheptane*-βδ-*diol*, b. p. 91°/11 mm., d^{22} 1·4638, n_D^{22} 1·026; γ-*bromo*-β-*methylhexane*-βδ-*diol*, b. p. 87°/22 mm.; γ-*bromo*-βζ-*dimethylheptane*-βδ-*diol*, b. p. 115—120°/20 mm., and γδ-*dibromo*-βζ-*dimethylheptan*-β-*ol*, d^{20} 1·5101, n_D^{20} 1·5023, are also described. The last-named, an unstable oil, rapidly decomposes on exposure to light into the tertiary alcohol and hydrogen bromide; on hydrolysis with potassium carbonate at 120°, it affords an unsaturated *bromo*-derivative, b. p. 62°/5 mm., d^{18} 1·175, n_D^{13} 1·485, either $CHMe_2\cdot CH_2\cdot CH{:}CBr\cdot CMe\cdot OH$ or $CHMe_2\cdot CH_2\cdot CH(OH)\cdot CBr{:}CMe_2$. R. BRIGHTMAN.

Hydroxymethylene ketones, particularly those derived from methyl ethyl ketone. E. BENARY (Ber., 1926, **59**, [*B*], 2198—2201; cf. this vol., 272, 500).—The product obtained by the action of benzenediazonium chloride on the sodium salt of methyl α-hydroxymethylene-ethyl ketone is identified as diacetylmonophenylhydrazone, the reaction consisting in the replacement of the hydroxymethylene group by the benzenediazonium radical. Although the ketone has the structure $COMe\cdot CMe{:}CH\cdot OH$, its sodium salt is derived in part from the isomeric form, $Et\cdot CO\cdot CH{:}CH\cdot OH$, since when treated with ammonia it affords 5-*propionyl*-2-*ethylpyridine*, b. p. 247—248° (corr.) [additive *compound* with mercuric chloride, m. p. 178° (decomp.); *picrate*, m. p. 217°; *oxime*, m. p. 104°]; the main product of the action is the *imine*, $(COMe\cdot CMe{:}CH)_2NH$, m. p. 162°. The product obtained by the condensation of methyl *n*-propyl ketone with ethyl formate appears to consist entirely of the normal derivative, since only 1-phenylpyrazole-5-carboxylic acid could be isolated by oxidation of the product obtained from its sodium salt and phenylhydrazine. H. WREN.

Action of acetic anhydride on methylglyoxal. B. SJOLLEMA and L. SEEKLES (Rec. trav. chim., 1926, **45**, 654—656).—By the interaction of acetic anhydride on anhydrous methylglyoxal in the presence of ferric chloride *methylglyoxal diacetate*, b. p. 111—113°/10 mm., m. p. 27° [p-*nitrophenylhydrazone*, m. p. 250° (indef.)], is produced. The substance has the properties of a ketone, and is therefore formulated $CH_3\cdot CO\cdot CH(OAc)_2$. W. J. POWELL.

Preparation of the chlorohydrins of mesityl oxide. J. PASTUREAU and BADER (Bull. Soc. chim., 1926, [iv], **39**, 1428—1430).—Fractionation of the chlorohydrin of mesityl oxide affords (yield 25%) the chlorohydrin (methyl α-chloro-β-hydroxy*iso*butyl ketone), b. p. 73°/10 mm., previously described (A., 1922, i, 717), together with 8% of *methyl* β-*chloro*-α-*hydroxyisobutyl ketone*, b. p. 68°/10 mm., which is more stable to light, and traces of methyl α-chloro-Δα-butenyl ketone, b. p. 39—41°/10 mm., d^{20} 1·0235, n_D^{20} 1·4570 [*semicarbazone*, m. p. 167° (decomp.)] (cf. A., 1900, i, 274). An unfractionated sample of the chlorohydrin of mesityl oxide after 4 months contained only traces of chlorohydrin. With semicarbazide, methyl α-chloro-β-hydroxy*iso*butyl ketone yields chloromesityl oxide semicarbazone (cf. A., 1910, i, 93; 1913, i, 444). R. BRIGHTMAN.

Function of phosphates in the dissimilation of hexoses. A. LEBEDEV (Z. physiol. Chem., 1926, **160**, 96).—A claim for priority over Kluyver and Struyk (this vol., 978). P. W. CLUTTERBUCK.

Carbohydrate oxidation. IV. Action of potassium hydroxide on *d*-glucose and *d*-galactose. W. L. EVANS, R. H. EDGAR, and G. P. HOFF (J. Amer. Chem. Soc., 1926, **48**, 2665—2677; cf. this vol., 149).—The action of various concentrations of aqueous potassium hydroxide on *d*-glucose and *d*-galactose at 25°, 50°, and 75° has been studied. The amount of lactic acid thus produced increases both with alkali concentration and with rise in temperature. It is formed by fission of the γδ-" enediol " with successive production of enolised glyceraldehyde and pyruvaldehyde, and its production can therefore be taken as a measure of the formation of this γδ-enediol. More lactic acid is obtained from *d*-glucose than from *d*-galactose under the same conditions. The formation of acetic and formic acids, which are probably derived from the decomposition of pyruvaldehyde into carbon monoxide and acetaldehyde, reaches a maximum, in the case of both sugars, at an alkali concentration of about 0·5*N*, thereafter diminishing owing to the increasing rate of formation of lactic acid. The total yield of formic acid, however, is greater than that obtained from pyruvaldehyde, and this is taken to indicate the formation of the αβ-enediol, which undergoes fission with formation of pentose and formaldehyde methylenenol. As alkali concentration and temperature are increased, the total yield of formic acid tends to approach that of the total acetic acid. The yield of pyruvaldehyde (isolated as the osazone) also passes through a maximum as alkali concentration and temperature are increased, beyond which point it yields lactic acid more rapidly than osazone. *d*-Galactose also yields *d*-galacto-α-metasaccharinic acid lactone, m. p. 143·5° (cf. Nef, A., 1908, i, 5), in amount increasing with alkali concentration and temperature. Its formation is taken as a measure of the existence of this carbohydrate as the βγ-enediol. A mechanism is suggested for the formation of saccharinic acid lactones from the three hexose enediols, through the intermediate hexose *o*-diketo-derivatives. F. G. WILLSON.

Action of aniline on dextrose in acetic acid solution. II. C. N. CAMERON (J. Amer. Chem. Soc., 1926, **48**, 2737—2743; cf. this vol., 1026).—The formation of glucoseanilide is catalysed by potassium dihydrogen phosphate as well as by acetic acid, and the former reagent is also an effective catalyst for the subsequent changes resulting in the production of the brown product from glucoseanilide. This coloured material, precipitated by water from alcoholic solutions of dextrose, aniline, and acetic acid, contains some 2 : 5-dianiloquinone, indicating that aniline is more readily oxidised in presence of dextrose. The more difficultly oxidisable benzylamine, however, also gives coloured products with dextrose and acetic acid. As the filtrate from the coloured material contains neither gluconic acid nor sorbitol, it is concluded that this product is chiefly a condensation product of aniline with some degradation product of the dextrose, possibly methylglyoxal. *o*- and *p*-Toluidines behave in the same way as aniline towards dextrose. Solutions of dextrose, aniline, and acetic acid show a greater reactivity than when either dextrose or aniline is absent, and it is concluded that the glucoseanilide is isomerised to a reactive form, probably the aldehyde isomeride (cf. Irvine and Gilmour, J.C.S., 1908, **93**, 1429). Dextrose has little effect on the coloration of methylaniline solutions in acetic acid. F. G. WILLSON.

New crystalline forms of trimethylglucose and dimethylglucose. W. N. HAWORTH and W. G. SEDGWICK (J.C.S., 1926, 2573—2580).—A mixture of the β-glucosides of (*a*) tetramethylglucose, (*b*) trimethylglucose, and (*c*) dimethylglucose, obtained by the methylation of dextrose with methyl sulphate, was separated into the corresponding fractions (A), b. p. 95°/0·01 mm., n_D 1·4455; (B), b. p. 124—127°/0·01 mm., n_D 1·4578, and (C), b. p. 146°/0·01 mm., n_D 1·4730. From (B) two crystalline trimethyl-β-methylglucosides were obtained (I), m. p. 67—68°, and (II), m. p. 64°. Hydrolysis of (I) yielded a *trimethylglucose* (2 : 4 : 6 suggested), m. p. 123°, $[\alpha]_D$ +89·7° → +71·9° in water, and +110° → +69·7° in methyl alcohol, identical with the trimethylglucose, m. p. 123°, obtained by the hydrolysis of heptamethylsucrose. From (C), by hydrolysis, a crystalline *dimethylglucose*, m. p. 156—157°, $[\alpha]_D$ +93·1° → +62·4° in water, and +110° → +64·7° in methyl alcohol, was obtained. H. BURTON.

Di*iso*propylideneglucose. III. Methylated methylglucosides prepared from mono*iso*propylideneglucose. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1926, **70**, 343—353).—On heating with methyl alcohol and hydrogen chloride and further methylation of the product, γεζ-trimethyl-*iso*propylideneglucose gave βγεζ-tetramethylmethylglucoside, b. p. 102°/0·3 mm., $[\alpha]_D$ −12·4°; the rate of hydrolysis of the latter compound was greater than that of the βγδζ-isomeride. The trimethyl*iso*propylideneglucose yielded trimethylglucose, $[\alpha]_D$ −8° to −11·4°; this yielded a methylglucoside, b. p. 135°/0·5 mm., $[\alpha]_D$ +13·3°, which in turn gave a tetramethylmethylglucoside, b. p. 105°/0·3 mm., $[\alpha]$ +29·2°; after distillation (b. p. 150°/0·3 mm.), the trimethylglucose gave two glucosides, (1) b. p. 110—115°/0·4 mm., $[\alpha]_D$ +50° (average); (2) b. p. 130°/0·2 mm., $[\alpha]_D$ −17° to −54°; these compounds yielded tetramethyl derivatives having, respectively, b. p. 98—100°/0·3 mm., $[\alpha]_D$ +63°, and b. p. 110°/0·5 mm., $[\alpha]_D$ −54·9°. None of these compounds, except the distilled trimethylglucose, reduced Fehling's solution in the cold; all gave strong orcinol reactions. It is concluded that the supposed power of γ-methylated sugars to reduce Fehling's solution in the cold is due to impurity, and that lævorotation is not necessarily a characteristic of methylated glucoses derived from di*iso*propylideneglucose. C. R. HARINGTON.

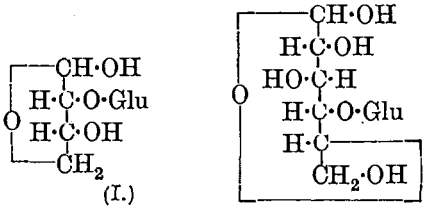
Mutarotation. VII. Third modification of galactose. C. N. RIIBER and J. MINSAAS (Ber., 1926, **59**, [*B*], 2266—2281; cf. A., 1925, i, 773).—The inference that two modifications of galactose are present in its aqueous solution, since the specific rotation follows a simple logarithmic law, is not theoretically valid, since three (or more) modifications in a solution may cause such change with respect to time as is consonant with a simple logarithmic law

within the limits of experimental error. An aqueous solution of α-galactose suffers initial expansion followed by contraction; the change in volume does not follow a simple logarithmic law until after about 50 min. Similarly, the refractive index of a similar solution increases slowly at first and then more rapidly, the curve gradually becoming simply logarithmic. Again, the temperature of a solution of α-galactose in water decreases rapidly at first and subsequently rises slowly. Similar relationships are not observed with β-galactose.

As judged by the specific rotation, the equilibrium solution of galactose (100 g. per litre) contains 69·19% of β-galactose and 30·81% of α-galactose. If only two modifications are actually present, the physical properties of a solution of the forms mixed in this proportion should be independent of the time. Actually this is not the case, and it is not possible to prepare a solution fulfilling these conditions. The existence of a third modification of galactose is therefore postulated (cf. Lowry, J.C.S., 1904, **85**, 1570). In aqueous solution, α-galactose appears to be transformed with great but measurable velocity into *galactose*-B, which, at a considerably slower rate, is converted partly into β-galactose. The physical constants of α-galactose, galactose-*B*, and β-galactose are: $V_{m\infty}$ 109·312, 109·538, and 109·128; M_∞ 62·10, 62·15, and 62·51; $[\alpha]_D$ +144·5°, +135·0°, and +52·2°. In the aged, aqueous solution of 10 g. galactose in 100 mol., 0·661 g. of α-galactose, 2·735 g. of galactose-*B*, and 6·604 g. of β-galactose are present. The isolation of galactose-*B* has not been achieved. H. WREN.

Stable γ-glucose. H. PRINGSHEIM and A. BEISER (Ber., 1926, **59**, [*B*], 2241—2243).—If rise of temperature is avoided as far as possible during evaporation of solutions of stable γ-glucose (cf. this vol., 822), the product has uniformly $[\alpha]_D$ +105° to +107° in water. Fractional precipitation of it from aqueous solution by ethyl alcohol affords evidence that it is homogeneous. Repeated evaporation of its aqueous solution on the water-bath causes the specific rotation to recede to +62·6° without increase of reducing power, and therefore without production of normal dextrose. Possibly mutarotation occurs at a high temperature which is impeded at a lower temperature by the particular position of the oxygen bridge. In support of this hypothesis, the isolation of two acetates is described, stable γ-glucose penta-acetate-*A*, m. p. 105°, $[\alpha]_D^{20}$ +86·5° in chloroform, prepared from acetic anhydride and sodium acetate and pyridine, and *stable γ-glucose penta-acetate*-B, m. p. 120—121°, $[\alpha]_D^{20}$ +116·8° in chloroform, prepared by means of acetic anhydride in the presence of a little zinc chloride. H. WREN.

Degradation of reducing bioses. III. Direct elucidation of the constitution of lactose. G. ZEMPLÉN (Ber., 1926, **59**, [*B*], 2402—2413; cf. Part II, following).—Lactose is converted by hydroxylamine into the non-crystalline oxime, which, with sodium acetate and glacial acetic acid, affords *octa-acetyl-lactobiononitrile* in about 70% yield. Treatment of the latter compound with sodium methoxide, whether or not followed by the use of silver acetate, affords *d*-galacto-*d*-arabinose, isolated as the *benzylphenylhydrazone*, m. p. 223—225° (decomp.), $[\alpha]^{24}$ +4·4° in a mixture of pyridine (4 vols.) and alcohol (6 vols.), not identical with the product isolated by Ruff through calcium lactobionate. The hydrazone is decomposed by benzaldehyde with formation of non-crystalline d-*galacto*-d-*arabinose*, $[\alpha]_D^{11}$ −58·1° in aqueous solution. The new sugar is hydrolysed by emulsin to *d*-arabinose and galactose; it yields a *phenylosazone*, m. p. about 242° (decomp.), and, apparently, a mixture of isomeric acetates. The non-crystalline *oxime* of *d*-galacto-*d*-arabinose is converted by acetic anhydride and sodium acetate into *hepta-acetyl*-d-*galacto*-d-*arabinonitrile*, m. p. 132°, $[\alpha]_D^{23\cdot5}$ +5·6° in chloroform, which, with sodium methoxide and chloroform, affords d-*galacto*-d-*erythrose*, $[\alpha]_D^{23\cdot5}$ +17·2° in aqueous solution. The latter compound is not hydrolysed by emulsin, but is converted by 1% hydrochloric acid into *d*-erythrose and *d*-galactose.



Since it is unable to yield an osazone, it must have the constitution (I), and consequently the structure (II) is assigned to lactose. H. WREN.

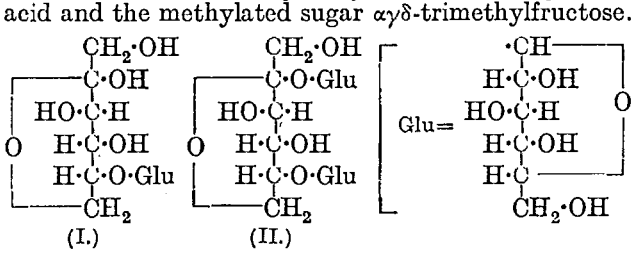
Irreversible hydrolysis of maltose by maltase. H. COLIN (Bull. Soc. chim., 1926, [iv], **39**, 1481—1483).—The hydrolysis of maltase by dried mycelium powder (*Mucor Boulard*) even in concentrated (40%) solution is complete, and no evidence of reversibility was obtained. The ferment is without action on dextrose at the ordinary temperature (cf. Hill, J.C.S., 1898, **73**, 684; 1903, **83**, 578). R. BRIGHTMAN.

Synthesis of melibiose. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1926, **9**, 805—809).—Diglucosan and digalactosan, when heated with zinc chloride, give a vitreous mass which, when treated with hydrochloric acid and then with silver carbonate, gives with alcohol a syrup, from which a *substance*, m. p. 196—197°, $[\alpha]_D$ +112·2° (acetate, m. p. 146°), separates. The alcoholic solution contains melibiose.
E. W. WIGNALL.

Degradation of reducing bioses. II. Constitution of turanose and melezitose. G. ZEMPLÉN and G. BRAUN (Ber., 1926, **59**, [*B*], 2230—2241; cf. this vol., 822).—Melezitose is converted by treatment with methyl sulphate and sodium hydroxide into *undecamethylmelezitose*, b. p. 195—200°/0·35 mm., $[\alpha]_D^{19}$ +105·25° in water, $[\alpha]_D^{19}$ +113·4° in alcohol, which is converted by hydrolysis with 20% acetic acid followed by methylation with methyl sulphate into a mixture of tetramethyl-α- and -β-methyl-glucoside and *octamethylturanose*, b. p. 159—162°/0·15 mm., $[\alpha]_D^{19}$ +106·7° in water, $[\alpha]_D^{19}$ +109·7° in alcohol. Hydrolysis of the latter compound with 2·5% hydrochloric acid gives as intermediate product *heptamethylturanose*, b. p. 162—163°/0·06 mm., $[\alpha]_D^{19}$ +106·0° to +104·8° in alcohol during 18 hrs., and as final products *αγδ-trimethylfructose*, b. p. 100—110°/0·08 mm., $[\alpha]_D^{16}$ +29·27° to +30·3° in water

during 18 hrs., $[\alpha]_D^{19}$ +23·97° to +24·96° in alcohol during 18 hrs., and tetramethylglucose. The trimethylfructose does not yield an osazone. When reduced by Haworth and Mitchell's method (J.C.S., 1923, **123**, 309), it yields a product of which the specific rotation does not change by addition of boric acid and therefore does not contain vicinal free hydroxy-groups. Oxidation of trimethylfructose with nitric acid and subsequently with permanganate gives a crystalline *hydroxydimethoxyglutaric acid*, $[\alpha]_D^{24}$ +36·9 to +34·5° in alcohol during 24 hrs.

Octa-acetylcellobiononitrile (Zemplén, *loc. cit.*) is degraded to glucosidoarabinose, which, when treated with methyl sulphate and sodium hydroxide, affords *hexamethylmethyl*-d-*gluco*-d-*arabinoside*, b. p. 167—168°/0·4 mm., m. p. 96·5—97°, $[\alpha]_D$ −35·26° in water, $[\alpha]_D^{21}$ −11·4° in alcohol, which is hydrolysed by 5% hydrochloric acid to tetramethylglucose and βδ-*dimethyl*-d-*arabinose*, b. p. 128—129°/0·32 mm., $[\alpha]_D^{24}$ −95·46° to −105·1° in alcohol during 24 hrs. The latter substance is oxidised by nitric acid to β-*hydroxy*-αα′-*dimethoxyglutaric acid*, b. p. 70°/0·24 mm., $[\alpha]_D^{23}$ −44·5° in alcohol. Since this acid is not identical with that obtained from trimethylfructose, the latter acid must be α-hydroxy-α′β-dimethoxyglutaric acid and the methylated sugar αγδ-trimethylfructose.



If the amylene oxide structure of fructose is accepted, the constitutions (I) and (II) are assigned to turanose and melezitose. H. WREN.

Location of the glucose residues in starch; degradation of monomethyltrihexosan to ζ-methylglucose. R. KUHN and W. ZIESE (Ber., 1926, 59, [*B*], 2314—2316).—Trihexosan, from potato starch, is converted by sodium hydroxide and methyl sulphate at the ordinary temperature into *monomethyltrihexosan*, $[\alpha]_D^{23}$ +116·7° in 1·15*N*-hydrochloric acid, the homogeneity of which is established by its unfermentability with malt, pancreas, or salivary amylase. When hydrolysed with acid, it yields ζ-methylglucose, identified as the osazone. Pringsheim's formulæ for trihexosan (A., 1924, i, 714), in which free ·CH_2·OH groups are not present, must therefore be rejected. In starch, the primary hydroxy-groups do not occupy the same preferential position as in trihexosan. When methylated under the conditions used above, the product contains much dimethylated substance and also non-methylated carbohydrate. Etherification does, however, occur in the ζ-position, so that the conception that all the primary hydroxy-groups are involved in the production of oxygen bridges in starch and in many of the products of its degradation is no longer tenable. H. WREN.

Inulin. M. BERGMANN and E. KNEHE (Annalen, 1926, **449**, 302—312).—By keeping mixtures of inulin, acetic anhydride, and pyridine for some days at temperatures between 20° and 60°, an 80% yield of *inulin hexa-acetate*, m. p. 135° after softening at 78°, $[\alpha]_D^{23}$ −39·5° in glacial acetic acid, is obtained. Determinations of the mol. wt. of this acetate by the cryoscopic method, using low (less than 1%) concentrations in glacial acetic acid (cf. A., 1925, i, 1384), show that the substance has the formula $C_{12}H_{14}O_{10}Ac_6$, and this suggests that inulin is a polymerised difructose anhydride, which agrees with the views of Schmid and Becker (A., 1925, i, 1386). Experiments on the fractionation of the acetate by diffusion yielded no evidence of further "dissociation" to a fructose anhydride. This acetate seems to be quite different from the triacetate of Pringsheim and Aronowsky (A., 1921, i, 545), to which the structure of a trebly polymerised anhydrotrifructose was given.

When hydrolysed with alcoholic potassium hydroxide solution, the hexa-acetate regenerates inulin, which in turn regenerates the hexa-acetate on acetylation. R. W. WEST.

Cellulose. XXI. Relation of βγζ-trimethylglucose to the constitution of cellulose; the movement of oxygen-bridges in carbohydrates. F. MICHEEL and K. HESS (Annalen, 1926, **449**, 146—155; cf. this vol., 715).—Treatment of trimethylglucose with methyl-alcoholic hydrogen chloride at 30° affords the hetero-methylglucoside, containing the amylene oxide ring (cf. Schlubach and von Bomhard, this vol., 600), whilst similar treatment at 100° yields the normal methylglucoside, containing the butylene oxide ring (cf. Irvine and Hirst, J.C.S., 1922, **121**, 1221). By treating the hetero-methylglucoside with methyl-alcoholic hydrogen chloride at 100°, it is quantitatively converted into the normal form, which is the more stable and cannot be made to undergo the reverse change. When trimethylglucose is dissolved in methyl-alcoholic hydrogen chloride, it is converted into a mixture of normal and hetero-forms, as is shown by the value for the initial specific rotation being 10—20° below normal (cf. Irvine and Hirst, *loc. cit.*). At 30°, only the hetero-form is converted into the glucoside, whilst at 100° the normal glucoside may be formed both directly and from the hetero-glucoside.

If Haworth's conception of the amylene oxidic structure of glucose be adopted (A., 1925, i, 1133), the prefixes *n*- and *h*- used in this paper must be interchanged.

Methylation of the trimethylmethylglucoside, $[\alpha]_D$ +87·2°, obtained from trimethylcellulose, yields a mixture of α- and β-forms of tetramethylmethylglucoside, $[\alpha]_D$ +92·6°, which suggests that the tetramethylglucoside and original trimethylglucoside consist of a mixture of 65% α-form and 35% β-form, and that the unknown 2 : 3 : 6-trimethyl-α-methylglucoside has $[\alpha]_D$ about +150°. The stability of α- and β-forms is suggested by the fact that octamethyl-lactose yields 2 : 3 : 6-trimethyl-β-methylglucoside (cf. Schlubach and Moog, A., 1923, i, 1063), which on methylation yields 2 : 3 : 5 : 6-tetramethyl-β-methylglucoside. Hydrolysis of octamethyl-lactose, however, yields tetramethylmethylgalactoside, $[\alpha]_D^{23}$ +133·9°, which is a mixture of

92% α-form and 8% β-form, showing that mixtures of the two forms may be obtained in reactions involving fission. R. W. WEST.

Comparative tests on the Mäule [permanganate] and phloroglucinol reactions for the detection of lignification. E. SIERSCH (Mikrochem., 1926, **4**, 188—198).—From a large number of comparative tests on various plants, it is shown that Mäule's permanganate method for the detection of lignified membranes is not a specific test and the reaction is due to substances other than those which give the phloroglucinol reaction. Starting with the lowest forms of vegetable life and passing upwards, the Mäule test gives positive results first with certain varieties of *Selaginellæ*, whilst the phloroglucinol test is already positive with the ferns.

A. R. POWELL.

Tenacity of organic residues. V. J. VON BRAUN, M. KÜHN, and J. WEISMANTEL (Annalen, 1926, **449**, 249—277; cf. this vol., 829).—Methylamine, treated with β-chloroallyl chloride, yields a mixture of *methyl-β-chloroallylamine*, b. p. 112° (*hydrochloride*, m. p. 156°; *picrate*, m. p. 110°), and *methyldi-β-chloroallylamine*, b. p. 70°/14 mm. (*hydrochloride*, m. p. 125°; *picrate*, m. p. 95°; *methiodide*, m. p. 130°), which with cyanogen bromide gives *methyltri-β-chloroallylammonium bromide*, m. p. 133°, β-chloroallyl bromide, and *methyl-β-chloroallylcyanamide*, b. p. 104—106°/13 mm. Similarly, β-bromoallyl bromide yields *methyl-β-bromoallylamine*, b. p. 135° (*hydrochloride*, m. p. 160°; *picrate*, m. p. 134—135°), and *methyldi-β-bromoallylamine*, b. p. 100—102°/14 mm. (*hydrochloride*, m. p. 160°; *picrate*, m. p. 96—98°; *methiodide*, m. p. 163°), which with cyanogen bromide gives *methyltri-β-bromoallylammonium bromide*, m. p. 162°, β-bromoallyl bromide, and *methyl-β-bromoallylcyanamide*, b. p. 114—116°/13 mm. *Methyl-β-chloroallyl-β-bromoallylamine*, b. p. 88°/14 mm. (*hydrochloride*, m. p. 151°; *picrate*, m. p. 95°), with cyanogen bromide, yields β-chloroallyl and β-bromoallyl bromides and the corresponding methylcyanamides. *Methylbenzyl-β-bromoallylamine*, b. p. 125—130° (*hydrochloride*, m. p. 140°; *picrate*, m. p. 124°; *methiodide*, m. p. 141°), with cyanogen bromide yields benzyl bromide and methyl-β-bromoallylcyanamide. Methylamine reacts with γ-chloroallyl chloride, yielding *methyl-γ-chloroallylamine*, b. p. 125° (*picrate*, m. p. 91°), and *methyldi-γ-chloroallylamine*, b. p. 88°/16 mm., which with cyanogen bromide gives *γ-chloroallyl bromide*, b. p. 130°, and *methyl-γ-chloroallylcyanamide*, b. p. 113—114°/14 mm. Similarly, *methyl-γ-chloroallyl-γ-bromoallylamine*, b. p. 102—103°/14 mm. (*hydrochloride*, *chloroaurate*, *picrate*, and *methiodide* are oils), yields γ-chloroallyl and γ-bromoallyl bromides and the corresponding methylcyanamides; *methylbenzyl-γ-chloroallylamine*, b. p. 120°/14 mm., yields benzyl bromide and methyl-γ-chloroallylcyanamide; *methyl-β-bromoallyl-γ-bromoallylamine*, b. p. 110—112°/14 mm. (*picrate*, m. p. 166°; *methiodide*, m. p. 140°), yields γ-bromoallyl bromide and methyl-β-bromoallylcyanamide; *methyl-β-chloroallyl-γ-bromoallylamine*, b. p. 98—100°/14 mm., yields γ-bromoallyl bromide and methyl-β-chloroallylcyanamide. It follows that the tenacities of the residues are in the ascending order: benzyl, γ-ehloro(bromo)allyl, β-chloro(bromo)allyl, methyl. The following quaternary salts are described: *trimethyl-β-chloroallylammonium bromide*, m. p. 147°; *trimethyl-β-bromoallylammonium bromide*, m. p. 202°; *benzyltrimethylammonium bromide*, m. p. 232°; *trimethyl-γ-chloroallylammonium bromide* (corresponding *gold* salt, m. p. 172°; *platinum* salt, m. p. 230°).

When ammonium thiocyanate is treated with β-bromoallyl bromide in alcoholic solution, it yields *β-bromoallylthiocarbimide*, b. p. 98—100°/14 mm., which reacts with aniline, yielding *phenyl-β-bromoallylthiocarbamide*, m. p. 110°.

Phenol reacts with β-bromoallyl bromide, yielding *phenyl β-bromoallyl ether*, b. p. 114—116°/14 mm., which on heating with decahydronaphthalene isomerises to *β-bromoallylphenol*, b. p. 135°/14 mm.

Di-*p*-chlorobenzylamine (*picrate*, m. p. 187°) yields a *benzoyl* derivative, m. p. 119°, which is decomposed by phosphorus pentachloride into *p*-chlorobenzyl chloride and benzonitrile. *Benzyl-*p*-chlorobenzylamine*, b. p. 195—196°/13 mm. (*hydrochloride*, m. p. 268°; *picrate*, m. p. 140°), yields a *benzoyl* derivative, m. p. 82°, which with phosphorus pentachloride gives benzyl chloride and benzoyl-*p*-chlorobenzylamine. Benzoyldi-*p*-bromobenzylamine, m. p. 187°, with phosphorus pentachloride gives *p*-bromobenzyl chloride. p-*Chlorobenzyl*-p-*bromobenzylamine*, m. p. 34° (*hydrochloride*, m. p. 280°; *picrate*, m. p. 191°), prepared from *p*-bromobenzylamine, b. p. 126—127°/15 mm., m. p. 20° (*benzoyl* derivative, m. p. 143°), yields a *benzoyl* derivative, m. p. 118°, which with phosphorus pentachloride gives *p*-chlorobenzyl chloride (p-*chlorobenzyltrimethylammonium chloride*, m. p. 235°) and *p*-bromobenzylbenzamide. *Methyl-*p*-chlorobenzyl-*p*-bromobenzylamine* (*hydrochloride*, m. p. 182°; *picrate*, m. p. 142°), prepared from *methyl-*p*-chlorobenzylamine*, b. p. 120—123°/15 mm. (*hydrochloride*, m. p. 193°; *picrate*, m. p. 130°), with cyanogen bromide yields mainly *p*-chlorobenzyl bromide (p-*chlorobenzyltrimethylammonium bromide*, m. p. 195°) and *p*-bromobenzylmethylcyanamide. p-*Bromobenzyl*-p-*iodobenzylamine*, m. p. 105—106° (*hydrochloride*, m. p. 248°; *picrate*, m. p. 197°), yields a *benzoyl* derivative, m. p. 119°, which with phosphorus pentachloride gives *p*-bromobenzyl chloride and benzoyl-*p*-iodobenzylamine. p-*Iodobenzyldimethylamine*, m. p. 32° (*hydrochloride*, m. p. 210°; *picrate*, m. p. 148°; *di*-p-*iodobenzyldimethylammonium bromide*, m. p. 229°), with cyanogen bromide gives *p*-iodobenzyl bromide and dimethylcyanamide. The tenacity series, benzyl<*p*-chlorobenzyl<*p*-bromobenzyl<*p*-iodobenzyl<methyl, is established by these results.

m-*Chlorobenzyl chloride*, b. p. 209—211°, m-*chlorobenzylamine*, b. p. 110—112°/17 mm. (*hydrochloride*, m. p. 225°; *picrate*, m. p. 203°; *benzoyl* derivative, m. p. 114°), and *di*-m-*chlorobenzylamine* (*picrate*, m. p. 126°; *hydrochloride*, m. p. 233°; *benzoyl* derivative, m. p. 100°) are described. m-*Chlorobenzyl-*p*-chlorobenzylamine* (*hydrochloride*, m. p. 236°; *picrate*, m. p. 156°) yields a *benzoyl* derivative, m. p. 196°, which with phosphorus pentachloride gives *p*-chlorobenzyl chloride and *m*-chlorobenzylbenzamide. Similarly, the *benzoyl* derivative, m. p. 74°, of o-*chloro-*

benzyl-m-*chlorobenzylamine* (*hydrochloride*, m. p. 172°; *picrate*, m. p. 137°) yields *m*-chlorobenzyl chloride and *o*-chlorobenzylbenzamide; the *benzoyl* derivative, m. p. 92°, of o-*chlorobenzyl*-p-*chlorobenzylamine*, b. p. 200—202°/16 mm. (*hydrochloride*, m. p. 220°; *picrate*, m. p. 129°), yields *p*-chlorobenzyl chloride and *o*-chlorobenzylbenzamide. o-*Chlorobenzyldimethylamine*, b. p. 90°/13 mm. (*hydrochloride*, m. p. 203°; *picrate*, m. p. 146°), reacts with cyanogen bromide, yielding dimethylcyanamide and *o*-chlorobenzyl bromide. *Di*-o-*chlorobenzylamine*, b. p. 211—213°/14 mm. (*hydrochloride*, m. p. 289°; *picrate*, m. p. 136°; *benzoyl* derivative, m. p. 86°), *di*-o-*chlorobenzyldimethylammonium bromide*, m. p. 185°, and o-*chlorobenzyltrimethylammonium bromide*, m. p. 160°, are described. The tenacity series, *p*-<*m*-<*o*-, is thus established. R. W. WEST.

Valency of nitrogen in quaternary ammonium compounds. F. D. HAGER and C. S. MARVEL (J. Amer. Chem. Soc., 1926, **48**, 2689—2698).—The preparation of nitrogen penta-alkyls has been attempted by treating lithium alkyls with quaternary ammonium iodides. The products, however, were tertiary amines and hydrocarbons, and it is concluded that the fifth valency of nitrogen always differs from the other four, and that there is never any exchange of groups between it and the remaining valencies (cf. Noyes, this vol., 154).

Lithium ethyl and triethyl-*n*-butylammonium bromide yield triethylamine and diethyl-*n*-butylamine, the former being also obtained from lithium *n*-butyl and tetraethylammonium bromide. Lithium *iso*amyl and triethyl-*n*-butylammonium bromide yield diethyl-*n*-butylamine. Lithium *n*-butyl and triethylbenzylammonium bromide yield diethylbenzylamine. Lithium *n*-heptyl and tetra-*n*-butylammonium iodide afford tri-*n*-butylamine, a trace of a hydrocarbon, b. p. above 100°, and, possibly, *n*-heptane. Lithium *n*-butyl and tri-*n*-butyl-*n*-heptylammonium iodide yield di-*n*-butyl-*n*-heptylamine. Lithium ethyl and tetraethylammonium bromide yield ethane and ethylene. The following compounds are described: *mercury di*-n-*heptyl*, b. p. 119—122°/0·005—0·01 mm., d_0^0 1·474, n_D^{21} 1·4935 (cf. Marvel and Gould, A., 1922, i, 329); *triethyl*-n-*butylammonium iodide*, m. p. 205° (decomp.); *benzyltriethylammonium bromide*, m. p. 195° (decomp.), and *iodide*, m. p. 128—135°; *tetra*-n-*butylammonium chloride* (non-crystalline), *bromide* (similar), and *iodide*, m. p. 144—145°; *tri*-n-*butyl*-n-*heptylammonium chloride*, *bromide* (both non-crystalline), and *iodide*; *diethyl*-n-*butylamine*, b. p. 136—137°, d_0^3 0·7614; and *di*-n-*butyl*-n-*heptylamine*, b. p. 119—120°/7 mm., n_D^{15} 1·4389, d_0^0 0·8088. Manipulative improvements in the preparation of lithium alkyls (cf. Schlenk and Holtz, A., 1916, i, 385; 1917, i, 262) are detailed. F. G. WILLSON.

Quaternary ammonium perhalides. T. H. READE (J.C.S., 1926, 2528—2531; cf. *ibid.*, 1923, **123**, 141; A., 1924, i, 277, 278).—The experimental study of the further halogenation of quaternary ammonium trihalides is expressed: $QmBr_3 \xrightarrow{Cl_2} QmCl_2Br \xrightarrow{I_2} QmCl_2I$, and $QmBr_3 \xrightarrow{I_2} QmBr_2I \xrightarrow{Cl_2} QmCl_2I$ (Qm=C_6H_5·NMe_3 or C_6H_4Br·NMe_3). These results support the hypothesis that phenyltrimethylammonium tribromide is represented as $Qm^{+} \ldots Br^{-} Br \ldots Br^{-}$. The solubilities of *p*-bromophenyltrimethylammonium chloride, bromide, and iodide in acetone are given and the reaction between *p*-bromophenyltrimethylammonium dichlorobromide and iodine is shown to be $2C_6H_4Br{\cdot}NMe_3Cl_2Br+2I_2 \rightarrow C_6H_4Br{\cdot}NMe_3ClBrI+C_6H_4Br{\cdot}NMe_3Cl_2I+ICl+IBr$. H. BURTON.

Basis for the physiological activity of -onium compounds. VII. Derivatives of betaines. R. R. RENSHAW and H. T. HOTCHKISS (J. Amer. Chem. Soc., 1926, **48**, 2698—2702; cf. this vol., 1027).—Treatment of trimethylamine with methyl bromoacetate in toluene at −10° affords *methylbetaine* [*trimethylcarbomethoxymethylammonium bromide*], m. p. 182·5°. *Trimethylcarbethoxymethylammonium bromide*, m. p. 158·4°, *trimethylcarbo*-n-*butoxymethylammonium bromide*, m. p. 100·4°, and *trimethylcarbobenzyloxymethylammonium bromide*, m. p. 111·5°, are obtained analogously. Ethyl bromopropionate and trimethylamine yield similarly *trimethyl*-α-*carbethoxyethylammonium bromide*, m. p. 146·5°. Ethyl-α-bromovalerate, ethyl bromo-*n*-hexoate, and ethyl phenylbromoacetate afford, in the same way, *trimethyl*-α-*carbethoxybutylammonium bromide*, m. p. 179·6°, *trimethyl*-α-*carbethoxyamylammonium bromide*, m. p. 144·5°, and *trimethylcarbethoxybenzylammonium bromide*, m. p. 197·5—198°, respectively. Treatment of chloroacetamide with trimethylamine in toluene at 70° affords *betaineamide* (*trimethylcarboxylamidomethylammonium chloride*), m. p. 194·5°. All these derivatives of betaine, in which the acidic hydrogen has been replaced, are physiologically active, and it is suggested that the inactivity of betaine is due to its existence in the blood-stream as the electrically neutral ion $^{+}[NMe_2{\cdot}CH_2{\cdot}CO_2]^{-}$, which is inert on account of this neutrality, whilst the activity of the above esters and amide is due to their yielding electrically active cations. F. G. WILLSON.

Pharmacological behaviour of aliphatic diamines. J. VON BRAUN, O. GOLL, and E. METZ (Ber., 1926, 59, [*B*], 2416—2425).—The pharmacological activity of substances of the type $NHR{\cdot}[CH_2]_n{\cdot}NH_2$ (*R* = β-1 : 2 : 3 : 4-tetrahydronaphthyl or the piperazine residue) attains its maximum when $n = 5$ and is almost absent when $n = 2$, 3, or 7.

β-*p*-Chloromethylphenylethylamine hydrochloride (cf. A., 1925, i, 1406) is converted by benzoyl chloride and alkali hydroxide into the corresponding *benzoyl* derivative, m. p. 120—122°.

Treatment of 1 : 2 : 3 : 4-tetrahydro-2-naphthylamine with β-bromoethylphthalimide and hydrolysis of the product by hydrochloric acid at 120° affords 2-β-*aminoethylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 155—160°/13 mm. (*dihydrochloride*, m. p. 218°; *picrate*, m. p. 207°). 2-γ-*Aminopropylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 193—197°/20 mm. (*picrate*, m. p. 200°; *dihydrochloride*, m. p. 217°), is similarly prepared. Tetrahydronaphthylamine and *N*-δ-chlorobutylbenzamide afford 2-δ-*benzamidobutyl*-

amino-1 : 2 : 3 : 4-*tetrahydronaphthalene hydrochloride*, m. p. 235°, from which 2-δ-*benzamidobutylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 320°/12 mm., and 2-δ-*aminobutylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 190°/12 mm. (*dihydrochloride*, m. p. not below 300°; *picrate*, m. p. 166°), are derived.

Similar methods lead to the preparation of 2-ε-*benzamidoamylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 322°/12 mm., m. p. 180° (*hydrochloride*, m. p. 215°), 2-ε-*aminoamylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 210°/14 mm. (*dihydrochloride*, m. p. 270°; picrate, m. p. 125°), 2-ζ-*benzamidohexylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. about 280°/2 mm. (slight decomp.) (*hydrochloride*, m. p. 236°), and 2-ζ-*aminohexylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 221°/12 mm. (*dihydrochloride*, m. p. 295°; *picrate*, m. p. 175°). 2-η-*Benzamidoheptylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. about 340°/12 mm., m. p. 140° (*hydrochloride*, m. p. 183°), and 2-η-*aminoheptylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 232°/12 mm. (*dihydrochloride*, m. p. 295°; *picrate*, m. p. 195°), are described. 2-p-β-*Benzamidoethylbenzylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 105° (*hydrochloride*, m. p. 224°), and 2-p-β-*aminoethylbenzylamino*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 270—280°/2 mm. (*dihydrochloride*, m. p. not below 300°; *picrate*, decomp. 120°), have been prepared. *N*-ε-Chloroamylbenzamide and β-phenylethylamine afford *phenylethyl*-ε-*benzamidoamylamine* β-*hydrochloride*, m. p. 184°, from which the corresponding free *base*, b. p. 300°/15 mm., and β-*phenylethyl*-ε-*aminoamylamine*, b. p. 185—187°/20 mm. (*dihydrochloride*, m. p. 300°; *picrate*, decomp. 173°; non-crystalline *dibenzoyl* derivative), are derived.

Similarly p-*benzamidoethylbenzyl*-β-*phenylethylamine hydrochloride*, m. p. 242°, yields successively the benzoylated *base*, m. p. 91°, and p-β-*aminoethylbenzyl*-β-*phenylethylamine*, b. p. 235—240°/15 mm. (*picrate*, m. p. 165°; *dihydrochloride*, m. p. not below 300°; *dibenzoyl* derivative, m. p. 135°; diquaternary *methiodide*, m. p. 250°).

Piperazine and β-bromoethylphthalimide readily yield 1 : 4-di-β-phthalimidoethylpiperazine (isolated as the *dihydrobromide*, which does not melt below 300°), which is hydrolysed to 1 : 4-*di*-β-*aminoethylpiperazine*, b. p. 130°/12 mm., m. p. 40° (non-crystalline *hydrochloride*; *picrate*, decomp. 228°; *picrolonate*, decomp. 250°). 1 : 4-*Di*-γ-*phthalimidopropylpiperazine hydrobromide*, decomp. 300°, and 1 : 4-*di*-γ-*aminopropylpiperazine*, b. p. 155—158°/14 mm. (*tetrahydrochloride*, m. p. not below 300°; *picrate*, decomp. 250°), are described. 1 : 4-*Di*-δ-*benzamidobutylpiperazine hydrochloride*, m. p. 248° (decomp.), is hydrolysed to 1 : 4-*di*-δ-*aminobutylpiperazine*, b. p. 175°/14 mm. [*tetrahydrochloride*; *picrate*, m. p. 242° (decomp.)]. 1 : 4-Di-ε-aminoamylpiperazine is converted by ε-chloroamylbenzamide into the *hydrochloride* of 1 : 4-di-ε-aminoamyl-ε-aminoamylpiperazine, from which the free *base*, $C_4H_8N_2([CH_2]_5{\cdot}NH{\cdot}[CH_2]_5{\cdot}NH_2)_2$, b. p. about 230°/0·1 mm. (non-crystalline *acetyl* and *benzoyl* derivatives and *methiodide*), is obtained. 1 : 4-*Di*-η-*benzamidoheptylpiperazine hydrochloride*, m. p. 205°, the corresponding non-crystalline benzoylated base, and 1 : 4-*di*-η-*aminoheptylpiperazine*, m. p. 54° (hygroscopic *hydrochloride*; *picrate*, m. p. 107—110°), are described. 1 : 4-*Di*-p-β-*benzamidoethylbenzylpiperazine dihydrochloride*, m. p. 260°, is hydrolysed to *di*-p-β-*aminoethylbenzylpiperazine*, m. p. 88—90° (*tetrahydrochloride*, m. p. not below 360°; *picrate*, m. p. 92°). Trimethylene bromide and 1 : 2 : 3 : 4-tetrahydro-β-naphthylamine yield *di*-2-1 : 2 : 3 : 4-*tetrahydronaphthyltrimethylenediamine dihydrobromide*, m. p. 271°; the corresponding *base*, $C_{10}H_{11}{\cdot}NH{\cdot}[CH_2]_3{\cdot}NH{\cdot}C_{10}H_{11}$, b. p. 295—297°/12 mm., m. p. 60°, gives a *dinitroso*-compound, m. p. 163° (decomp.). *Di*-2-1 : 2 : 3 : 4-*tetrahydronaphthylheptamethylenediamine*, its *hydrochloride*, m. p. 265°, non-crystalline *picrate*, and *picrolonate*, m. p. 248—249°, are described. Ethylene bromide and 1 : 2 : 3 : 4-tetrahydro-β-naphthylamine give almost exclusively the diquaternary *piperazine* derivative,

$$(Br)C_{10}H_{11}N<\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}>N{\cdot}C_{10}H_{11}(Br),$$ m. p. 292°.

Catalytic hydrogenation of *p*-ethoxymethylphenylacetonitrile yields a very considerable proportion of the corresponding secondary base, converted by hydrogen chloride in alcohol at 100° into *di*-β-*p*-*chloromethylphenylethylamine hydrochloride*, m. p. 253°.

H. WREN.

Catalytic reduction of dimethylglyoxime. βγ-Diaminobutane. J. FREJKA and L. ZAHLOVA (Publ. Fac. Sci. Masaryk, 1926, [73], 3—39; cf. A., 1890, 954).—Dimethylglyoxime is reduced when agitated with hydrogen in glacial acetic acid in presence of platinum-black, the products being a mixture (b. p. 56—60°/55 mm., d_4^{20} 0·90024, n_D^{20} 1·44496) of the mono- and hemi-hydrates of βγ-diaminobutane in addition to other fractions. Besides the *diacetyl* and *dibenzoyl* derivatives of βγ-diaminobutane, the following have been prepared: *dihydrochloride*, *dihydrobromide*, *dihydriodide*, *sulphate*, *chromate*, *chloroplatinate*, chloroaurate, oxalate, *succinate*, *picrate*, and *picrolonate*. With phenylcarbimide, a *compound*, $CHMe(NH{\cdot}CO{\cdot}NHPh){\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}NHPh$, m. p. 230°, is formed, and with ethyl acetoacetate a *compound*, $CHMe(NH{\cdot}CMe{:}CH{\cdot}CO_2Et){\cdot}CHMe{\cdot}NH{\cdot}CMe{:}CH{\cdot}CO_2Et$, m. p. 59°.

B. W. ANDERSON.

Configuration of bistriaminopropane metallic complexes. F. G. MANN and (SIR) W. J. POPE (J.C.S., 1926, 2675—2681; cf. A., 1924, i, 1049).—Complex compounds of the type $[Co\ ptn_2]Cl_3$ [ptn = $NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2$] should exist in three isomeric forms, one of which is symmetric and the other two disymmetric, assuming the hexamminocobaltic complex to have an octahedral configuration. Spatial considerations indicate that the symmetrical form is the most stable, a conclusion supported by the failure to resolve the bistriaminopropanecobaltic complex into optically active forms. An improved method for preparing bistriaminopropanecobaltic chloride is given, and *bistriaminopropanecobaltic thiocyanate*, $[Co\ ptn_2](SCN)_3$, m. p. 286—288° (decomp.), is described.

Bistriaminopropanecobaltic d-*camphor*-β-*sulphonate*, $[Co\ ptn_2](C_{10}H_{15}SO_4)_3,EtOH$, m. p. (alcohol-free) 285—286° (decomp.), $[\alpha]_{5780}$ (alcohol free) +17·4° in

water, prepared from the corresponding cobaltic iodide and silver *d*-camphor-β-sulphonate, on treatment with excess calcium chloride solution, gave bistriaminopropanecobaltic chloride, $[\alpha]_{5780}$ +3·6° in water. The cobaltic *l*-camphor-β-sulphonate, $[\alpha]_{5780}$ −17·4° in water, gave a completely inactive chloride.

Bistriaminopropanecobaltic d-α-*bromocamphor-π-sulphonate*, $[Co\ ptn_2](C_{10}H_{14}SO_4Br)_3,5H_2O$, m. p. (anhydrous) 266—267° (decomp.), $[\alpha]_{5780}$ (anhydrous) +75·3° in water, when dried over calcium chloride at atmospheric pressure gave a stable *dihydrate*. *Bistriaminopropanecobaltic* d-*camphor*-α-*nitronate*, $[Co\ ptn_2](C_{10}H_{14}O{\cdot}NO_2)_3$, m. p. 242—245° (decomp.), gave an inactive bromide. The following *bistriaminopropanenickelous* salts are described: the *iodide*, $[Ni\ ptn_2]I_2$; *sulphate pentahydrate*, $[Ni\ ptn_2]SO_4,5H_2O$. Attempts to prepare $[Co(NH_3)_3\ ptn]Cl_3$ resulted in the formation of the $[Co\ ptn_2]$ complex. Nickel salts gave similar results. *Triaminopropane dihydrochloride monohydriodide*, m. p. 303—304° (decomp.), is obtained by treating a highly concentrated aqueous solution of the trihydrochloride with potassium iodide solution. H. BURTON.

Complex salts of αβγ-triaminopropane with copper and platinum. F. G. MANN (J.C.S., 1926, 2681—2688; cf. preceding abstract).—Triaminopropane forms two types of complexes with cupric salts in which the metal shows a co-ordination number of four. No compounds with the metal showing a co-ordination number of six could be obtained. Examples of the first type are: *tetratriaminopropanetricupric hexaiodide*, $[Cu_3\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2\}_4]I_6$, m. p. 236—237° (decomp.), and the *hexathiocyanate*, m. p. 184—185° (decomp.), where four molecules of the base are co-ordinated with three atoms of copper. In the second type of compound, one atom of copper is associated with two molecules of the base, but one amino-group in each molecule of triaminopropane is free, forming salts, such as *bis(triaminopropanemonothiocyanate)cupric thiocyanate*, $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HSCN\}_2](SCN)_2$ or $[Cu\{NH_2{\cdot}CH_2{\cdot}CH(NH_2,HSCN){\cdot}CH_2{\cdot}NH_2\}_2](SCN)_2$, m. p. 174—175° (decomp.), and *bis(triaminopropanemonohydrobromide)cupric bromide dihydrate*. The configuration of the second type of compound is discussed fully. With platinum, the following compounds have been prepared: *tetrachloro(triaminopropanemonohydrochloride)platinum monohydrate*, $[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CH_2{\cdot}NH_2,HCl]H_2O$, m. p. 272—273° (decomp.), m. p. (anhydrous) 273—274° (decomp.); *tetrachloro(triaminopropanemonohydrochloride)platinum chloroplatinate monohydrate*, $\{[Cl_4PtNH_2{\cdot}CH_2{\cdot}CH(NH_2)]{\cdot}CH_2{\cdot}NH_2,HCl\}_2PtCl_4,H_2O$, and *tetrabromo(triaminopropanemonohydrochloride)-platinum monohydrate*, m. p. 262—263° (decomp.). H. BURTON.

Synthesis of spermine. H. W. DUDLEY, O. ROSENHEIM, and W. W. STARLING (Z. physiol. Chem., 1926, **159**, 199—200).—See this vol., 1128.

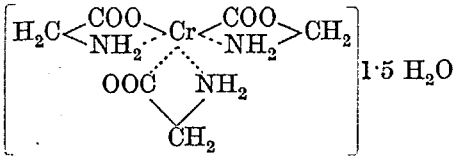
Action of Grignard reagent on amino-acids. VIII. F. BETTZIECHE and A. EHRLICH (Z. physiol. Chem., 1926, **160**, 1—24; cf. A., 1925, i, 250, 251, 257; this vol., 154, 155).—Leucine ester hydrochloride with magnesium phenyl bromide gives β-*amino-αα-diphenyl*-β-iso*butylethanol*, m. p. 112·5°, yield 62% (*benzoyl* derivative, m. p. 184°). Leucine ester hydrochloride with magnesium benzyl bromide gives β-*amino-αα-dibenzyl*-β-iso*butylethanol*, m. p. 102·5°, yield 61%. The diphenylethanol treated with sodium nitrite in acetic acid solution gave iso*butyldeoxybenzoin*, m. p. 77°, yield 80%. The diphenylethanol when heated with alcoholic sodium hydroxide for 6 hrs. is unchanged, but when heated in aqueous solution at 200° in a sealed tube for 5 hrs. yields benzophenone and *iso*amylamine. The dibenzylethanol, treated similarly, is unchanged when heated with alkali, but in a sealed tube at 210° yields dibenzyl ketone and *iso*amylamine. β-Amino-αα-dibenzylethanol, β-amino-αα-diphenyl-β-*iso*butylethanol, β-amino-β-phenyl-αα-dibenzylethanol, and β-amino-αα-dibenzyl-β-*iso*butylethanol when heated for 8 hrs. with 20% hydrochloric acid and β-amino-αα-dibenzylethanol, β-amino-αα-dibenzylpropanol, β-amino-αα-dibenzyl-β-*iso*butylethanol, β-amino-β-phenyl-αα-dibenzylethanol, and β-amino-ααβ-tribenzylethanol, on keeping for several hours with concentrated sulphuric acid are unchanged. β-Amino-β-phenyl-αα-dibenzylethanol, heated for 5 hrs. at 160° in an autoclave, gives a 3-*phenyl*-2-*benzylindene*, m. p. 101°, yield 94%, oxidised by permanganate to benzoic and *o*-benzoylbenzoic acids. This substance in ethereal solution, on passing a slow stream of nitrogen trioxide for a short time, gives an isomeric hydrocarbon, m. p. 92°, yield 90%; with a quick stream of trioxide passed for a longer time, a *substance*, $C_{22}H_{18}O_4N_2$, m. p. 163—164°, is obtained in small amount. ωω-Dibenzylacetophenone when treated with 20% hydrochloric acid in a sealed tube for 5 hrs. at 150° or when kept with sulphuric acid is unchanged and cannot therefore be intermediate in the formation of the indene. Ethyl mandelate and magnesium benzyl bromide give αβ-*dihydroxy*-β-*phenyl*-αα-*dibenzylethane*, m. p. 116°, yield 54%, which both on heating in a sealed tube for 5 hrs. at 145° with 25% hydrochloric acid and on shaking in benzene with phosphoric oxide and keeping gives αγδ-triphenylbutan-β-one, m. p. 77°. P. W. CLUTTERBUCK.

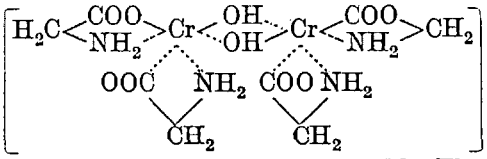
Synthetic preparation of substances containing adsorbed amino-acid. I. Action of aluminium amalgam on formylglycine. II. Action of aluminium amalgam on *dl*-formylleucine. A. FODOR and M. FRANKEL (Z. physiol. Chem., 1926, **159**, 133—149, 150—162).—I. Formylglycine heated with aluminium amalgam in aqueous solution for 12—13 hrs., yields on filtration a yellow, opalescent solution which shows the Tyndall effect, dense aggregates, and sporadically moving particles under the ultramicroscope, and the phenomenon of cataphoresis, the solution migrating to the cathode. The liquid contains a considerable amount of aluminium, gives a strong ninhydrin reaction, and with ferric chloride and silver nitrate gives the reactions for free formic acid. The liquid still contains amino-acid after ultradialysis for 20 hrs., and with alcohol gives a milky fluid from which the larger particles can be filtered off on a collodion membrane. This residue, after carefully washing, when suspended in

water still gives the ninhydrin reaction, contains aluminium, and shows the Brownian movement under the ultramicroscope.

II. A similar result is obtained on treating *dl*-leucine with aluminium amalgam in alcohol. Part of the colloidal material may be separated by ultrafiltration, but both the filtrate and the residue suspended in alcohol give the ninhydrin reaction, show the Brownian movement, and contain aluminium. The alcoholic sol on addition of water gives a milky fluid from which almost the whole of the colloidal material is separated by ultrafiltration. P. W. CLUTTERBUCK.

Complex compounds of chromium with amino-acids. P. B. SARKAR (Bull. Soc. chim., 1926, [iv], **39**, 1385—1389).—Contrary to the conclusions of Florence and Couture (this vol., 715), the red and violet compounds of chromium and glycine are considered to have the structures (I) and (II), respectively, whilst the asparagine compound described by these authors can be represented by a structure

(I.) 

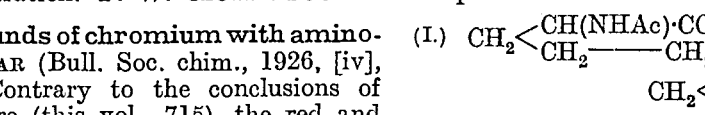
(II.) 

analogous to (I). The structure proposed by Florence and Couture for their chlorohydratoglycine compound of chromium is not accepted. A. S. CORBET.

α-Amino-*N*-carboxylic anhydrides. III. High molecular compounds. F. WESSELY and F. SIGMUND (Z. physiol. Chem., 1926, **159**, 102—119).—Sarcosine-*N*-carboxylic anhydride on exposure to moist air for 3 days at the ordinary temperature decomposes into sarcosine, sarcosine anhydride, and an anhydride, mol. wt. in molten phenol >350, which decomposes on sublimation into sarcosine anhydride. By the action of pyridine on sarcosine-*N*-carboxylic anhydride at the ordinary temperature, an anhydride is obtained, mol. wt. 630 in molten phenol, having the composition of sarcosine anhydride. It is not identical with the anhydride obtained by the action of water vapour (cf. A., 1925, i, 1151; this vol., 960). P. W. CLUTTERBUCK.

Aminohydroxy-compounds which show the biuret reaction. II. Synthesis of γ-hydroxyornithine. M. TOMITA and T. FUKAGAWA (Z. physiol. Chem., 1926, **158**, 58—61).—Ethyl sodiophthalimidomalonate, freed from alcohol, is condensed with γ-chloro-β-hydroxypropylphthalimide at 150—190° to form *ethyl phthalimido-(γ-phthalimido-β-hydroxypropyl)malonate* [*ethyl αδ-diphthalimido-γ-hydroxy*-n-*butane-αα-dicarboxylate*], which without purification is hydrolysed by hydrochloric acid to *γ-hydroxyornithine* (*αδ-diamino-γ-hydroxy*-n-*valeric acid*) [*picrolonate*, m. p. 250° (decomp.)]. The product shows the biuret reaction. C. HOLLINS.

Arginine and its conversion into ornithine. M. BERGMANN and H. KÖSTER (Z. physiol. Chem., 1926, **159**, 179—189).—*d*-Arginine on shaking for 3 hrs. with acetic anhydride gives *monoacetyl*-dl-*arginine*, m. p. 266°, yield 90%. On boiling with 2*N*-hydrochloric acid, inactive arginine is obtained. *d*-Arginine, heated with excess of acetic anhydride, yields optically inactive *triacetylanhydro*-dl-*arginine* (I), m. p. 164°, which, on keeping in aqueous solution for 24 hrs., yields diacetylcarbamide and *acetyl-anhydro*-dl-*ornithine* (dl-3-*acetamido*-2-*piperidone*), m. p. 187—188°. Formula II is assigned, since the

(I.)  (II.)

substance reacts neither acid nor alkaline. The piperidone on heating for 4 hrs. with *N*-hydrochloric acid yields *dl*-ornithine. P. W. CLUTTERBUCK.

Exhaustive methylation of *l*-leucylproline. Formation of hydroxyacylamido-acid amides from halogenoacylamido-acids in aqueous ammonium hydroxide. E. ABDERHALDEN and H. SICKEL (Z. physiol. Chem., 1926, **159**, 163—171).—Prolyl-*l*-leucine, m. p. 231—232°, is prepared in small yield (20%) by the action of *l*-leucine and dibromovaleryl chloride in alkaline solution, the product being kept in aqueous ammonium hydroxide for 4 days. When heated at 180° in a vacuum over phosphoric oxide, it yields *prolyl*-l-*leucine anhydride*, m. p. 158—159°. When the anhydride is treated for 2 days with *N*-barium hydroxide solution, *l*-leucylproline, m. p. 100° after softening at 90°, $[\alpha]_D^{17}$ +50·96°, is obtained. The ninhydrin reaction is positive, the carbonyl reaction negative. It reacts faintly acid to litmus. Exhaustive methylation with diazomethane gives a small amount of *methyl dimethyl-N-leucylproline*. In the preparation of prolyl-*l*-leucine above, the chief product is an optically inactive powder, $C_5H_9O_2N,0{\cdot}5H_2O$, m. p. 190—192° (cf. this vol., 748). P. W. CLUTTERBUCK.

Transformations of peptide substances. XI. Dehydrogenation of asparagines. M. BERGMANN, E. KANN, and A. MIEKELEY (Annalen, 1926, **449**, 135—145; cf. this vol., 743).—When asparagine reacts with α-bromopropionyl bromide in sodium hydroxide solution, it yields the *α-bromopropionyl* derivative, m. p. 158—159°, $[\alpha]_D^{19}$ −6·6° in water, which on treatment with acetyl chloride yields *propionamidomaleic* (or *fumaric*) *monoamide*, $CO_2H{\cdot}C(NH{\cdot}COEt){:}CH{\cdot}CO{\cdot}NH_2$, m. p. 180—181°. This monoamide yields: with diazomethane, a substance which is probably *propionamidomaleinimide*, m. p. 174—175°; with boiling water, *ammonium hydrogen propionamidomaleate*, m. p. 141°, which with excess of diazomethane in methyl-alcoholic solution yields the *dimethyl* ester, b. p. 130°/1 mm.; with acetic anhydride or sulphuric acid, *propionamidomaleic anhydride*, m. p. 108°; with boiling 5*N*-hydrochloric acid, oxalacetic acid, which decomposes, yielding pyruvic acid. Reduction of the dimethyl ester using hydrogen and palladium-black gives a quantitative yield of *methyl* dl-*propionamido-*

succinate, b. p. 150°/1·5 mm., m. p. 46—48°, n_D^{18} 1·4592, which is readily hydrolysed to *dl*-aspartic acid. R. W. WEST.

Transformations of peptide substances. XIII. Synthesis of dipeptides and their anhydrides. M. BERGMANN, F. STERN, and C. WITTE (Annalen, 1926, **449**, 277—302).—When *d*-glutamic acid is treated with the lactimide of α-acetamidocinnamic acid (cf. Bergmann and Stern, this vol., 743), it yields *α-acetamidocinnamoyl-d-glutamic acid*, m. p. 170° (corr., decomp.), $[\alpha]_D^{21}$ −4·19° in pyridine, which on reduction with hydrogen and palladium-black yields a mixture of N-*acetyl*-l-*phenylalanyl*-d-*glutamic acid*, m. p. 140° (corr.), $[\alpha]_D^{23}$ +5·6° in ethyl alcohol [*dimethyl* ester, m. p. 135° (corr.), $[\alpha]_D^{21}$ −9·12° in methyl alcohol], and N-*acetyl*-d-*phenylalanyl*-d-*glutamic acid* (*dimethyl* ester, m. p. 129°, $[\alpha]_D^{23}$ −21·2° in methyl alcohol). The two acids last named on hydrolysis with concentrated hydrochloric acid yield *l*- and *d*-phenylalanine, whilst they are converted by dilute acid into l-*phenylalanyl*-d-*glutamic acid*, m. p. 235° (corr.), $[\alpha]_D^{20}$ +20·27° in water [*anhydride*, m. p. 242—244° (corr.)], and d-*phenylalanyl*-d-*glutamic acid*, m. p. 216° (corr.).

Similarly, if *l*-tyrosine is used instead of *d*-glutamic acid, the following compounds are obtained: *α-acetamidocinnamoyl*-l-*tyrosine*, m. p. 217—218° (corr.), $[\alpha]_D^{20}$ +47·1° in pyridine; N-*acetyl*-d-*phenylalanyl*-l-*tyrosine*, m. p. 237° (corr.), $[\alpha]_D^{20}$ +25·2° in pyridine; d-*phenylalanyl*-l-*tyrosine anhydride*, m. p. 267° (corr.); l-*phenylalanyl*-l-*tyrosine anhydride* (?), m. p. 300°.

N-Acetyl-*dl*-phenylalanine yields a *lactimide* (dl-2-*methyl*-4-*benzyloxazolin*-5-*one*), b. p. 118°/0·8 mm., which with aqueous ammonia yields the *amide*, m. p. 165°, and with glycine ester gives *ethyl acetyl*-dl-*phenylalanylamidoacetate*, m. p. 135°, a substance which is hydrolysed by dilute hydrobromic acid to dl-*phenylalanylglycine hydrobromide*, m. p. 211° (decomp.).

Similarly, acetyl-*dl*-leucine yields a *lactimide*, b. p. 73—75°/0·4 mm., and an *amide*, m. p. 202°; the lactimide yielding with glycine ester *ethyl* N-*acetyl*-dl-*leucylamidoacetate*, m. p. 121°, and with *dl*-alanine an *acetyl-leucylalanine*, m. p. 203°.

When aspartic acid is treated with acetic anhydride, it yields *acetamidosuccinic anhydride*, m. p. 141°, which reacts with glycine ester, yielding the *glycine* ester salt of *ethyl* N-*acetamidosuccinylamidoacetate*, m. p. 142°. R. W. WEST.

Nucleic acid structure as determined by electrometric titration data. P. A. LEVENE and H. S. SIMMS (J. Biol. Chem., 1926, **70**, 327—341).—Application of the graphical method (this vol., 1265) to the comparison of the experimentally determined titration curve of yeast nucleic acid with the theoretical curve constructed from the dissociation constants on the basis of the authors' theory of the nucleic acid structure, shows a close correspondence over the range p_H 5·5—11·5, no evidence being found of the existence of the secondary phosphoric acid group which is required by the theory of Jones. Samples of nucleic acid from the thymus and the spleen also showed good agreement between the theoretical and observed curves; such deviations from the theoretical as were observed could be correlated with the presence of small amounts of impurity, and also with a certain degree of anhydride formation involving partial suppression of the primary phosphoric acid groups. C. R. HARINGTON.

Supposed isomeride of methyleneaminoacetonitrile. Methylenebisiminodiacetonitrile. M. DELÉPINE (Bull. Soc. chim., 1926, [iv], **39**, 1439—1443).—See this vol., 943.

β-Hydroformamine cyanide. H. W. RINEHART (J. Amer. Chem. Soc., 1926, **48**, 2794—2798).—Alkaline hydrolysis of β-hydroformamine cyanide, $C_9H_{12}N_6$ (cf. Rinehart and Johnson, A., 1924, i, 1052), yields ammonia only as a volatile base, and in presence of hydrochloric acid the compound reacts with liquid hydrogen cyanide to give nitrilotriacetonitrile, $N(CH_2{\cdot}CN)_3$. The crystalline hydrolysis compound previously described is now shown to be the hydrochloride of iminodiacetic acid, probably produced from iminodiacetonitrile formed as an intermediate hydrolysis product, and 2 mols. of this appear to be incorporated in the molecule of the β-isomeride. These facts suggest that the latter is identical with methylenebisiminodiacetonitrile, $C_9H_{10}N_6$ (cf. Klages, A., 1903, i, 469): $CH_2[N(CH_2{\cdot}CN)_2]_2+H_2O \longrightarrow CH_2O+2NH(CH_2{\cdot}CN)_2$; $2NH(CH_2{\cdot}CN)_2+4H_2O \longrightarrow 2NH(CH_2{\cdot}CO_2H)_2+4NH_3$; also $CH_2[N(CH_2{\cdot}CN)_2]_2+HCN \longrightarrow NH(CH_2{\cdot}CN)_2+N(CH_2{\cdot}CN)_3$. This conclusion is confirmed by the synthesis of methylenebisiminodiacetonitrile by the condensation of formaldehyde with iminodiacetonitrile at the ordinary temperature, the product being identical with β-hydroformamine cyanide. Evidence has been obtained that two of the nitrile groups in the compound are not disclosed by interaction with hydrogen sulphide. S. K. TWEEDY.

Esters of formiminic and formhydroximic acids. J. HOUBEN and E. PFANKUCH (Ber., 1926, 59, [*B*], 2392—2397; cf. A., 1923, i, 1077).—*Ethyl formiminate hydrochloride*, $CH(OEt){:}NH,HCl$, is prepared by the action of hydrogen chloride on a solution of anhydrous ethyl alcohol and hydrocyanic acid in light petroleum. The corresponding *methyl* and *benzyl* esters are analogously prepared in the presence of toluene and absence of a solvent, respectively. Treatment of the benzyl compound with hydroxylamine hydrochloride and pyridine in anhydrous ether affords *benzyl formhydroximate*, $OH{\cdot}N{:}CH{\cdot}OCH_2Ph$, m. p. 140°; ethyl acethydroximate (cf. A., 1914, i, 26) is analogously prepared. The ability of alcohols to react with hydrocyanic acid and similar compounds extends to secondary alcohols, as shown by the isolation of *bornyl formiminate hydrochloride*, *bornyl acetiminate hydrochloride*, m. p. 185° (decomp.), and *bornyl acetiminate*, b. p. 70—72°/5 mm., m. p. 46°. *Bornyl acethydroximate* has m. p. 103°. The formhydroximic esters decompose readily into alcohols and a polymeride of cyanic acid, appearing, therefore, to be *anti*-derivatives, $\begin{matrix} H{\cdot}C{\cdot}OAlk \\ \| \\ N{\cdot}OH \end{matrix}$. Acethydroximic esters and phosphorus pentachloride give phosphoric esters of hydroximic esters and hence are also *anti*-derivatives. H. WREN.

Esters of oximinic and α-hydroxyoximinic acids. J. HOUBEN and E. PFANKUCH (Ber., 1926,

59, [*B*], 2397—2402).—Glycollonitrile, prepared by the action of potassium cyanide and dilute sulphuric acid on formaldehyde, is converted by ethyl alcohol and hydrogen chloride in the presence of ether into *ethyl α-hydroxyacetimate hydrochloride*, converted by potassium carbonate in the presence of ether into monomeric *ethyl α-hydroxyacetimate*, m. p. 38—39°, from which *ethyl α-hydroxyacethydroximate*, $CH_2(OH)\cdot C(:N\cdot OH)\cdot OEt$, m. p. 57—58°, is derived. Acetaldehyde gives rise to *ethyl α-hydroxypropimate*, $CH_3\cdot CH(OH)\cdot C(:NH)\cdot OEt$, m. p. 78° (*hydrochloride*), and *ethyl α-hydroxyprophydroximate*, m. p. 74° after softening. *β-Chloro-α-hydroxypropionitrile*, b. p. 77°/0·4 mm., from αβ-dichloroethyl ether and potassium cyanide, is converted by ethyl alcohol and hydrogen chloride in ether into *ethyl β-chloro-α-hydroxypropimate*, m. p. 110—112° (decomp.) when rapidly heated, which gives non-crystalline products with hydroxylamine hydrochloride, probably by reason of the absence of basic properties. *β-Chloro-α-acetoxypropionitrile*, b. p. 96—97°/10 mm., yields *ethyl β-chloro-α-acetoxypropimate hydrochloride*, m. p. 120° (decomp.). *β-Chloro-α-ethoxypropionitrile*, b. p. 75°/13 mm., from αβ-dichloroethyl ether and mercuric cyanide in ether, yields *ethyl β-chloro-α-ethoxypropimate hydrochloride*, converted by water into ammonium chloride and *ethyl β-chloro-α-ethoxypropionate*, b. p. 108°/25 mm.; when heated at 100—120°, the hydrochloride passes into *β-chloro-α-ethoxypropionamide*, m. p. 114°. H. WREN.

Optically active phosphine oxides. J. MEISENHEIMER, J. CASPER, M. HÖRING, W. LAUTER, L. LICHTENSTADT, and W. SAMUEL (Annalen, 1926, 449, 213—248).—When treated with aqueous sodium hydroxide, methylphosphenyl chloride is quantitatively converted into phenyldimethylphosphine (phenyltrimethylphosphonium iodide, m. p. 232°) and phosphenyl chloride. Similarly, ethylphosphenyl chloride ultimately yields phenylmethyldiethylphosphonium iodide, m. p. 108—109°, which reacts with silver oxide, yielding *methyldiethylphosphine oxide*, b. p. 230°. Diphenylethylphosphine, best prepared by the interaction of magnesium ethyl bromide and diphenylchlorophosphine, reacts with propyl iodide, yielding *diphenylethylpropylphosphonium iodide*, m. p. 153—154°, which readily yields dl-*phenylethylpropylphosphine oxide*, m. p. 44—45°. *dl*-Phenylmethylethylphosphine oxide is resolved by conversion into the bromocamphorsulphonate, yielding the *d*-oxide, b. p. 159°/8 mm., $[\alpha]_D$ +22·3° in water, $[\alpha]_D$ +28° in benzene (cf. Meisenheimer and Lichtenstadt, A., 1911, i, 344), and *l-hydroxyphenylmethylethylphosphonium l-bromocamphorsulphonate*, m. p. 94—95°, $[\alpha]_D$ −65·3° in water. Diphenylmethylphosphine, prepared similarly to the ethyl analogue, reacts with propyl bromide, yielding *diphenylmethylpropylphosphonium bromide*, m. p. 158°, which is converted by silver oxide into dl-*phenylmethylpropylphosphine oxide*, b. p. 308—310°.

Phenyldimethylphosphine reacts with benzyl chloride, yielding *phenylbenzyldimethylphosphonium chloride*, m. p. 101°, which with silver oxide yields *phenyldimethylphosphine oxide*, m. p. 100° (*mercuric chloride* compound, m. p. 163°). *Phenylbenzyldiethylphosphonium chloride*, m. p. 194—195°, similarly yields phenyldiethylphosphine oxide, and is decomposed on heating, yielding phenylbenzylethylphosphine, b. p. 204—206°/33 mm., which was purified through the *phenylbenzylmethylethylphosphonium iodide*, m. p. 167—168° (d-*bromocamphorsulphonate*, m. p. 129—130°). When a current of air is passed through a benzene solution of phenyldibenzylphosphine (from phosphenyl chloride and magnesium benzyl chloride), it yields *phenyldibenzylphosphine oxide*, m. p. 174°. *Phenyldibenzylethylphosphonium iodide*, m. p. 150—151°, yields *phenylbenzylethylphosphine oxide*, m. p. 110—111°. *Phenylmethyldibenzylphosphonium iodide*, m. p. 206—208° (*nitrate*, m. p. 162—164°), with silver oxide yields dl-*phenylbenzylmethylphosphine oxide*, m. p. 148—149°, which is resolvable into l-*hydroxyphenylbenzylmethylphosphonium* d-*camphorsulphonate*, m. p. 94°, yielding with ammonia l-*phenylbenzylmethylphosphine oxide*, m. p. 135°, $[\alpha]_D$ −72·5° in water, and the *d*-oxide *l*-sulphonate previously described.

By heating together the appropriate phosphine and alkyl halide, and treating the phosphonium halide with silver oxide, the following substances are obtained: from phenyldiethylphosphine, *phenyltriethylphosphonium bromide*, m. p. 187—189°, and *phenyldiethylallylphosphonium bromide*, m. p. 152—153°; from phenyldimethylphosphine, *phenyl-[β-phenylethyl]dimethylphosphonium bromide*, m. p. 172—172·5°, [β-*phenylethyl*]*dimethylphosphine oxide*, m. p. 58—60° (*mercuric chloride* compound, m. p. 115°), and *phenyldimethylallylphosphonium bromide*, m. p. 113—114°, of which the corresponding hydroxide decomposes on heating into phenyldimethylphosphine oxide (cf. Michaelis and Graeff, A., 1876, i, 274); from diphenylmethylphosphine, *diphenylmethylallylphosphonium bromide*, m. p. 161—163°, which reacts with silver oxide, yielding diphenylmethylphosphine oxide.

When diphenylchlorophosphine, the preparation of which is described, reacts with benzyl bromide, it yields *diphenylbenzylphosphonium chlorobromide*, m. p. 171°, which readily decomposes, yielding diphenylbenzylphosphine oxide. Phosphorus diphenyl bromide is readily obtained by the action of hydrogen bromide on the chloride. R. W. WEST.

Coupling action of the Grignard reagent. II. Magnesium methyl iodide and benzyl halides. R. C. FUSON (J. Amer. Chem. Soc., 1926, 48, 2681—2689; cf. this vol., 604).—When benzyl halides are treated with excess of magnesium methyl iodide, about 25% of the former is converted into ethylbenzene, whilst the remainder yields ethane and dibenzyl in equivalent amounts, according to the equation $2PhCH_2X+2MeMgI=CH_2Ph\cdot CH_2Ph+C_2H_6+2MgIX$. The formation of αβγ-triphenylpropane was not observed (cf. Späth, A., 1914, i, 1). F. G. WILLSON.

Compound of chromium sulphate with acetic acid. A. RECOURA (Compt. rend., 1926, 183, 719—721).—When treated with an excess of acetic anhydride, chromium sulphate is slowly transformed into the *compound*, $Cr_2(SO_4)_3,4H_2O,4Ac_2O$, stable in an atmosphere containing acetic anhydride, decomposing in a dry atmosphere slowly, giving the *substance*

$Cr_2(SO_4)_3,4H_2O,Ac_2O$, and decomposing in a damp atmosphere, giving chromium sulphate tetrahydrate.

L. F. HEWITT.

1 : 2-Dimethyl*cyclo*pentane compounds. M. VAN RYSSELBERGE (Bull. Soc. chim. Belg., 1926, **35**, 311—328).—2-Methyl*cyclo*pentanone, prepared in good yield by a modification of the method of Bouveault (A., 1900, i, 171), is converted by magnesium methyl bromide into 1 : 2-*dimethyl*cyclo*pentan*-1-*ol*. The product is a mixture of stereoisomerides, partly separable by distillation, the extreme fractions (probably mainly *cis* and *trans*, respectively) showing m. p. below −20°, +25°, b. p. 145°, 151°/760 mm., 54°, 60·8°/16 mm., n_D^{23} 1·4463, 1·4523, d_4^{20} 0·9064, 0·9156. All fractions are dehydrated on heating with *p*-toluenesulphonic acid to the same 1 : 2-dimethyl*cyclo*pentene, b. p. 100·3—105·3°, d_4^{20} 0·7924—0·7947, n_D^{20} 1·4416—1·4411. This is a mixture of Δ^1- and Δ^5-dimethyl*cyclo*pentenes, since on oxidation the former is converted into heptane-$\beta\zeta$-dione (*semicarbazone*, m. p. 219·8°), and the latter into benzoic acid, presumably by the following stages:

$CH_2<\begin{matrix}CH{=}CMe\\ CH_2{\cdot}CHMe\end{matrix}\rightarrow$
$Me{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CHMe{\cdot}OH\rightarrow$
$CMe(OH){:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH_2\rightarrow Ph{\cdot}Mo\rightarrow Ph{\cdot}CO_2H$.

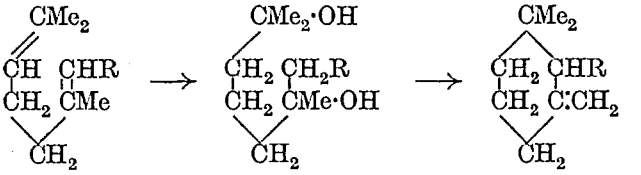
Catalytic reduction of this dimethyl*cyclo*pentene in acetic acid, using platinum-black, affords a dimethyl*cyclo*pentane, b. p. 94—98°/760 mm., d_4^{20} 0·7664, n_D^{20} 1·4187, t_{cs} in aniline, 42°. This probably contains an excess of the *cis*-isomeride, whilst that obtained in other ways by Kijner (A., 1908, i, 865) must be mainly the *trans*-derivative.

H. E. F. NOTTON.

Spatial structure of *cyclo*paraffins. II. Structure of 1 : 1-disubstituted *cyclo*hexanes. W. A. WIGHTMAN (J.C.S., 1926, 2541—2545).—Pentamethylene dibromide condensed with methyl disodiomalonate yields *dimethyl* cyclo*hexane*-1 : 1-*dicarboxylate*, b. p. 119°/14 mm., which on partial hydrolysis gives 1-*methyl* 1′-*hydrogen* cyclo*hexane*-1 : 1′-*dicarboxylate*, m. p. 75°. Treatment of the latter with hydrazine furnishes cyclo*hexane*-1′-*carboxylic acid*-1-*hydrazide*, m. p. 156° (decomp.), which is converted through the azoimide into 1-*carbamyl*cyclo*hexane*-1′-*carboxylic acid*, m. p. 149° (decomp.). Treatment of this acid with diazomethane yields 1′-*methyl* 1-*carbamyl*cyclo*hexane*-1′-*carboxylate*, m. p. 90—91°, identical with 1-*methyl* 1′-*carbamyl*cyclo*hexane*-1-*carboxylate*, m. p. 91·5°, which is obtained from 1-methyl 1′-hydrogen *cyclo*hexane-1 : 1′-dicarboxylate by treatment with thionyl chloride followed by ammonia. These results show that in this series of derivatives the rigid form of the *cyclo*hexane ring does not exist as a static modification (see A., 1925, i, 894).

H. BURTON.

Cyclic compounds [γ-*cyclo*geraniolenes]. III. R. ESCOURROU (Bull. Soc. chim., 1926, [iv], **39**, 1460—1470).—The tertiary methylheptenols previously described (this vol., 1022) when heated with anhydrous oxalic acid, 70% sulphuric acid, orthophosphoric acid (*d* 1·7), or pyrophosphoric acid are converted into new cyclic hydrocarbons, γ-cyclo*geraniolenes*. They contain a methylene group, affording formaldehyde on treatment with ozone, and the ring-formation is accordingly represented:



The presence of the tertiary hydroxyl is not essential, since with anhydrous oxalic acid at 150° or with oxalic acid +1 mol. of water $\beta\zeta$-dimethyloctadiene affords the same cyclic hydrocarbon as $\beta\zeta$-dimethyl-Δ^β-octen-ζ-ol. With 20% oxalic acid, the latter yields mainly the diolefine previously obtained by the action of metaphosphoric acid. Further evidence in support of the structure proposed for these γ-*cyclo*geraniolenes is afforded by the failure of ζ-phenyl-β-methyl-Δ^β-hepten-ζ-ol to give a corresponding compound. The new compounds absorb very little bromine in chloroform solution and do not yield crystalline nitroso-derivatives by Wallach's method. The following are described: γ-cyclo*geraniolene* (3 : 3-*dimethyl*-1-*methylene*cyclo*hexane*), b. p. 138—141°/739 mm., d^{10} 0·8013, $d^{16·5}$ 0·7970, n_D^{10} 1·44837; *methyl*-γ-cyclo*geraniolene* (2 : 3 : 3-*trimethyl*-1-*methylene*cyclo*hexane*), b. p. 164°/738 mm., d^{11} 0·8320, n_D^{15} 1·46274; *ethyl*-γ-cyclo*geraniolene* (3 : 3-*dimethyl*-2-*ethyl*-1-*methylene*cyclo*hexane*), b. p. 182—184°/745 mm., d^{10} 0·8160, n_D^{10} 1·46235; *dimethyl*-γ-cyclo*geraniolene* (2 : 2 : 3 : 3-*tetramethyl*-1-*methylene*cyclo*hexane*), b. p. 181—183°/756 mm., d^{11} 0·8246, n_D^{12} 1·46275; *propyl*-γ-cyclo*geraniolene* (3 : 3-*dimethyl*-2-*propyl*-1-*methylene*cyclo*hexane*), b. p. 200—202°/741 mm., d^{10} 0·8126, $n_D^{10·5}$ 1·46176; iso*butyl*-γ-cyclo*geraniolene* (3 : 3-*dimethyl*-2-iso*butyl*-1-*methylene*cyclo*hexane*), b. p. 212—213°/742 mm., d^{11} 0·8123, $n_D^{10·5}$ 1·46086, and *phenyl*-γ-cyclo*geraniolene* (2-*phenyl*-3 : 3-*dimethyl*-1-*methylene*cyclo*hexane*), b. p. 105—107°/5 mm., d^{11} 0·9403, n_D^{11} 1·53117.

R. BRIGHTMAN.

Reactions of *cyclo*hexene oxide. P. BEDOS (Compt. rend., 1926, **183**, 562—565).—Alkyl halides react with *cyclo*hexene oxide when heated at 150—190° for 48 hrs., and the following compounds have been obtained: 2-*methoxy*cyclo*hexyl iodide*, b. p. 101°/13 mm., d_{25}^{25} 1·5929, n_D^{25} 1·5340, 2-ethoxy*cyclo*hexyl iodide, b. p. 110°/15 mm., d_{25}^{25} 1·5020, n_D^{23} 1·5206 (cf. Brunel, Diss., Paris, 1905), 2-*ethoxy*cyclo*hexyl bromide*, b. p. 80°/9 mm., d_{25}^{25} 1·2738, n_D^{25} 1·4804, and 2-*propoxy*-cyclo*hexyl bromide*, b. p. 103—104°/14 mm., d_{25}^{25} 1·2330, n_D^{25} 1·4778. Acyl halides react with *cyclo*hexene oxide at low temperatures, and the following products are described: 2-*chloro*cyclo*hexyl acetate*, b. p. 95—96°/11 mm., d_{25}^{25} 1·1182, n_D^{25} 1·4620, 2-*chloro*-cyclo*hexyl propionate*, b. p. 106—107°/11 mm., d_{25}^{25} 1·0835, n_D^{25} 1·4597, and 2-*bromo*cyclo*hexyl acetate*, b. p. 109—110°/11 mm., d_{25}^{25} 1·3603, n_D^{23} 1·4834. The compounds obtained are capable of stereoisomerism. No compound was isolated from the product of reaction of hydroxylamine with *cyclo*hexene oxide.

L. F. HEWITT.

Stereochemistry of *o-cyclo*hexanediols and structure of *cyclo*hexene oxide. P. BEDOS (Compt. rend., 1926, **183**, 750—753).—*cyclo*Hexene oxide yields the same *cyclo*hexane-1 : 2-diol, m. p. 104° (dibenzoate, m. p. 92—93°), by each of the six methods

of hydration investigated. The *trans*-configuration of the glycol, m. p. 104° (cf. Böeseken, A., 1921, i, 663; Godchot, *ibid.*, 1923, i, 327), is confirmed, and *cyclo*hexene oxide must have a similar structure.

L. F. HEWITT.

Coloured secondary fluorenyl halides and the synthesis of α-naphtha-derivatives of difluorenyl. A. WANSCHEIDT (Ber., 1926, 59, [*B*], 2092—2100).—αα-Dinaphthafluorene (cf. Schmidlin and Massini, A., 1909, i, 562), suspended in acetone, is converted by methyl-alcoholic potassium methoxide in the presence of air into *αα-dinaphthafluorenone*, m. p. 272° (corr.), which is reduced by zinc dust and acetic acid to *αα-dinaphthafluorenol*, m. p. 260—270° according to the mode of heating. The carbinol is converted by hydrogen bromide in glacial acetic acid into *αα-dinaphthafluorenyl bromide*, b. p. 234° (decomp.), transformed by sodium iodide in acetone into *αα-dinaphthafluorenyl iodide*, decomp. about 160°. *Chrysofluorenyl chloride*, m. p. 146° (decomp.), and the corresponding *bromide*, m. p. 142° (decomp.), and *iodide*, decomp. 103°, are described. Chrysofluorene is prepared by treating a solution of chrysofluorenol in glacial acetic acid with concentrated hydriodic acid; fluorene and αα-dinaphthafluorene are analogously produced. *9-Iodofluorene*, decomp. about 98°, is prepared from 9-bromofluorene and sodium iodide in acetone. *Dichrysofluorenyl*, $\begin{matrix}C_{10}H_6\\C_6H_4\end{matrix}\!>\!CH\cdot CH<\!\begin{matrix}C_{10}H_6\\C_6H_4\end{matrix}$, m. p. 221° (corr.), is obtained from chrysofluorenyl bromide and sodium iodide in acetone. Bisdi-α-naphthafluorenyl, m. p. 353—355° (cf. Magidson, A., 1925, i, 384), is almost quantitatively obtained from di-α-naphthafluorenone and α-dinaphthafluorenyl bromide. *Fluorenyl-αα-dinaphthafluorene*, $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!>\!CH\cdot CH<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$, m. p. 270° (corr.), is prepared by addition of 9-chlorofluorene dissolved in acetone to a boiling suspension of αα-dinaphthafluorene in acetone containing potassium methoxide. *Chrysofluorenyl-αα-dinaphthafluorene*, $\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\!>\!CH\cdot CH<\!\begin{matrix}C_{10}H_6\\C_6H_4\end{matrix}$, m. p. 267° (corr.), is described.

H. WREN.

Nitration of fluorene. 2 : 5-Dinitrofluorene. G. T. MORGAN and R. W. THOMASON (J.C.S., 1926, 2691—2696).—Nitration of fluorene with fuming nitric acid in glacial acetic acid solution yields mainly 2 : 7-dinitrofluorene, m. p. 269° (decomp.), and a small amount of 2 : 5-*dinitrofluorene*, m. p. 207°. Similar results are obtained by the further nitration of 2-nitrofluorene. Oxidation of 2 : 5-dinitrofluorene with chromium trioxide yields 2 : 5-*dinitrofluorenone*, m. p. 241°, which is identical with the substance obtained by nitrating 4(or 5)-nitrofluorenone prepared from 4-nitrodiphenyleneglycollic acid. Acetylation of 2 : 7-diaminofluorene with acetic anhydride gives the following *acetyl* derivatives, *di-*, m. p. 281°; *tri-*, m. p. 234°; *tetra-*, m. p. 179—181°, whilst boiling acetic acid yields mainly the diacetyl derivatives; a *formyl* derivative, m. p. 272°, is described. Reduction of 2 : 5-dinitrofluorene with sodium hyposulphite gives 2 : 5-*diaminofluorene*, m. p. 175° (*diacetyl* derivative, m. p. 289°).

H. BURTON.

Is the effect produced by a substituent in a benzenoid ring transmitted by the carbon chain, as the theory of induced alternate polarities requires? S. C. J. OLIVIER and G. BERGER (Rec. trav. chim., 1926, 45, 710—721; cf. this vol., 805).—The Friedel and Crafts reaction has been studied from the point of view of the theory of alternate polarities. The velocity constants of the reactions between the three nitrobenzyl chlorides with benzene in presence of aluminium chloride are, for the *o*-derivative $k>0{\cdot}025$, *m*-derivative $k=0{\cdot}025$, and *p*-derivative $k=0{\cdot}0046$ at 30°. The order required by the theory is *meta*>*para*>*ortho*, and it is therefore concluded that in this reaction the determining factor is the direct influence of the catalyst rather than the effect of the alternate polarities induced on the reactivity of the chlorine atom. The reactions of *p*-nitrobenzyl chloride with toluene ($k=0{\cdot}0105$), with benzene ($k=0{\cdot}0045$), and with chlorobenzene ($k=0{\cdot}00084$) were also studied.

W. J. POWELL.

Reaction between organo-magnesium halides and the esters of some sulphur acids. H. GILMAN, J. ROBINSON, and N. J. BEABER (J. Amer. Chem. Soc., 1926, 48, 2715—2718).—The action of magnesium phenyl bromide on di-*n*-butyl and diphenyl sulphites, *n*-butyl *p*-toluenesulphinate, methyl phenylsulphenate(?), ethyl thiolbenzoate, ethyl thionbenzoate, and ethyl dithiobenzoate, and of magnesium benzyl chloride on ethyl *p*-toluenesulphinate, has been examined. In no case was an alkylating action observed similar to that obtaining with alkyl sulphonates and Grignard reagents (cf. Gilman and Beaber, A., 1925, i, 802), the reaction proceeding in all cases analogously with that observed in the case of carboxylic and other esters.

F. G. WILLSON.

Synthesis of tetrahydronaphthalenes and naphthalenes. G. DARZENS (Compt. rend., 1926, 183, 748—750).—β-Phenyl-α-allylpropionic acid, when treated with sulphuric acid, yields 1-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene-3-carboxylic acid*, m. p. 121°, b. p. 203—204°/20 mm. (*methyl* ester, b. p. 170°/15 mm.). When treated with sulphur, the acid is dehydrogenated to 1-*methyl*-3-*naphthoic acid*, m. p. 198—199° (*methyl* ester, b. p. 188°/15 mm., m. p. 39°), which yields 1-methylnaphthalene when its calcium salt is distilled.

L. F. HEWITT.

Substitution of the halogen atom or alkyloxy-radical in 2-chloro-(2-bromo-) and 2-methoxy-(2-ethoxy-)1 : 6 : 8-trinitronaphthalene and in 1-chloro-2 : 4-dinitrobenzene by amino-residues and other groups or atoms. E. J. VAN DER KAM (Rec. trav. chim., 1926, 45, 722—733; cf. this vol., 1029).—The nitro-groups present render the halogen atom or alkyloxy-radical in the trinitronaphthalene derivatives readily replaceable by ·OH, ·OMe, ·OEt, ·OPh, ·S·, and ·S_2·. With aromatic primary amines and with secondary amines, 2-chloro-(2-bromo-)1 : 6 : 8-trinitronaphthalene reacts readily, whilst 1 : 6 : 8-trinitro-2-methoxy-(2-ethoxy-)naphthalene does not react. It is claimed that the large variations in m. p. of the products and their ready isolation render them particularly suitable for the identification of alcohols and amines. The following derivatives of 1 : 6 : 8-trinitronaphthalene were pre-

pared : 2-*phenoxy*-, m. p. 189°; 2-*amino*-, m. p. 300° (decomp.); 2-*methylamino*-, m. p. 257° (decomp.); 2-*ethylamino*-, m. p. 216°; 2-n-*propylamino*-, m. p. 186°; 2-n-*butylamino*-, m. p. 156°; 2-n-*amylamino*-, m. p. 181°; 2-n-*heptylamino*-, m. p. 136°; 2-iso*propylamino*-, m. p. 209°; 2-iso*butylamino*-, m. p. 179°; 2-iso*amylamino*-, m. p. 164°; 2-*allylamino*-, m. p. 158°; 2-*dimethylamino*-, m. p. 226°; 2-*diethylamino*-, m. p. 135°; 2-*di*-n-*propylamino*-, m. p. 135°; 2-*di*-iso*butylamino*-, m. p. 173°; 2-*piperidino*-, m. p. 198° (decomp.); 2-*anilino*-, m. p. 247°; 2-o-*toluidino*-, m. p. 199°; 2-m-*toluidino*-, m. p. 234°; 2-p-*toluidino*-, m. p. 233°; 2-m-*nitroanilino*-, m. p. 251°; 2-p-*nitroanilino*-, m. p. 250°; 2-o-, 2-m-, and 2-p-*chloroanilino*-, m. p. 216°, 239°, and 230°, respectively; 2-o-, 2-m-, and 2-p-*bromoanilino*-, m. p. 216°, 235°, and 245° (all decomp.), respectively; 2-m- and 2-p-*iodoanilino*-, m. p. 249° and 257° (decomp.), respectively; 2-*benzylamino*-, m. p. 238°; 2-α- and -β-*phenylethylamino*-, both of m. p. 219°; 2-*methylanilino*-, m. p. 201°; 2-*ethylanilino*-, m. p. 181°; 2-α-*naphthylamino*-, m. p. 245°; 2-β-*naphthylamino*-, m. p. 243° (decomp.); 2-ac-*tetrahydro*-β-*naphthylamino*-, m. p. 258°; 2-*bornylamino*-, m. p. 288° (decomp.); 2-*camphylamino*-, m. p. 210°; 2-*acetamido*-, m. p. 239—240°. The following are described: *acet*-1 : 6 : 8-*trinitro*-β-*naphthyl*-n-*propylamide*, m. p. 179—180°; 1 : 6 : 8 : 1′ : 6′ : 8′-*hexanitrodinaphthyl sulphide*, m. p. 296—300° (decomp.); 1 : 6 : 8 : 1′ : 6′ : 8′-*hexanitrodinaphthyl disulphide*, $C_{10}H_4(NO_2)_3{\cdot}S{\cdot}S{\cdot}C_{10}H_4(NO_2)_3$, decomp. 255—257°; 2 : 4-*dinitro*-n-*butylaniline*, m. p. 90°; 2 : 4-*dinitro*-n-*amylaniline*, m. p. 81°; 2 : 4-*dinitro*-n-*heptylaniline*, m. p. 20°; 2 : 4-*dinitro*iso*amylaniline*, m. p. 91°; 2 : 4 : 4′-*trinitrodiphenylamine*, m. p. 186° (decomp.); 2 : 3′ : 4-*trinitrodiphenylamine*, m. p. 193°. Other derivatives of 2 : 4-dinitrodiphenylamine prepared were the 2′-, 3′-, and 4′-*chloro*-, m. p. 150°, 184°, and 167°; 2′-, 3′-, and 4′-*bromo*-, m. p. 161°, 178°, and 158°; 3′- and 4′-*iodo*-, m. p. 133° and 176°, respectively. The following are also described: 2 : 4-*dinitro*-α-*phenylethylaniline*, m. p. 118°; 2 : 4-*dinitro*-[ac-*tetrahydro*-β-*naphthyl*]*aniline*, m. p. 152°; 2 : 4-*dinitrobornylaniline*, m. p. 142°; 2 : 4-*dinitrocamphylaniline*, m. p. 103°. W. J. POWELL.

Relation between m. p. and chemical constitution. E. J. VAN DER KAM (Rec. trav. chim., 1926, **45**, 734—744; cf. A., 1897, ii, 542).—A study of the variation of m. p. with constitution of two series of closely-related compounds, viz., the *N*-derivatives of 1 : 6 : 8-trinitro-2-aminonaphthalene and of 2 : 4-dinitroaniline. The introduction of alkyl radicals of ascending mol. wt. causes a progressive decrease in m. p., although the amyl group is abnormal in this respect. Two *N*-alkyl groups each containing *n* carbon atoms depress the m. p. to about the same extent as one such group containing 2*n* carbon atoms, *e.g.*, the ethyl group causes about the same lowering as two methyl groups. Unsaturated radicals such as allyl bring about a greater depression than the corresponding saturated radicals. W. J. POWELL.

Physical properties of nitro-derivatives. L. DESVERGNES (Mon. Sci., 1926, **16**, 201—208).—The following corrected m. p. were determined with a Maquenne block; the figures in brackets denote solubility in 100 g. of water at 50° : 2 : 4 : 6-trinitrobenzoic acid, m. p. 228·5° (decomp.) [4·180]; 2 : 4 : 6-trinitroethylaniline, m. p. 81·2° [0·031]; 2 : 4 : 6-trinitrodiethylaniline, m. p. 167° [0·005]; 2 : 4-dinitrophenyl picrate, m. p. 210° [0·017, with gradual decomp. into picric acid and dinitrophenol]; 2 : 4 : 6-trinitrophenylethylnitroamine, m. p. 95·7° [0·026 with decomp. on heating into *iso*picric acid]. Solubilities in the usual organic solvents are given in all cases. 2 : 4 : 6-Trinitrobenzoic acid and 2 : 4 : 6-trinitrophenylethylnitroamine are decomposed by pyridine, affording 1 : 3 : 5-trinitrobenzene and picolinic acid in the former case and *iso*picric acid in the second. 2 : 4-Dinitrophenyl picrate is decomposed by pyridine on warming and also by ethyl and methyl alcohols, affording picric acid and the corresponding ether of 2 : 4-dinitrophenol.

R. BRIGHTMAN.

Optically active amine oxides. IV. J. MEISENHEIMER, H. GLAWE, H. GREESKE, A. SCHORNING, and E. VIEWEG (Annalen, 1926, **449**, 188—213; cf. A., 1922, i, 813).—When dl-*phenylmethylallylamine* N-*oxide hydrochloride*, m. p. 100—104°, is treated with silver *d*-π-bromocamphorsulphonate, it yields d-*phenylmethylallylamine* N-*oxide* d-π-*bromocamphorsulphonate*, m. p. 161—162°, $[\alpha]_D$ +63·3° in water; the corresponding *picrate* has m. p. 97—98°, $[\alpha]_D$ +4·0° in alcohol. d-*Phenylethylallylamine* N-*oxide* d-*bromocamphorsulphonate* has m. p. 144—145°, $[\alpha]_D$ +58·2° in water, the *picrate* m. p. 124—125°, $[\alpha]_D$ +1° in alcohol, and the *hydrochloride* $[\alpha]_D$ +4·5° in water. dl-*Phenylmethylpropylamine* N-*oxide picrate*, m. p. 104—105°, yields the d-*bromocamphorsulphonate* of the *d*-amine oxide, m. p. 160—161°, $[\alpha]_D$ +66·8°; the corresponding d-*hydrogen tartrate* has m. p. 137—142°, $[\alpha]_D$ +25·1°, and the *picrate* m. p. 99—102°, $[\alpha]_D$ +6·6° in alcohol. dl-*Phenylethylpropylamine* N-*oxide hydrochloride* (*picrate*, m. p. 144—145°; *tartrate*, m. p. 134°) yields the d-*bromocamphorsulphonate* of the *d*-amine oxide, m. p. 166—167°, $[\alpha]_D$ +58·1°, and thence the *picrate*, m. p. 142—144°, $[\alpha]_D$ +1·3° in alcohol, and the *hydrochloride*, $[\alpha]_D$ +5°. d-*Phenylbenzylmethylamine* N-*oxide* d-π-*bromocamphorsulphonate*, m. p. 141°, $[\alpha]_D$ +54°, yields the *picrate*, m. p. 131°, and the *hydrochloride*, $[\alpha]_D$ +4°; l-*phenylbenzylmethylamine* N-*oxide* d-*tartrate*, m. p. 127°, $[\alpha]_D$ +7·1°, yields the *hydrochloride*, m. p. 135°, $[\alpha]_D$ −3·2°. When benzylethylaniline is treated in alcoholic solution with perbenzoic acid, it yields *phenylbenzylethylamine* N-*oxide benzoate*, m. p. 98°, whilst the mother-liquor with picric acid yields the *picrate*, m. p. 137°. dl-*Phenylbenzylethylamine* N-*oxide hydrochloride* has m. p. 125°, the *d*-amine oxide gives a d-*bromocamphorsulphonate*, m. p. 153·5°, $[\alpha]_D$ +83·4°; d-*hydrogen tartrate*, m. p. 101°, $[\alpha]_D$ +52·8°, which crystallises with $2H_2O$; *picrate*, m. p. 127°, $[\alpha]_D$ +54°, and *hydrochloride*, m. p. 130°, $[\alpha]_D$ +67·1°; and the *l*-amine oxide gives a d-*tartrate*, m. p. 137°, $[\alpha]_D$ −44°, and *picrate*, m. p. 127°, $[\alpha]_D$ −54° in alcohol. Similarly, *benzylmethyl*-p-*toluidine*, b. p. 175°/12 mm., yields dl-p-*tolylbenzylmethylamine* N-*oxide benzoate*, m. p. 99°, and the corresponding *picrate*, m. p. 139°. From dl-p-*tolylbenzylmethylamine* N-*oxide hydrochloride*, m. p. 134°, the following compounds were obtained: d-*tartrate* of the *l*-amine oxide, m. p. 139°, $[\alpha]_D$ −27·8°,

which yields the *picrate*, m. p. 50°, and the *hydrochloride*, m. p. 135°, $[\alpha]_D$ −45°; d-*hydrogen tartrate* of the *d*-amine oxide, m. p. 144°, $[\alpha]_D$ +42·4°, which yields the *picrate*, m. p. 50°, and the *hydrochloride*, m. p. 135°, $[\alpha]_D$ +45°; d-*bromocamphorsulphonate* of the *d*-amine oxide, m. p. 165°, $[\alpha]_D$ +73°; l-*bromocamphorsulphonate* of the *l*-amine oxide, m. p. 165°, $[\alpha]_D$ −72·8°. R. W. WEST.

Diphenyl series. II. Substitution reactions. F. BELL and J. KENYON (J.C.S., 1926, 2705—2713).—Among the products of dinitration of diphenyl, 2 : 2′-dinitrodiphenyl, m. p. 127—128°, has been identified. 2-Nitrodiphenyl gives a mixture of 4 : 2′- and 2 : 2′-dinitrodiphenyls, whilst 4-nitrodiphenyl furnishes a mixture of the 4 : 4′- and 4 : 2′-dinitro-derivatives. 2′-*Nitro*-4-*dimethylaminodiphenyl*, prepared from 2′-nitro-4-aminodiphenyl and methyl sulphate, has m. p. 100°. The nitration of 4-*benzylideneaminodiphenyl*, m. p. 148°, in sulphuric acid furnishes 4′-nitro-4-aminodiphenyl, m. p. 200°, in small yield, whilst 4-*p*-toluenesulphonamidodiphenyl with warm dilute nitric acid yields the 3-*nitro*-derivative, m. p. about 118°, from which 3-nitro-4-aminodiphenyl is obtained by hydrolysis, and 4-acetamidodiphenyl, when nitrated according to the method of Fichter and Sulzberger (A., 1904, i, 325), gives the 3-nitro-derivative, m. p. 132°, in good yield. By reducing 3-nitro-4-aminodiphenyl with aluminium amalgam in moist ether, 3 : 4-*diaminodiphenyl*, m. p. 103°, is obtained. It yields a *diacetyl* derivative, m. p. 163°, a *dibenzoyl* derivative, m. p. 248°, and a *quinoxaline* derivative, m. p. 148°. 3-*Amino*-4-*acetamidodiphenyl*, m. p. 155°, obtained by reducing 3-nitro-4-acetamidodiphenyl with aluminium amalgam, gives 3-*benzamido*-4-*acetamidodiphenyl*, m. p. 186°, with benzoyl chloride in pyridine solution. 3-Amino-4-acetamidodiphenyl, with sodium nitrite and hydrochloric acid, yields 1-*acetyl*-5-*phenyl*-1 : 2 : 3-*benztriazole*, m. p. 130—132°, and 5(or 6)-phenyl-1 : 2 : 3-benztriazole, m. p. 156°, from which the above 5-phenyl compound and 1-*acetyl*-6-*phenyl*-1 : 2 : 3-*benztriazole* (not quite pure), m. p. 97°, is obtained by acetylation. The 5-phenyl compound is partly converted into the 6-phenyl isomeride by heating with acetic anhydride. 3-*Amino*-4-*benzamidodiphenyl*, m. p. 221° (3-*acetyl* derivative, m. p. 211°), is obtained by reducing 3-nitro-4-benzamidodiphenyl with aluminium amalgam. 4-Aminodiphenyl with methyl sulphate and sodium hydroxide forms 4-dimethylaminodiphenyl, m. p. 123°, and diphenylyltrimethylammonium hydroxide (bromide, m. p. 222°), whilst with methyl iodide and sodium carbonate a considerable quantity of 4-dimethylaminodiphenyl methiodide, m. p. 218° (decomp.), is produced. 3-Nitro-4-dimethylaminodiphenyl, m. p. 74°, formed together with 3(5 ?)-*dinitro*-4-*nitrosomethylaminodiphenyl*, m. p. 122°, by adding an excess of sodium nitrite to 4-dimethylaminodiphenyl in acetic acid, yields 3-*acetamido*-4-*dimethylaminodiphenyl*, m. p. 167°, after reduction and acetylation, and 3 :(5 ?)-dinitro-4-nitrosomethylaminodiphenyl, m. p. 122°, together with a *compound*, m. p. 290—292°, with fuming nitric acid in acetic acid solution. The dinitronitroso-compound, the constitution of which is confirmed by its preparation from 4-nitrosomethylaminodiphenyl, has been erroneously described by García Banús and Tomás (A., 1922, i, 333) as 3 : 5 : 2′ : 4′-tetranitro-4-dimethylaminodiphenyl. 3 : (5 ?)-*Dinitro*-4-*methylaminodiphenyl* has m. p. 142—143°. The nitration of 3-nitro-4-dimethylaminodiphenyl in sulphuric acid furnishes the 3 : (4′ ?)-dinitro-derivative, m. p. 137—138°, probably identical with the dinitro-compound, m. p. 134°, described by Vorländer (A., 1925, i, 1258), whilst similar treatment of 4-dimethylaminodiphenyl gives a *product*, m. p. 170—171° [probably the 2 : 4′(?)-dinitro-derivative] and a *compound*, $C_{14}H_{17}O_5N_3S$, m. p. 215—217°, which forms an explosive *derivative*, m. p. above 300°, when treated with hydrochloric acid. 2 : 2′-Diaminotetramethylbenzidine (*diacetyl* derivative, m. p. 191—192°), prepared by the method of Ullmann and Dieterle (A., 1904, i, 269), has m. p. 166°. Tetramethylbenzidine, on mononitration in sulphuric acid, yields the 2-*nitro*-derivative, m. p. 164°, which on further nitration yields the 2 : 2′-dinitro-compound. The former is converted into 2 : (3′ ?)-*dinitrotetramethylbenzidine*, m. p. 145°, by sodium nitrite and acetic acid, whilst tetramethylbenzidine under similar conditions furnishes the (3 : 3′ ?)-*dinitro*-derivative, m. p. 188° (cf. Michler and Pattinson, A., 1882, 199; García Banús and Tomás, *loc. cit.*). The derived diamine, m. p. 165—166°, forms a *diacetyl* derivative, m. p. 281—282°. 2 : 2′-Dinitrotetramethylbenzidine yields a *compound*, m. p. 185°, possibly a trinitrotetramethylbenzidine, on further nitration in sulphuric acid. 4-Amino-4′-hydroxydiphenyl forms a *benzylidene* derivative, m. p. 200°, and a *diacetyl* derivative, m. p. 218—220°. The latter is converted by benzoyl chloride into 4-*acetylbenzamido*-4′-*acetoxydiphenyl*, m. p. 142—143°, giving 4-benzamido-4′-hydroxydiphenyl on hydrolysis (cf. J.C.S., 1926, 1239). Attempts to resolve diphenyl-2-carboxylic acid into optical isomerides were unsuccessful. J. S. H. DAVIES.

Stability of benzenediazonium chloride solutions. I. Reaction of benzenediazonium chloride with water. H. A. H. PRAY.—See this vol., 1214.

Aminotriarylmethanes and azo-dyes derived from them. BRIT. DYESTUFFS CORPN. and K. H. SAUNDERS.—See B., 1926, 866.

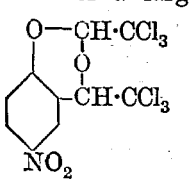
Additive compounds between phenols and ammonia. I. E. BRINER, O. AGATHON, and A. FERRERO (Helv. Chim. Acta, 1926, **9**, 905—912).—Thermal measurements indicate the formation of a molecular compound between phenol and ammonia (*ammonium phenoxide*); similar indications are obtained in the systems resorcinol–ammonia and naphthol–ammonia. Measurement of the vapour pressure of the system *o*-nitrophenol–ammonia as the volume of ammonia added increases, shows that *ammonium* o-*nitrophenoxide*, orange-yellow, is rapidly formed, with a calculated free energy change of 15 g.-cal. per g.-mol. *Ammonium* p-*nitrophenoxide*, yellow, is formed very slowly at the ordinary temperature. E. W. WIGNALL.

Mechanism of the transformation of phenyl allyl ethers. II. L. CLAISEN and E. TIETZE (Ber., 1926, **59**, [*B*], 2344—2351; cf. A., 1925, i, 389).—Methylvinylcarbinol, b. p. 96—98°, advantageously prepared by the addition of acraldehyde dissolved in

ether to a boiling ethereal solution of magnesium methyl bromide, is converted by hydrobromic acid (45%) at the ordinary temperature into Δ^{β}-butenyl bromide, b. p. 103—106°, hydrolysed exclusively to Δ^{β}-butenyl alcohol. When treated with phenol dissolved in acetone in the presence of potassium carbonate, the bromide yields *phenyl* Δ^{β}*-butenyl ether*, m. p. 98—98·5°/14 mm., the constitution of which follows from its hydrogenation to phenyl *n*-butyl ether. The ether is isomerised when heated at 200—210° or, preferably, when boiled with diethylaniline, to o-α-*methylallylphenol*, b. p. 111—112°/14 mm., 229—230°/762 mm. (*phenylcarbamate*, m. p. 89·5—90·5°), converted by glacial acetic and hydrobromic acids into 2 : 3-*dimethylcoumaran*, b. p. 209—210°. Direct action of Δ^{β}-butenyl bromide on sodium phenoxide in the presence of benzene affords o-Δ^{β}-*butenylphenol*, b. p. 117·5—118·5°/13 mm., 239·5—240·5°/atm. pressure (*phenylcarbamate*, m. p. 65—66°; *methyl ether*, b. p. 111—112°/17 mm., d_4^{19} 0·965, n_D^{18} 1·526), converted into 2-methylchroman, b. p. 219·5—221°/767 mm. Isomerisation of phenyl Δ^{β}-butenyl ether, like that of phenyl cinnamyl ether (*loc. cit.*), leads to the attachment of the alkyl group to the benzene nucleus by the γ- instead of the α-carbon atom. H. WREN.

Organic phosphoric acid compounds. IV. Determination of iron. II. F. ZETZSCHE and M. NACHMANN (Helv. Chim. Acta, 1926, 9, 705—708).—The *magnesium, calcium, strontium, barium, nickel, cobalt, zinc, manganese, ferrous, copper, mercuric, cadmium, aluminium, chromium, lead,* and *tin* salts of bis-*p*-chlorophenylphosphoric acid, and of phenyl-, diphenyl-, *p*-bromophenyl-, bis-*p*-bromophenyl-, bistrichlorophenyl-, guaiacol-, anilinophenyl-, β-naphthyl-, and benzyl-phosphoric acids have been prepared in order to ascertain their effect on the determination of ferric iron by the method previously described (this vol., 705). All but the last four metals form crystalline salts, all of which are decomposed by 1% mineral acid, and hence it is found that only in the presence of manganese, stannic, lead, and mercury salts is the determination of ferric iron by this method untrustworthy. In the presence of manganese, trustworthy results can be obtained if the ferric hydroxide is redissolved in 2*N*-hydrochloric acid and reprecipitated. The presence of other organic substances does not affect the method, but when reducing agents, *e.g.*, pyrogallol, are present, the precipitation must be carried out in the presence of an oxidising agent, 3% hydrogen peroxide solution being employed. J. W. BAKER.

Condensation of phenols with chloral. F. D. CHATTAWAY (J.C.S., 1926, 2720—2727).—*p*-Nitrophenol (1 mol.) and chloral (2 mols.) combine in presence of a large excess of sulphuric acid to form



anhydro-5-*nitro*-2-ββββ-*trichloro*-α-*hydroxyethoxy*-1-ββββ-*trichloro*-α-*hydroxyethylbenzene* (annexed formula), m. p. 146° (crystallographic data given), which is insoluble in dilute alkalis and is unchanged by boiling acetic anhydride. It reacts vigorously with alcoholic potassium hydroxide, liberating chloroform and ethyl orthoformate, and forming dl-5-*nitro*-2-*ethoxyphenylglycollic acid*, m. p. 138° (*silver* and *ammonium* salts described; *acetyl* derivative, m. p. 147·2°), together with a small amount of 5-*nitro*-2-*ethoxybenzoic acid*, m. p. 163° (*sodium* salt described). On reduction with tin and acetic acid, it yields the corresponding 5-*amino*-compound, m. p. 176° (*hydrochloride*, decomp. on heating; *acetyl* derivative, m. p. 206°; 5-*diazonium chloride*; *azo*-β-*naphthol* derivative, m. p. 196°; *sodium* salt described), which is converted by the Sandmeyer reaction into *anhydro*-2-ββββ-*trichloro*-α-*hydroxyethoxy*-1-ββββ-*trichloro*-α-*hydroxyethylbenzene*, m. p. 119°. *dl*-5-Nitro-2-ethoxyphenylglycollic acid is decomposed by sulphuric acid into formic acid and 5-nitro-2-ethoxybenzaldehyde [*semicarbazone* exists in two polymorphic forms, m. p. 234—235° (decomp.)], and yields on oxidation with alkaline permanganate 5-nitro-2-ethoxybenzoic acid, which is also obtained from salicylic acid by successive nitration, ethylation, alkaline hydrolysis, and acidification.

J. S. H. DAVIES.

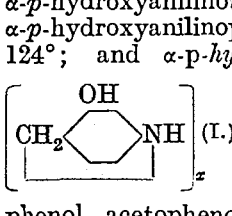
Effect of substituents in the formation and reactions of certain ethers. L. C. RAIFORD and J. C. COLBERT (J. Amer. Chem. Soc., 1926, 48, 2652—2662).—The formation of phenyl alkyl ethers by treatment of halogenated nitrobenzenes with alcohols in presence of aqueous potassium hydroxide is dependent on the number and relative positions of the nitro-groups, the reducing action of the alcohol, the concentrations of the reactants, and the temperature. The reaction between a halogenated nitrobenzene and a phenol is influenced by the substituents in the latter. If the phenol contains a nitro-group, the reaction will not take place unless the halogenated nitrobenzene contains more than one nitro-group. The phenyl radical of phenyl alkyl ethers is not readily brominated if two of the three possible positions are occupied by substituents other than hydrogen. Where the alkyl group is allyl, the latter will take up bromine. Phenyl benzyl ethers are decomposed into the corresponding brominated phenol and benzyl bromide, indicating that substitution in the phenyl nucleus occurs first, the ether then being decomposed by the hydrogen bromide formed. The bromination of diphenyl ethers is hindered by the presence of a nitro-group. Diphenyl ethers are unaffected by hydrobromic acid under certain conditions, whilst the decomposition of phenyl alkyl ethers under similar conditions is incomplete and apparently dependent on the substituents in the phenyl group, except in the case of the phenyl allyl ethers, when the fission is nearly quantitative.

4-Chloro-*o*-anisidine, m. p. 82—83° (*benzoyl* derivative, m. p. 77·5°), is obtained in 51·6% yield by reduction of the corresponding nitro-compound (D.R.-P. 140133) with aluminium amalgam in alcohol. 4-Chloro-*o*-nitrophenetole, obtained analogously to the chloronitroanisole, did not yield a bromo-derivative; by reduction with stannous chloride it gave 4-chloro-*o*-phenetidine, not obtained pure, giving a *benzoyl* derivative, m. p. 119°. Attempts to prepare 4-chloro-2-nitrophenyl allyl ether by Blom's method (A., 1922, i, 38) gave no reaction at 60°, but at 70°

and 85° the product was a mixture from which tetrachloroazoxybenzene, m. p. 145° (cf. Laubenheimer, A., 1875, 759), was isolated. 4-*Chloro*-o-*nitrophenyl allyl ether*, m. p. 46°, is obtained from allyl iodide and the silver salt of the appropriate phenol. 2 : 4-Dinitrophenyl allyl ether, m. p. 46—47° (cf. Fairbourne and Toms, J.C.S., 1921, **119**, 1038), is obtained by treating chloro-2 : 4-dinitrobenzene with allyl alcohol and potassium hydroxide. Treatment with bromine affords an additive compound, m. p. 108·5°, whilst the ether is decomposed almost quantitatively by hydrobromic acid. 4-Chloro-*o*-nitrophenyl benzyl ether, m. p. 85—86°, is obtained by heating benzyl chloride with an aqueous solution of the potassium salt of the appropriate phenol (cf. D.R.-P. 142899; Gomberg and Buchler, A., 1920, i, 839). When treated with 5 mols. of bromine in ether in presence of iodine, it yields 4-chloro-6-bromo-*o*-nitrophenol. 2 : 4-Dinitrophenyl benzyl ether, m. p. 149·5° (cf. Kumpf, A., 1884, 1005), is obtained in 51·6% yield by heating chloro-2 : 4-dinitrobenzene with benzyl chloride and water for 10 hrs. at 150°. *p*-Nitrodiphenyl ether, m. p. 60—61°, is obtained by heating *p*-chloronitrobenzene with concentrated aqueous potassium phenoxide at 150° for 6 hrs. (cf. Jones and Cook, A., 1916, i, 644; Haeussermann and Teichmann, *ibid.*, 1896, i, 533). The following substituted diphenyl ethers were also prepared: 2 : 4-dinitro-, m. p. 70°; 4′-*bromo*-2 : 4-*dinitro*-, m. p. 138·5°; 4′-*chloro*-2 : 4-*dinitro*-, m. p. 123°; 2 : 4 : 2′-trinitro-, m. p. 137·5° (cf. Willgerodt and Huetlein, A., 1884, 1328); 2 : 4 : 3′-trinitro-, m. p. 135° (cf. D.R.-P. 281053); 2 : 4 : 4′-trinitro-, m. p. 116° (Willgerodt and Huetlein, *loc. cit.*); 2′ : 4′ : 6′-*tribromo*-2 : 4-*dinitro*-, m. p. 130·5°; 4′-*chloro*-2 : 4 : 2′-*trinitro*-, m. p. 154°; 4′-*bromo*-2 : 4 : 2′-*trinitro*-, m. p. 148·5°; 4′-*chloro*-2-*nitro*-, m. p. 45·5°; 4′-*bromo*-2-*nitro*-, m. p. 71°; 4′-*chloro*-4-*nitro*-, m. p. 76·5°; 4′-*bromo*-4-*nitro*-, m. p. 65—66°; 4-*chloro*-2-*nitro*-, m. p. 36—37°, b. p. 201°/12 mm.; 4-*chloro*-4′-*bromo*-2-*nitro*-, m. p. 93—94°; 4 : 4′-*dichloro*-2-*nitro*-, m. p. 79° (cf. D.R.-P. 216642); 4 : 4′-*dibromo*-2-*nitro*-, m. p. 94·5°; and 4′-*chloro*-4-*bromo*-2-*nitro*-*diphenyl ether*, m. p. 100·5°.

F. G. Willson.

Derivatives of hydroxyphenylglycine. I. K. Shimo (Bull. Chem. Soc. Japan, 1926, **1**, 202—207; cf. A., 1906, i, 349; 1921, i, 556).—Condensation of *p*-aminophenol in glacial acetic acid with formaldehyde and potassium cyanide yields *p*-hydroxyanilinoacetonitrile, m. p. 103—104°, and similar condensations using acetaldehyde, acetone, benzaldehyde, and acetophenone instead of formaldehyde give α-p-*hydroxyanilinopropionitrile*, m. p. 111—112°; α-*p*-hydroxyanilino*iso*butyronitrile, m. p. 140—142°; α-*p*-hydroxyanilinophenylacetonitrile, m. p. 122—124°; and α-p-*hydroxyanilino*-α-*phenylpropionitrile*, m. p. 128—130°. Similarly, *o*-aminophenol, formaldehyde, and potassium cyanide condense to form o-*hydroxyanilinoacetonitrile*, m. p. 74—75°, and *m*-aminophenol, acetophenone, and potassium cyanide form α-m-*hydroxyanilino*-α-*phenylpropionitrile*, m. p. 135—137°. The colour reactions of the above compounds with ferric chloride, silver nitrate, and other reagents are tabulated. *m*-Aminophenol treated with formaldehyde and potassium cyanide solution yields a pale yellow powder, m. p. >300°, insoluble in organic solvents and hydrochloric acid—probably *anhydro*-p-*amino*-o-*hydroxybenzyl alcohol* (I).


(I.)

B. W. Anderson.

p-Anisylurethane and its nitration products. F. Reverdin (Helv. Chim. Acta, 1926, **9**, 793—798).—*p*-Anisylurethane, m. p. 66—67°, is prepared from *p*-anisidine and ethyl chloroformate. Nitric acid, *d* 1·185, converts it into 3-*nitro*-p-*anisylurethane*, m. p. 61°; in acetic acid, nitric acid *d* 1·4 gives the 2 : 5-(or 2 : 6-)*dinitro*-derivative, m. p. 162—163°, or, under different conditions, the 3 : 5-*dinitro*-compound, m. p. 140°, whilst nitric acid *d* 1·5 gives 2 : 3-*dinitro*-p-*anisylurethane*, m. p. 157—158°. The last nitrates further to the 2 : 3 : 5-*trinitro*-derivative, m. p. 212°. The 2 : 3-dinitro-compound gives with ammonia a red *substance*, m. p. 146°; the trinitro-compound similarly a red *substance*, m. p. 150°, possibly an amino-derivative of a dinitro-compound, $MeO{\cdot}C_6H(NH_2)(NO_2)_2{\cdot}NH{\cdot}CO_2Et$.

E. W. Wignall.

Phototropic aminoaryl disulphides. R. Child and S. Smiles (J.C.S., 1926, 2696—2702).—Among aminoaryl disulphoxides, only the *para* compounds are phototropic; acetylation of the amino-group tends to diminish, or may obliterate, the phototropy, which is also not observed in the dicarbomethoxy- or dicarboethoxy-derivatives. The presence of ono amino-group in the thiol-substituted nucleus of an unsymmetrical disulphoxide suffices to produce phototropy. *p*-Aminophenyl disulphoxide and its acetyl derivative are inactive, but may be rendered phototropic by admixture with about 0·1% of the corresponding disulphide, or a disulphide containing a 4-amino- or substituted 4-aminophenyl group. It is suggested that the formation of mixed crystals is necessary to induce phototropy. These results support the idea of a close connexion between phosphorescence and phototropy.

p-Aminophenyl disulphoxide with methyl and ethyl chloroformate and sodium carbonate yields *di*-p-*carbomethoxy*- and *di*-p-*carboethoxy*-*aminophenyl disulphoxide*, m. p. 186° and 162°, respectively. The *disulphide* corresponding with the latter has m. p. 136—137°. Acetanilide-*p*-sulphinic acid on methylation forms p-*acetamidophenylmethylsulphone*, m. p. 183°, and *acetanilide*-p-*disulphone*, not phototropic, m. p. 245—250° (decomp.), on successive treatment with potassium permanganate and sulphurous acid. p-*Acetamidophenyl* p-*acetamidobenzenesulphonate* has m. p. 218°. o-*Acetamidophenyl sulphoxide*, m. p. 140°, is obtained by oxidising the *diacetyl* derivative, m. p. 156°, of *o*-aminophenyl disulphide with hydrogen peroxide in acetic acid. *Acetanilide*-m-*sulphinic acid*, m. p. 145°, from the sulphonyl chloride and alkaline sodium sulphite, with hydriodic and sulphurous acids, yields m-*acetamidophenyl disulphoxide*, m. p. 212—213° (decomp.). *Aceto*-o-*toluidide*-5-*sulphonyl chloride*, m. p. 159°, by treatment with alkaline sodium sulphite and acidification, yields the corresponding *sulphinic acid*, m. p. 147°, which furnishes the disulphide with hydriodic and sulphurous acids.

5-*Thiolaceto*-o-*toluidide*, m. p. 143°, forms 5-*methylthiolaceto*-o-*toluidide*, m. p. 134°, with methyl sulphate. The mercaptan on oxidation with ferric chloride yields 2-*acetamidotolyl* 5-*disulphide*, m. p. 222°, which is converted by hydrolysis into 2-*aminotolyl* 5-*disulphide*, m. p. 112°. The derived 2-*acetamidotolyl* 5-*disulphoxide*, m. p. 183° (decomp.), contains a trace of the disulphide. 1-*Acetamidonaphthalene*-4-*sulphinic acid*, m. p. 176° (decomp.), prepared from the corresponding sulphonyl chloride, yields in the usual manner 4-*acetamidonaphthyl disulphoxide* (containing a trace of disulphide), m. p. 234° (decomp.), which with 2 : 5-dibromophenylmercaptan furnishes 1-acetamidonaphthalene-4-sulphinic acid and 2 : 5-*dibromophenyl* 4-*acetamidonaphthyl disulphide*, m. p. 189°. *Acetanilide*-p-*sulphonyl iodide*, from sodium acetanilide-*p*-sulphinate and alcoholic iodine, has m. p. 97° (decomp.), and with silver *p*-tolylmercaptide forms *p*-tolyl disulphide and p-*tolyl* p-*acetamidobenzenethiolsulphonate*, m. p. 169° (decomp.), which is not phototropic. *p*-Bromothiolacetanilide and silver *p*-chlorobenzenesulphinate form *p*-acetamidophenyl disulphide and p-*acetamidophenyl* p-*chlorobenzenethiolsulphonate*, m. p. 200—201° (decomp.).

J. S. H. Davies.

Preparation of diazophenolsulphonic acids. V. M. Rodionov, V. K. Matweev, and "Aniltrust."—See B., 1926, 867.

Diazotisation of aminophenols. Rheinische Kämpfer-Fabr. G.m.b.H., S. Skraup, and K. Steinruck.—See B., 1926, 867.

Distinguishing α- and β-naphthols. F. Lewisch.—See B., 1926, 909.

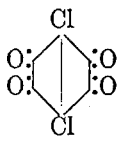
Preparation of chloro-derivatives of β-naphthol with free 1-position. I. G. Farbenind. A.-G., W. Herzberg, O. Spengler, and A. Schmid.—See B., 1926, 869.

Preparation of 4-halogeno-1 : 8-naphthasultones. Soc. Chem. Ind. in Basle.—See B., 1926, 870.

[Synthesis of] 2 : 4-dihydroxydiphenylethane. E. Klarmann, and Lehn and Fink, Inc.—See B., 1926, 931.

New complex metallic compounds with pyrocatechol and their application to microchemical analysis. A. Martini (Anal. Asoc. Quím. Argentina, 1926, **14**, 177—184).—Solutions of pyrocatechol acetate and aniline or pyrocatechol acetate and piperazine are sensitive micro-reagents for molybdenum, tungsten, and vanadium. The crystalline precipitates obtained are described with photomicrographs. G. W. Robinson.

Action of chlorosulphonic acid on phenols. III. J. Pollak and E. Gebauer-Fülnegg (Monatsh., 1926, **47**, 109—118).—The action of chlorosulphonic acid on pyrocatechol for 24 hrs. at the ordinary temperature yields the disulphonic acid, isolated as the barium salt, but if the reaction mixture is heated at 110° for 1·5 hrs., *pyrocatechol*-3 : 5-*disulphonyl chloride*, m. p. 149—150°, is obtained. Heated at 150° for 8 hrs., the reaction mixture yields the neutral *sulphate* of pyrocatechol-3 : 5-disulphonyl chloride, $(SO_2Cl)_2C_6H_2<^{O}_{O}>SO_2$, m. p. 143° [*disulphonanilide*, m. p. 304° (decomp.); *disulphomethylanilide*, m. p. 146°]. Quinol treated with chlorosulphonic acid (10 parts) at the ordinary temperature yields no products which are insoluble in water or hydrochloric acid, but heated at 150—160° for 8 hrs. it yields chloroanil together with by-products which are best obtained by using 50 parts of chlorosulphonic acid and heating for 80 hrs.; these are pentachlorophenol, m. p. 189°, together with 1% of p-*dichlorobenzodiquinone* (I), which yields no acetyl derivative, but on reduction and acetylation yields the known tetra-acetylhydrochloroanilic acid. Salicylic acid treated with chlorosulphonic acid (10 parts) at 130—140° for 1·5 hrs. yields the *disulphonyl chloride*, m. p. 185°.


(I.)

J. W. Baker.

Orientation in the benzene ring. Chlorination of pyrogallol 1 : 3-dimethyl ether. A. A. Levine (J. Amer. Chem. Soc., 1926, **48**, 2719—2721; cf. this vol., 516).—Chlorination of pyrogallol 1 : 3-dimethyl ether in carbon disulphide affords 4-*chloropyrogallol* 1 : 3-*dimethyl ether*, (I), b. p. 154—156°/12 mm. (*benzoate*, m. p. 89—90°), which, on bromination in the same solvent, yields 4-*chloro*-5 : 6-*dibromopyrogallol* 1 : 3-*dimethyl ether*, (II), m. p. 124—125° (*acetate*, m. p. 107—108°; *benzoate*, m. p. 119—120°). Oxidation of (I) with chromium trioxide in glacial acetic acid affords 2 : 2′-*dichloro*-3 : 5 : 3′ : 5′-*tetramethoxydiphenoquinone* (*dichlorocedriret*), together with a *product*, probably 3-*chloro*-2 : 6-*dimethoxy*-1 : 4-*benzoquinone*. Oxidation of (II) with chromium trioxide in carbon disulphide affords 3-chloro-5-bromo-2 : 6-dimethoxy-1 : 4-benzoquinone (*loc. cit.*), which, on reduction with sulphur dioxide in aqueous acetone, yields the corresponding *quinol*, m. p. 146° (*diacetate*, m. p. 85—86°). F. G. Willson.

Hydrogenation of triphenylcarbinol and phenylfluorenylcarbinol under pressure. V. Ipatiev and B. Dolgov (Bull. Soc. chim., 1926, [iv], **39**, 1456—1460).—See this vol., 949.

Isomeric forms of didiphenylylcarbinol. F. Straus and H. Demus (Ber., 1926, **59**, [*B*], 2426—2431).—A second *modification* of didiphenylylcarbinol, m. p. 106°, is obtained together with the known form, m. p. 151°, when didiphenylyl ketone is subjected to prolonged reduction with zinc dust in alkaline solution. Each form is remarkably stable towards infection from the other. Conversion of the form of higher into that of lower m. p. is effected by treatment with warm alcohol during 1—2 days. The converse change is brought about by rapidly cooling a solution of the modification of higher m. p. in alcohol which has been boiled for 70 hrs. The isomeric carbinols are converted by hydrogen chloride into the corresponding *didiphenylmethyl chlorides*, m. p. 97° and 130—131°, respectively. The chloride of m. p. 130—131° is reconverted into the carbinol of m. p. 151°, whereas that of m. p. 97° yields a mixture of the isomeric carbinols. H. Wren.

Influence of general electron displacement on the reactivity of conjugated systems in the

molecules of carbon compounds. R. ROBINSON (Nature, 1926, **118**, 627).—The proportion of the *m*-nitrobenzoic acid derivative obtained on nitration of benzoic esters rises in the series : $C_6H_5\cdot CO_2 \leftarrow CR_3$ (R=alkyl), $C_6H_5\cdot CO_2Me$, $C_6H_5\cdot CO_2 \rightarrow CH_2 \rightarrow C_6H_4\cdot NO_2$; the arrows show the assumed direction of displacement of electrons, methyl benzoate being the standard of reference. The result supports the author's theoretical views (cf. Baker and Ingold, this vol., 1131). A. A. ELDRIDGE.

Nitration of cinnamic acid derivatives. J. VAN DER LEE (Rec. trav. chim., 1926, **45**, 674—709).—In the nitration of *o*-, *m*-, and *p*-nitrocinnamic acids with nitric acid (*d* 1·52), the corresponding ω-dinitrostyrenes, $NO_2\cdot C_6H_4\cdot CH{:}CH\cdot NO_2$, are formed. It is assumed that addition of nitric acid to the double linking in the side-chain first takes place, followed by elimination of carbon dioxide and water. *p*-Chloro- and *p*-bromo-cinnamic acid with nitric acid (*d* 1·48) give chloro(bromo)nitrocinnamic acid, and with nitric acid (*d* 1·52) *p*-chloro-(bromo-)ω-dinitrostyrene, but the products are mixtures of isomerides and cannot be separated into their components. *p*-Chloro-*o*-nitrocinnamic acid with nitric acid (*d* 1·52) affords 4-*chloro*-ω : 2-*dinitrostyrene*, m. p. 98—99°; 4-*bromo*-ω : 2-*dinitrostyrene*, m. p. 114—116·5°, 4-*chloro*-ω : 3-*dinitrostyrene*, m. p. 150—151°, and 4-*bromo*-ω : 3-*dinitrostyrene*, m. p. 147—149°, were prepared in a similar way.

By nitrating the esters of cinnamic acid derivatives, the elimination of carbon dioxide is prevented and intermediate products can be isolated. Thus, ethyl *p*-nitrocinnamate gives *ethyl* α-*nitro*-β-*nitrato*-β : p-*nitrophenylpropionate*, $NO_2\cdot C_6H_4\cdot CH(O\cdot NO_2)\cdot CH(NO_2)\cdot CO_2Et$, m. p. 73—74·5°. This loses nitric acid with extreme readiness, yielding two forms of ethyl α : *p*-dinitrocinnamate; one form (m. p. 110—111°) is probably identical with that previously described (A., 1882, 401), the second *form* (m. p. 86·5—87°) is new. The two forms can be separated by fractional crystallisation from benzene, and may be geometrical isomerides. *Ethyl* α-*nitro*-β-*nitrato*-β-m-*nitrophenylpropionate*, m. p. 76·5°, readily passes by loss of nitric acid into a mixture of two forms of *ethyl* α-m-*dinitrocinnamate*, m. p. 105·5—106° and 74—74·5°, respectively. The nitration of ethyl *o*-nitrocinnamate yielded an uncrystallisable oil.

A new method for the preparation of *p*-chloro-*o*-nitrobenzaldehyde from *p*-chloro-*o*-nitrotoluene is described, 4 : 4′-*dichloro*-2 : 2′-*dinitrodibenzyl*, m. p. 195°, being obtained as a by-product. 4 : 4′-*Dibromo*-2 : 2′-*dinitrodibenzyl* has m. p. 210—212°. Other new compounds produced are p-*chloro*-m-*nitrocinnamic acid*, m. p. 184—185° (sinters at 180°), and p-*bromo*-m-*nitrocinnamic acid*, m. p. 198—199° (indefinite). W. J. POWELL.

Three-carbon system. VIII. Tautomeric systems terminated by a phenyl group. R. P. LINSTEAD and L. T. D. WILLIAMS (J.C.S., 1926, 2735—2747).—The presence of a γ-phenyl group confers an unusual degree of stability on the double linking in the βγ-position of butenoic acids. The action of forty times the theoretical quantity of 20% sodium hydroxide for 105 hrs. on styrylacetic acid, m. p. 87° [prepared by condensing phenylacetaldehyde with malonic acid in presence of diethylamine : *potassium* salt, m. p. 245° (decomp.); *acid chloride*, m. p. 42°; *ethyl* ester, b. p. 164—165°/25 mm., 184°/44 mm., $d_4^{20\cdot5}$ 1·0340, $n_D^{20\cdot5}$ 1·53271, $[R_L]_D$ 56·73], produces a mixture of 0·5% of the αβ-acid (γ-phenylcrotonic acid), 10% of the β-hydroxy-acid (β-hydroxy-γ-phenylbutyric acid), and a trace of lactone (cf. Fittig, A., 1883, 471; 1895, 223). γ-Phenylcrotonic acid, m. p. 58—59°, is best prepared by the action of acetic anhydride on β-hydroxy-γ-phenylbutyric acid, and furnishes the αβ-acid when treated with 10% sodium hydroxide. In the presence of sodium ethoxide, ethyl styrylacetate, b. p. 164—165°/25 mm., becomes mobile, and the αβ-phase, ethyl γ-phenylcrotonate, condenses with ethyl sodioacetoacetate, giving a resorcinol ester, which forms 3 : 5-*diketo*-1-*benzyl*cyclo*hexane*, m. p. 118°, on hydrolysis. In these condensations, the ester is unique amongst the βγ-butenoic acids. *Styrylacetone*, b. p. 262°/75 mm., 150°/15 mm. (*semicarbazone*, m. p. 160°), which is best obtained by the action of zinc methyl iodide on styrylacetyl chloride, resists alkylation (styrylacetic acid being occasionally formed), and resembles the corresponding ester in that the equilibrium mixture produced by interaction with sodium ethoxide readily adds on ethyl sodiomalonate to form the above resorcinol ester. That ethyl α-cyano-α-styrylacetate, b. p. 192°/16 mm., $d_4^{17\cdot5}$ 1·0912, $n_D^{17\cdot5}$ 1·53635, $[R_L]_D$ 61·22, formed from phenylacetaldehyde and ethyl cyanoacetate in presence of diethylamine, is an equilibrium mixture containing a large proportion of the βγ-form is shown by addition to the αβ-phase by treatment with alcoholic ammonia and ethyl cyanoacetate, when *α-cyano-γ-phenylbutyramide*, m. p. 151—152°, and 3 : 5-*dicyano*-6-*hydroxy*-4-*benzyl*-2-*pyridone*, m. p. 279° (*monoammonium* salt chars without melting at 320°), are formed, although none of the reactions cited by Haworth (J.C.S., 1909, **95**, 482) provides definite proof of its βγ-structure. When phenylacetaldehyde and ethyl cyanoacetate are condensed in presence of sodium ethoxide, a compound, m. p. 220°, probably the hydroxynitrile, $CHPh{:}CH\cdot CH(CN)\cdot CH(OH)\cdot CH_2Ph$, is obtained as a by-product. Ethyl α-cyano-α-styrylacetate is oxidised quantitatively to benzoic acid by a mixture of chromic and acetic acids.

J. S. H. DAVIES.

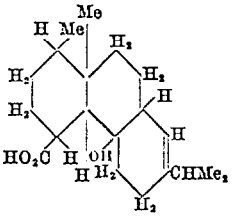
Three-carbon system. IX. The αβ–βγ-change in the β-alkylcinnamic acids. J. D. A. JOHNSON and G. A. R. KON (J.C.S., 1926, 2748—2759).—It has been shown (see preceding abstract) that a terminal phenyl group cannot cause mobility in a three-carbon system, and a study of the αβ–βγ-change in a series of β-phenyl compounds shows that the β-methyl-, ethyl-, propyl-, and *iso*propyl-cinnamic acids have a greater degree of mobility than the corresponding aliphatic compounds, the increased mobility being due to the influence of the phenyl group, which is discussed. Nevertheless, none of the esters of this series could be alkylated.

β-*Phenyl*-Δ^{β}-*butenoic acid* (*methyl* ester, b. p. 138°/16 mm.; *anilide*, m. p. 127°) is formed in small quantity (2%) during the preparation (described) of

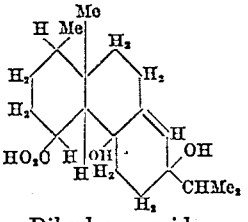
β-methylcinnamic acid. The former (βγ-) acid is rapidly converted by boiling concentrated alkali into β-methylcinnamic acid, which remains unchanged under these conditions. Sulphuric acid (50%) does not cause conversion of the αβ-form, but a little α-methylstyrene, b. p. 160°, is produced. The chloride, b. p. 132°/18 mm., of the stable αβ-acid is unaffected by heat. *β-Phenyl-Δ$^{\beta}$-pentenoic acid* (*anilide*, m. p. 127°; *acid chloride*, b. p. 140°/18 mm.; *ethyl* ester, b. p. 143°/14 mm., $d_4^{13\cdot5}$ 1·0285, $n_D^{13\cdot5}$ 1·52953, $[R_L]_D$ 61·26 : the αβ-ethyl ester has b. p. 145°/14 mm., $d_4^{13\cdot5}$ 1·0234, $n_D^{13\cdot5}$ 1·52827, $[R_L]_D$ 61·45), gives an equilibrium mixture of the two isomerides under the action of alkali. A similar change occurs with boiling 50% sulphuric acid, in which case a lactone, apparently, *β-phenylvalerolactone*, b. p. 170°/16 mm., and *α-ethylstyrene*, b. p. 81—82°/20 mm., are also formed. β-Ethylcinnamanilide melts at 86°, and β-ethylcinnamoyl chloride boils at 142°/18 mm. On pouring either acid chloride into water, a mixture of the αβ- and βγ-acids is produced. *β-Phenyl-Δ$^{\beta}$-hexenoic acid* (*acid chloride*, not pure, b. p. 159°/40 mm.; *methyl* ester, b. p. 133°/12 mm., $d_4^{19\cdot5}$ 1·0297, $n_D^{19\cdot5}$ 1·53305, $[R_L]_D$ 61·53; *ethyl* ester, not pure, b. p. 148°/16 mm.) and β-propylcinnamic acid, m. p. 96·5° (*anilide*, m. p. 114°; *acid chloride*, not pure, b. p. 160°/40 mm.; *methyl* ester, b. p. 135°/12 mm., $d_4^{18\cdot2}$ 1·0017, $n_D^{18\cdot2}$ 1·52146, $[R_L]_D$ 62·10; *ethyl* ester, not pure, b. p. 161°/31 mm.), are interconvertible with alkalis and with 50% sulphuric acid. In the latter case, a *lactone*, m. p. 94—97°, b. p. 178°/14 mm., and α-propylstyrene, b. p. 86°/14 mm., were isolated. The two acids give the same *amide*, m. p. 101°, and *anilide*, m. p. 108°—probably the βγ-compounds—when these are prepared from the acid chloride, because the latter, produced by phosphorus pentachloride from either acid, is the βγ-derivative. β-iso*Propylcinnamic acid*, m. p. 94° (*anilide*, m. p. 99°; *acid chloride*, not pure, b. p. 153°/26 mm.; *methyl* ester, not pure, b. p. 166°/42 mm.; *ethyl* ester, not pure, b. p. 161°/31 mm.), and *β-phenyl-γ-methyl-Δ$^{\beta}$-pentenoic acid*, m. p. 95° (*anilide*, m. p. 121°; *acid chloride*, not pure, b. p. 153°/30 mm.; *methyl* ester, not pure, b. p. 166°/42 mm.; *ethyl* ester, not pure, b. p. 161°/33 mm.), give the same *amide*, presumably the βγ-compound, m. p. 113°. The isomerisation of the acids was carried out as indicated above. With sulphuric acid, *α-iso*propylstyrene, b. p. 89°/15 mm. (also obtained by distilling either acid), and a *lactone*, b. p. 178°/16 mm., were also isolated. iso*Butyrophenone semicarbazone* melts at 182°. The β-propyl- and *β-iso*propyl-cinnamic acids have much less tendency to pass into the βγ-forms than the β-ethyl derivative. *δ-Phenyl-Δ$^{\gamma}$-penten-β-one*, m. p. 100°, b. p. 133—136°/12 mm. (*semicarbazone*, m. p. 191°), shows little tendency to pass into the βγ-form, and cannot be alkylated. *δ-Phenyl-Δ$^{\gamma}$-hexen-β-one*, b. p. 138°/14 mm. (*semicarbazone*, m. p. 158°), and *δ-phenyl-Δ$^{\delta}$-hexen-β-one*, b. p. 138°/14 mm. (*semicarbazone*, m. p. 185°), readily form an equilibrium mixture in presence of alcoholic alkalis, sodium ethoxide, and acids. On ethylation, they both furnish the same (βγ-) *ethyl* derivative, b. p. 140—146°/14 mm. (*semicarbazone*, m. p. 174°). None of the ketones or esters of this series undergoes the Michael reaction. Attempts to synthesise satisfactorily the above two ketones from propiophenone and acetone resulted chiefly in the formation of a compound, b. p. 194—199°/16 mm. (*semicarbazone*, m. p. 204°), possibly $CEtPh{:}CH{\cdot}CO{\cdot}CH{:}CMe_2$. J. S. H. Davies.

β-Naphthol-6-carboxylic acid. F. Andre, and Grasselli Dyestuffs Corpn.—See B., 1926, 869.

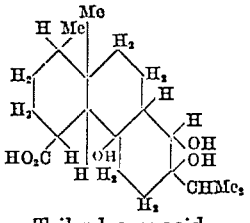
Constituents of some Indian essential oils. XVIII. Derivatives of abietic acid. M. G. Rau and J. L. Simonsen (J. Indian Inst. Sci., 1926, 9A, 111—116).—The main product of the oxidation with potassium permanganate of the monohydroxyabietic acid previously described (A., 1925, i, 687) is a *trihydroxy[tetrahydro]abietic acid*, $C_{20}H_{34}O_5$, m. p. 210—212° (*methyl* ester, m. p. 172°). When treated with a mixture of methyl alcohol and sulphuric acid, the acid yields a *dihydroxy[dihydro]abietic acid*, $C_{20}H_{32}O_4$, m. p. 278° [*methyl* ester (from the *silver* salt), m. p. 144°; *acetyl* derivative, m. p. 186°; *ammonium*, *calcium*, *barium*, *lead*, and *silver* salts], no methylation occurring. The three hydroxy-acids are considered to have the following constitutions :



Monohydroxy-acid.



Dihydroxy-acid.



Trihydroxy-acid.

It is pointed out that the hydroxyabietic acids are properly derivatives of di- and tetra-hydroabietic acid, but have never been so called.

E. H. Sharples.

Three-carbon system. VII. Derivatives of malonic acid. G. A. R. Kon and E. A. Speight (J.C.S., 1926, 2727—2735).—Ethyl *iso*propylidenemalonate, in presence of sodium ethoxide and methyl iodide, gives the *ester*, $CH_2{:}CMe{\cdot}CMe(CO_2Et)_2$, b. p. 124°/18 mm., $d_4^{24\cdot6}$ 1·01159, $n_D^{24\cdot6}$ 1·44020, $[R_L]_D$ 55·81. The corresponding *acid*, m. p. 135° (decomp.), loses carbon dioxide when heated and yields an *acid*, $CH_2{:}CMe{\cdot}CHMe{\cdot}CO_2H$, b. p. 108°/25 mm. (*anilide*, m. p. 88°), not identical with αββ-trimethylacrylic acid, but being converted into this by boiling with strong alkalis. The *anilide* of αββ-trimethylacrylic acid has m. p. 94°. *Ethyl* cyclo*pentylidenemalonate*, b. p. 139—141°/10 mm., $d_4^{19\cdot3}$ 1·06164, $n_D^{19\cdot3}$ 1·47241, $[R_L]_D$ 59·59, is best obtained by condensing ethyl malonate with *cyclo*pentanone in presence of acetic anhydride and the compound of aniline with zinc chloride, or from the silver salt of the derived cyclo*pentylidenemalonic acid*, m. p. 169° (decomp.), with methyl iodide, but not from 1-chloro-Δ^1-*cyclo*pentene and ethyl sodiomalonate; it has the αβ-structure.

*cyclo*Pentylidenemalonic acid on oxidation with alkaline permanganate yields oxalic and glutaric acids, whilst *cyclo*pentanone is obtained from the ozonide of the acid or of the ester. Ethyl *cyclo*pentylidenemalonate with sodium methoxide and methyl iodide yields *ethyl* cyclo*pentylidene-α-methylmalonate*, b. p. 150°/20 mm., d_4^{22} 1·03457, n_D^{22} 1·45853, $[R_L]_D$ 63·24, (*acid*, m. p. 136·5°). The methylated ester furnishes the semialdehyde of glutaric acid on oxidation with ozone, and ethyl α-Δ^1-*cyclo*pentenylpropionate and ethyl carbonate with alcoholic sodium ethoxide. Ethyl *cyclo*pentylidenemalonate with hydrogen cyanide gives a product which furnishes 1-carboxy-*cyclo*pentane-1-acetic acid, m. p. 156°, with dilute sulphuric acid. It does not condense with ethyl sodioacetoacetate, but with ethyl cyanoacetate and ammonia it furnishes the *imide*,

$$\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH(CO_2Et)\cdot CO\\ CH(CN)\text{—}CO\end{matrix}>NH,$$

m. p. 163°, which with dilute sulphuric acid yields *cyclo*pentane-1 : 1-diacetic acid, m. p. 176—177°. *Ethyl* Δ^1-cyclo*hexenylmalonate*, b. p. 160°/20 mm., $d_4^{22\cdot5}$ 1·04419, $n_D^{22\cdot5}$ 1·46470, $[R_L]_D$ 63·42, prepared from *cyclo*hexanone [Δ^1-cyclo*hexenylmalonic acid*, m. p. 150° (decomp.)], has the βγ-structure, and is oxidised by ozone to Δ^1-*cyclo*pentenyl methyl ketone. The acid is oxidised by permanganate to adipic acid, and yields Δ^1-*cyclo*hexenylacetic acid when heated. Methylation furnishes *ethyl* Δ^1-cyclo*hexenyl-α-methylmalonate*, b. p. 152—154°/16 mm., $d_4^{19\cdot8}$ 1·03723, $n_D^{19\cdot8}$ 1·46748, $[R_L]_D$ 68·06, hydrolysed to the *acid*, m. p. 155°. Ethyl Δ^1-*cyclo*hexenylmalonate does not condense with hydrogen cyanide or ethyl acetoacetate, nor does the pure ester (prepared through the silver salt) condense with ethyl cyanoacetate and ammonia, but with all other samples the ω-imide of αα′-dicyano*cyclo*hexane-1 : 1-diacetic acid is formed. The condensation with ethyl sodiocyanoacetate proceeds to some extent, for a nitrogenous product, probably ethyl α-cyano*cyclo*hexylideneacetate, is isolated which condenses readily with ethyl cyanoacetate and ammonia to give the imide. J. S. H. DAVIES.

Preparation of diphenylsuccinodinitrile. I. G. FARBENIND. A.-G.—See B., 1926, 899.

[Iminolactones and salts of unsaturated nitriles.] J. HOUBEN and E. PFANKUCH (Ber., 1926, **59**, [*B*], 2432; cf. this vol., 951).—A correction of certain errata. H. WREN.

Isomeric fluorobenzaldehydes and their derivatives. J. B. SHOESMITH, C. E. SOSSON, and R. H. SLATER (J.C.S., 1926, 2760—2761).—m-*Fluorobenzaldehyde*, b. p. 173°/760 mm., unlike the *o*- and *p*-isomerides, b. p. 175°/760 mm., and 181·5°/763 mm., respectively, cannot be obtained pure from the corresponding sodium hydrogen sulphite compound, but is prepared in 60% yield by passing a current of dry hydrogen for 24 hrs. into a xylene solution of *m*-fluorobenzoyl chloride in contact with palladised barium sulphate. The following m. p. are recorded: fluorobenzaldoximes, *o*-, 63°; *m*-, 63°; *p*-, 86·5°; *fluorobenzaldehydephenylhydrazones*, *o*-, 89·5°; *m*-, 114°; *p*-, 147°; *fluorobenzaldehyde*-p-*nitrophenylhydrazones*, *o*-, 205°; *m*-, 202°; *p*-, 212°. J. S. H. DAVIES.

Mechanism of the photochemical reactions of *o*-nitrobenzaldehyde and some of its condensation products. I. TANASESCU (Bull. Soc. chim., 1926, [iv], **39**, 1443—1453).—It is shown by Zerewitinoff's method (A., 1907, ii, 509) that a mobile hydrogen atom is present in all *o*-nitrobenzaldehyde derivatives which are sensitive to light, *e.g.*, *o*-nitrobenzylidenepentaerythritolspiran, *o*-nitrobenzylideneglycol, *o*-nitrobenzylidene-erythritol, and *o*-nitrotriphenylmethane. 2 : 4 : 2′ : 4′-Tetranitrodiphenylmethane and hexanitrotriphenylmethane are insensitive, but, owing to their slight solubility in pyridine, it was not possible to examine them for a mobile hydrogen atom. *o*-Nitrodiphenylmethane is sensitive, but requires special study. It is suggested that in *o*-nitrobenzaldehyde the equilibrium $C_6H_4<\begin{matrix}CHO\\ NO_2\end{matrix}\rightleftharpoons C_6H_4<\begin{matrix}CO\\ NO\cdot OH\end{matrix}$ exists, and that the action of light causes a migration of a hydroxyl group from the nitrogen to the carbon atom.

By insolation of a pyridine solution of *o*-nitrotriphenylmethane, *o-nitrosotriphenylcarbinol* was obtained, m. p. 185° to a green liquid; *acetyl* derivative, m. p. 125°. A blue *mono-* and a brown *di-pyridyl* derivative (m. p. above 300°) of hexanitrotriphenylmethane are described. A. S. CORBET.

Beckmann transformation of oximes of α-keto-formhydroxamic acids [hydroxyglyoximes]. C. GASTALDI, M. LONGIAVE, and F. SIRCANA (Gazzetta, 1926, **56**, 550—556; cf. A., 1925, i, 987; Ponzio, this vol., 850).—By analogy with Meisenheimer's γ-benzildioxime, the α-form of phenylhydroxyglyoxime is considered to have the structure

$$\begin{matrix}Ph\cdot C\text{——}C\cdot OH\\ \|\quad\quad\|\\ N\cdot OH\ N\cdot OH\end{matrix}$$

since phosphorus pentachloride transforms it into β-oximino-oxanilide (phenylhydroxyloxamide, A., 1896, i, 209). The β-form gives benzonitrile and a *substance*, m. p. 170—175° (decomp.), which is not 3-hydroxy-5-phenyl-1 : 2 : 4-oxadiazole, since *benzamidoformhydroxamic acid*, COPh·NH·C(:NOH)·OH, from which it would be derived, has been prepared from hydroxylamine and benzoylurethane, and is stable to acetic anhydride. Acetyl chloride gives with the sodium salt of the α-form, 3-phenyl-1 : 2 : 4-oxadiazole, and another substance. E. W. WIGNALL.

New type of rearrangement of oximes. P. W. NEBER and A. VON FRIEDOLSHEIM (Annalen, 1926, **449**, 109—134).—When benzyl methyl ketoxime, m. p. 68—70°, is treated in pyridine solution with *p*-toluenesulphonyl chloride, it yields the p-*toluenesulphonate*, $CH_2Ph\cdot CMe{:}NO\cdot SO_2\cdot C_6H_4Me$, m. p. 78°, which on long exposure to the air changes to *acetobenzylamide* p-*toluenesulphonate*, m. p. 81—82°, and is converted by ethyl alcohol into *benzylamine* p-*toluenesulphonate*, m. p. 180°. According to experimental conditions, the *p*-toluenesulphonate of the oxime reacts with potassium ethoxide solution yielding either 3 : 6-diphenyl-2 : 5-dimethyl-*p*-diazine or α-*amino*-ββ-*diethoxy*-α-*phenylpropane* (*acetate*, m. p. 141°; *picrate*, m. p. 142°; p-*toluenesulphonyl* derivative, m. p. 124°; *benzoyl* derivative, m. p. 133°, which reacts with dilute hydrochloric acid, yielding

α-benzamidobenzyl methyl ketone, m. p. 98°). Similarly, the α-oxime of *o*-nitrobenzyl methyl ketone yields a benzenesulphonate and a p-*toluenesulphonate*, m. p. 109°, which yield the following substances: o-*nitrobenzylamine benzenesulphonate*, m. p. 167° (p-*toluenesulphonate*, m. p. 168°); with alcoholic ammonia, 3 : 6-*di*-o-*nitrophenyl*-2 : 5-*dimethyl*-3 : 6-*dihydro*-p-*diazine*, m. p. 186° (*dibenzoyl* derivative, m. p. 158°; *diacetyl* derivative, m. p. 84—85°); with potassium ethoxide solution and treatment of the product with hydrochloric acid, o-*nitro*-α-*aminobenzyl methyl ketone hydrochloride*, m. p. 184°. R. W. WEST.

Isomeric relationships in the chalkone series. III. Addition of bromine and aniline to substituted chalkones. C. WEYGAND and A. MATTHES (Ber., 1926, 59, [*B*], 2247—2249; cf. A., 1924, i, 521; this vol., 1041).—Addition of bromine to *p*-tolyl styryl ketone affords very small amounts of a *dibromide*, m. p. 140—141° (decomp.), with greatly preponderating quantities of the dibromide, m. p. 175—176°, previously reported. The constitution assigned previously to *p*-tolyl β-anilino-β-phenylethyl ketone is confirmed, Mayer's observation (A., 1905, i, 791) that the product of the condensation of benzylideneaniline and *p*-methylacetophenone has m. p. 171° not being confirmed. The following compounds are described: p-*ethylphenyl* β-*anilino*-β-*phenylethyl ketone*, m. p. 141°; the *substance*, $(CHPh{:}CH{\cdot}CO{\cdot}C_6H_4Et)_2,PhNH_2$, m. p. 187—188°; p-n-*propylphenyl* β-*anilino*-β-*phenylethyl ketone*, m. p. 141°; p-*tolyl* β-p-*toluidino*-β-*phenylethyl ketone*, m. p. 150°. H. WREN.

Isomeric relationships in the chalkone series. IV. β-Ethoxychalkone [phenyl β-ethoxystyryl ketone]. C. WEYGAND and H. HENNIG (Ber., 1926, 59, [*B*], 2249—2253).—The existence of phenyl β-ethoxystyryl ketone in the γ-form, m. p. 63° (cf. Sluiter, A., 1905, i, 796), and in the β-form, m. p. 78° (cf. Wislicenus, *ibid.*, 1900, i, 37), has been confirmed and quantitative interconversion has been effected. In addition, a new α-*modification*, m. p. 81°, has been isolated. Conversion of the α- into the β-variety is effected by crystallisation from absolute ethyl alcohol in a sealed tube. H. WREN.

Truxillic and truxinic ketones. I. Polymerides of phenyl *p*-methoxystyryl ketone and other chalkones. H. STOBBE and A. HENSEL (Ber., 1926, 59, [*B*], 2254—2265).—Exposure of phenyl *p*-methoxystyryl ketone dissolved in glacial acetic acid, alcohol, or chloroform in presence or absence of air to the light of the sun or quartz-mercury lamps gives mainly a neutral resin, mixed occasionally with *p*-anisic acid. Solid phenyl *p*-methoxystyryl ketone is converted into a mixture of resin and 1 : 2-*dibenzoyl*-3 : 4-*di*-p-*methoxyphenyl*cyclo*butane*, m. p. 164°, production of resin being mainly due to the light of shorter wave-length. In aqueous suspension, the ketone is also readily polymerised, whereas hydrochloric acid favours resinification at the expense of polymerisation. The dimeride *A* is stable towards ice-cold, alkaline permanganate or bromine, and hence is saturated. It is far more transparent to light than the simple ketone. Oxidation with chromic acid affords carbon dioxide, anisic and benzoic acids, and resin. Its constitution rests mainly on the observation that it yields monomeric ketone and di-*p*-methoxystilbene when subjected to dry distillation, whereas the hydrocarbon is derived in much smaller yield when the monomeric ketone is very slowly distilled; analogy with the truxillic and truxinic acids leads the authors to suggest the term di-*p*-methoxydiphenyltruxin ketone for the dimeride *A*. The latter compound is isomerised by acetic anhydride, glacial acetic acid, concentrated hydrochloric acid, alcoholic potassium hydroxide, pyridine, piperidine, or when heated at 180—200° to 1 : 2-dibenzoyl-3 : 4-di-*p*-methoxyphenyl*cyclo*butane *B* (di-*p*-methoxydiphenyltruxin ketone *B*], prepared synthetically by Stobbe and Striegler (A., 1912, i, 781); it is stable to bromine and ice-cold, alkaline permanganate, and resembles dimeride *A* in its absorption spectrum. The dimerides *A* and *B* are not affected by phosphorus pentasulphide, but are converted by alcoholic ammonia into the *ketimine*,

$$OMe{\cdot}C_6H_4{\cdot}CH<\begin{matrix}CH(C_6H_4{\cdot}OMe)\\ CHBz\end{matrix}>CH{\cdot}CPh{:}NH,$$

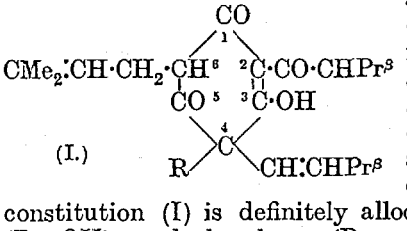
m. p. 154° [corresponding *phenylhydrazone*, m. p. 178° (decomp.)], which is regarded as a derivative of the *B* compound. Dimeride *A* is converted by hydrazine hydrate into an amorphous compound, whereas dimeride *B* gives a *dihydrazone*, m. p. 215°. Hydroxylamine and dimeride *A* afford a *monoxime*, m. p. 199° (decomp.), whereas dimeride *B* does not react. Both ketones are indifferent to semicarbazide. Dimeride *A* is unchanged by treatment with sodium and moist benzene and mainly isomerised to *B* by amalgamated zinc and hydrochloric acid. Hydriodic acid causes resinification of *A* and *B*. Hydroxylamine hydrochloride causes isomerisation of *A* to *B* at 130°, whereas at 140—150° profound decomposition is induced, accompanied by the production of di-*p*-methoxystilbene. From analogy with the truxinic acids, it is suggested that dimerides *A* and *B* are *cis*- and *trans*-compounds, respectively. The great resistance of the substances to intramolecular ring closure is thereby explained, since the stable derivative *B* is constitutionally unsuited to this type of change and compound *A* is too prone to isomerisation. Phenyl *o*-methoxystyryl ketone is largely resinified when illuminated in benzene containing iodine, chloroform, or methyl alcohol; in the last case, a small proportion of a *dimeride*, m. p. 162, is produced; in the solid condition, the particles of ketone become coated with resin when illuminated. Phenyl styryl ketone in glacial acetic acid or chloroform gives much resin and little *dimeride*, m. p. 124°; in aqueous suspension in presence of mercuric chloride, a photodimeride, m. p. 220—222°, probably 1 : 2-dibenzoyl-3 : 5-diphenyl*cyclo*butane, is produced. H. WREN.

[Simplest *O*-alkyl ethers of benzoylacetone.] C. WEYGAND (Ber., 1926, 59, [*B*], 2253; cf. A., 1925, i, 1289; Claisen, this vol., 406).—Claisen's conclusion that the product of the action of ethyl orthoformate on benzoylacetone has the constitution CHBz:CMe·OEt is confirmed further by the presence of ethyl acetate among the substances formed by fission with ozone. The b. p. of phenylmethyl*iso*-

oxazole, m. p. 42°, is incorrectly given. In agreement with Claisen, the b. p. of the isomeric phenylmethyl*iso*oxazoles are found to lie very close together. H. WREN.

Salt formation from 1 : 3-diketones. I. Beryllium and aluminium salts of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione. C. WEYGAND and H. FORKEL (Ber., 1926, 59, [*B*], 2243—2247).—5 : 5-Dimethyl*cyclo*hexane-1 : 3-dione does not yield metallic compounds when treated with aluminium or beryllium sulphate in aqueous alkaline solution. The *aluminium* compound, $C_{24}H_{33}O_6Al$, m. p. about 270° (decomp.), is prepared by heating a mixture of the diketone with ethyl aluminoacetoacetate or aluminium ethoxide in a vacuum at 110° or, preferably, from the diketone and aluminium ethoxide in boiling xylene. The *beryllium* compound, $C_{12}H_{18}O_6Be$, m. p. 315—355° (decomp.), is analogously prepared. The compounds differ from typical enolates in their non-volatility and insolubility in indifferent media. They are readily hydrolysed and behave like salts of weak acids and weak bases. The aluminium derivative is decomposed by ethyl acetoacetate into the free diketone and ethyl aluminoacetoacetate. *Ethyl beryllioacetoacetate*, m. p. 63°, b. p. 166°/13 mm., is incidentally described. H. WREN.

Resin acids of hops. III. H. WIELAND and E. MARTZ (Ber., 1926, 59, [*B*], 2352—2356; cf. A., 1925, i, 276, 1422).—The hydrocarbon, $C_{15}H_{18}$, b. p. 108—110°/11 mm., is obtained homogeneous when humulic acid is reduced by Clemmensen's method under particular conditions. It is hydrogenated in presence of platinum oxide (but not of platinum-black on spongy platinum) to 1 : 3-*di*iso*amyl*cyclo*pentane*, b. p. 110—112°/11 mm., prepared also by treatment of dihydrohumulic acid with amalgamated zinc and hydrochloric acid. Ozonisation of the unsaturated hydrocarbon affords acetone and 2-iso*amyl*-β-1-cyclo*pentylacetaldehyde*, b. p. 74—76°/11 mm.; acetone is also obtained similarly from humulic acid. The position of the double linking in the side-chain attached to carbon atom 6 of humulone and its derivatives is thereby established and the constitution (I) is definitely allocated to humulone (R=OH) and lupulone (R=amylene). Suitable interruption of the reduction of dihydrohumulic acid by Clemmensen's method affords *deoxyhumulic acid*, $\begin{matrix}CH_2\text{-}CH(CH_2\cdot CH_2Pr^\beta)\\ C(OH){:}C(CH_2\cdot CH_2Pr^\beta)\end{matrix}>CO$, m. p. 146°. H. WREN.



(I.)

Hydroxybenzophenones and hydroxyxanthones. H. ATKINSON and I. M. HEILBRON (J.C.S., 1926, 2688—2691).—Although phloroglucinol and salicylonitrile condense to yield finally 1 : 3-dihydroxyxanthone (Nishikawa and Robinson, *ibid.*, 1922, **121**, 839), the condensation between salicylonitrile and resorcinol, salicylonitrile and pyrogallol, β-resorcylonitrile and pyrogallol does not take place unless the hydroxy-groups of the nitrile are protected. The normal course of the reaction when the acetyl derivatives are used is, however, complicated by side reactions. In none of the condensations was the intermediate ketimine or its hydrochloride isolated pure, owing to the partial removal of the acetyl groups during the condensation. *o*-Acetoxybenzonitrile and resorcinol furnish 3-hydroxyxanthone, m. p. 246° (Ullmann and Denzler, A., 1907, i, 142, give m. p. 242°), and 2 : 4 : 2′-trihydroxybenzophenone. Pyrogallol and *o*-acetoxybenzonitrile give 2 : 3 : 4 : 2′-tetrahydroxybenzophenone, together with a little 3 : 4-dihydroxyxanthone and gallacetophenone. Pyrogallol and diacetyl-β-resorcylonitrile give 2 : 3 : 4 : 2′ : 4′-pentahydroxybenzophenone, $C_{13}H_{10}O_6,2H_2O$, m. p. 187° (D.R.-PP. 49149, 50451 give m. p. 168—170°), and a little gallacetophenone. Resorcinol and diacetyl-β-resorcylonitrile yield 2 : 4 : 2′ : 4′-tetrahydroxybenzophenone and a little 3 : 6-dihydroxyxanthone. J. S. H. DAVIES.

New oxidation product from *p*-benzoquinone. E. M. TERRY and N. A. MILAS (J. Amer. Chem. Soc., 1926, **48**, 2647—2652).—When treated with aqueous sodium chlorate, acidified with hydrochloric acid, in presence of a trace of osmium tetroxide, quinol is converted (with intermediate, exothermic formation of quinhydrone) into a colourless *compound*, $C_6H_6O_4$, decomp. 177—178°, which is tentatively regarded as 2 : 3-*dihydroxy*-2 : 3-*dihydro*-1 : 4-*benzoquinone*. The yield is more than 50%, and oxalic acid and at least one other *product*, as well as carbon dioxide, are also formed. When boiled for 48 hrs. with excess of acetic anhydride, the new compound yields a *tetra-acetate*, m. p. 139° (decomp.), which is possibly identical with the tetra-acetate of 1 : 2 : 3 : 4-tetrahydroxybenzene (apionol) (cf. Einhorn, Cobliner, and Pfeiffer, A., 1904, i, 238). The tautomeric nature of the compound, which the formation of apionol tetra-acetate would demand, is indicated by the production of an intense absorption band on the addition of alkali to its aqueous solution, the original solution showing only general absorption. The fresh aqueous solution is only slowly attacked by bromine and gives no coloration with ferric salts, but the reacidified alkaline solution absorbs bromine rapidly and gives a red coloration with ferric chloride, whilst excess of ferric chloride yields an intense blue coloration. When the new compound is treated with acetic anhydride and a small proportion of concentrated sulphuric acid, a vigorous reaction takes place, and a *compound*, $C_{20}H_{16}O_{10}$, m. p. 217—218°, is obtained. If the proportion of sulphuric acid be reduced, the reaction is correspondingly moderated, and the product is a mixture of the above compound and a *compound*, $C_{24}H_{22}O_{13}$. Benzoyl chloride and pyridine convert the dihydroxydihydrobenzoquinone into a *tetrabenzoate*, m. p. 191—192°, whilst the reacidified alkaline solution affords, on treatment with sodium bromide and bromate, a *bromine* derivative, yellow, m. p. 285°. 2 : 3-Dihydroxy-2 : 3-dihydrobenzoquinone in alkaline solution appears to form slowly a disodium salt, which suggests tautomerisation to 2 : 3-dihydroxy-5 : 6-dihydro-1 : 4-benzoquinone. Phenylhydrazine affords a condensation product, apparently a *dihydrazone-dihydrazide*, whilst crystalline derivatives are also obtained from hydroxylamine, aniline, and

mercuric acetate, and heavy metals yield insoluble *salts*. F. G. WILLSON.

Arylidoanthraquinone derivatives. FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 866.

Benzanthrone derivatives containing sulphur [sulphinic acids]. I. G. FARBENIND. A.-G.—See B., 1926, 867.

Intermediates [mercaptans, sulphides, disulphides] of the benzanthrone series. BADISCHE ANILIN- UND SODA-FABRIK and FARBW. VORM. MEISTER, LUCIUS, UND BRÜNING.—See B., 1926, 867.

[Halogeno-alkoxybenzanthrones and *iso*dibenzanthrones.] R. F. THOMSON, J. THOMAS, and SCOTTISH DYES LTD.—See B., 1926, 868.

Halogenated dibenzpyrenequinones. I. G. FARBENIND. A.-G., G. KRÄNZLEIN, R. SEDLMAYR, and H. VOLLMANN.—See B., 1926, 868.

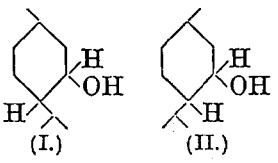
Mordant dyes of the phenanthraquinone series. K. BRASS.—See B., 1926, 868.

Association of double linking with lactone group in cardiac aglucones. W. A. JACOBS, A. HOFFMANN, and E. L. GUSTUS (J. Biol. Chem., 1926, 70, 1—11).—Like strophanthidin and its derivatives (this vol., 430), digitoxigenin and gitoxigenin reduce Tollens' reagent and give a colour reaction with sodium nitroprusside, these reactions being no longer obtainable after hydrolysis or hydrogenation; these substances further resemble one another in failure to absorb bromine; it was, however, found that the products of hydrolysis of these substances, as of the strophanthidin derivatives, were not keto-acids, but apparently hydroxy-acids. In the case of the angelolactones, the $\Delta^{\beta\gamma}$-form gives an immediate reduction of Tollens' solution, the $\Delta^{\alpha\beta}$-form a slower reduction, and α-substituted derivatives no reduction; the reaction appears to be dependent, therefore, on the presence of the α-methylene group, which can exist only in the $\Delta^{\beta\gamma}$-form. The similarity in these reactions between the crotonolactones and the strophanthidin derivatives, and the failure of the latter to yield keto-acids on hydrolysis, are explained by assuming that, in the latter, the double linking is attached to the β-carbon atom, but outside the lactone ring; in the anhydrostrophanthidin compounds, which do yield keto-acids on hydrolysis, the newly-formed double linking may have caused a shift of the original one to the βγ-position within the lactone ring. The ethylal of oxidoanhydrostrophanthidin, after alkaline hydrolysis, gave an *oxime*, m. p. 153—155°; the tetrahydrodilactone, $C_{23}H_{30}O_4$ (this vol., 73), similarly yielded an *oxime*, m. p. 248—249°. C. R. HARINGTON.

Saponins. IV. Oxidation of hederagenin methyl ester. W. A. JACOBS and E. L. GUSTUS (J. Biol. Chem., 1926, 69, 641—652; cf. A., 1925, i, 948).—By oxidation of hederagenin methyl ester with chromic acid, there were obtained an *acid*, $C_{31}H_{48}O_5$, m. p. 133—135°, $[\alpha]_D^{28}$ +117° in alcohol, and a *ketone*, $C_{31}H_{48}O_3$, m. p. 208—210°, $[\alpha]_D^{30}$ +87° in pyridine. The acid proved to be the monomethyl ester of an acid, $C_{30}H_{46}O_5$, *dimethyl* ester, m. p. 161—163°; it gave an *oxime*, m. p. 180° (softening at 160°). The ketone yielded an *oxime*, m. p. 198°; on reduction by Clemmensen's method, it gave a *substance*, $C_{31}H_{50}O_2$, m. p. 190—191°, $[\alpha]_D^{21}$ +82° in pyridine. The ketone was probably formed by oxidation to carboxyl of the primary alcoholic group of hederagenin methyl ester and subsequent loss of carbon dioxide from the resulting β-keto-acid. On further oxidation with chromic acid, it yielded a *diketone*, $C_{31}H_{46}O_4$, m. p. 238—240°, $[\alpha]_D$ +81° in pyridine, *monoxime*, m. p. 156—158°, which, on reduction, gave a *substance*, $C_{31}H_{50}O_2$, m. p. 192—194°, $[\alpha]_D$ +45° in pyridine, not identical with the above-mentioned substance of the same formula, and a *hydroxyketone*, $C_{31}H_{48}O_4$, m. p. 215—216°, $[\alpha]_D$ +10° in pyridine, *oxime*, m. p. 200° (softening at 170°), which, on reduction, gave a *substance*, $C_{31}H_{50}O_3$, m. p. 180—182°, $[\alpha]_D$ +20·6° in pyridine. Neither the diketone nor the hydroxyketone absorbed bromine. In the light of the above results, the recent conclusions of van der Haar (A., 1925, i, 946), particularly in relation to the position of the carboxyl group of hederagenin, are criticised. C. R. HARINGTON.

Caoutchouc—formula and ozonide. F. EVERS (Kautschuk, 1926, 204—206).—Reconsideration of the fission behaviour of caoutchouc ozonide and of recent physical investigations of the constitution of caoutchouc indicates Harries' formula as the most satisfactory for the fundamental particle. D. F. TWISS.

Stereoisomerism in the menthol series. O. ZEITSCHEL and H. SCHMIDT (Ber., 1926, 59, [*B*], 2298—2307).—*neo*Menthol is converted far more readily than *l*-menthol by dehydrating agents into menthene. The latter hydrocarbon is also the principal product of the action of phosphorus pentachloride or thionyl chloride on *neo*menthol, whereas the hydroxy-group of *l*-menthol is smoothly replaced by chlorine by the former reagent and untouched by the latter reagent. Contrary to Vavon, therefore (this vol., 837), it appears that the hydroxy-group and a tertiary hydrogen atom are vicinal in *neo*menthol. The relative positions of the methyl and *iso*propyl groups in menthol and *neo*menthol are established by oxidising them respectively to *l*-menthone, m. p. —7°, b. p. 210°/760 mm., d_{20}^{15} 0·8937, n_D^{20} 1·44952, $[\alpha]_D$ —25·55°, and *d-iso*menthone, m. p. about —35°, b. p. 212°/760 mm., d_{20}^{15} 0·902, n_D^{20} 1·45302, $[\alpha]_D$ +85·10°. The interpretation of the physical constants according to the Auwers–Skita rule indicates the *trans*-position of methyl and *iso*propyl groups in *l*-menthone and the *cis*-position in *d-iso*menthone. The structures (I) and (II) are hence assigned to menthol and *neo*menthol, respectively.



(I.) (II.)

The following constants are recorded: *l*-menthol, m. p. 42—43°, b. p. 216°/760 mm., d_{20}^{15} 0·900, n_D^{27} 1·45412, $[\alpha]_D$ —48·5° (formate, m. p. +9°, b. p. 222—223°/760 mm., d_{15}^{15} 0·940; acetate, b. p. 228°/760 mm., d_{15}^{15} 0·930, n_D^{20} 1·44562; α-naphthylurethane, m. p. 126°); *r*-menthol, m. p. 34°, b. p. 216°/760 mm., d_{20}^{15} 0·900, n_D^{20} 1·46150 (acetate, b. p. 228—229°/760 mm., d_{15}^{15}

0·931, n_D^{20} 1·44600; phenylurethane, m. p. 103—104°); *d-neo*menthol, m. p. —15°, b. p. 211·5—211·8°/755 mm., d_{15}^{15} 0·903, n_D^{20} 1·46030, $[\alpha]_D$ +19·6° (*acetate*, m. p. 37·2—37·8°, b. p. 227°/760 mm., d_{25}^{15} 0·921, n_D^{25} 1·44381; *formate*, m. p. —21°, b. p. 221—222°/760 mm., d_{15}^{15} 0·940, n_D^{20} 1·44902; *propionate*, b. p. 239—240°/760 mm., d_{15}^{15} 0·922, n_D^{20} 1·44560; *phenylurethane*, m. p. 108°; *α-naphthylurethane*, m. p. 126°; *allophanate*, m. p. 215·5°); *r-neo*menthol, m. p. 51°, b. p. 211·4—211·8°/755 mm., d_{15}^{15} 0·903, n_D^{20} 1·46040 (acetate, m. p. 27°, b. p. 227°/760 mm., d_{15}^{15} 0·928, n_D^{20} 1·44580; phenylurethane, m. p. 114°; α-naphthylurethane, m. p. 132°). H. WREN.

Borneol, *iso*borneol, and their esters. P. PEIGNIER (Diss., Nancy, 1926; Parfums de France, 1926, 4, 196—201).—The following data are recorded. *l*-Borneol, m. p. 208° (corr.); $[\alpha]_{578}$ (0·02 or 0·05% solution) —35° to —42·2°; rotatory dispersion $[\alpha]_{436}/[\alpha]_{578}$, 1·94—1·98. *l-iso*Borneol, m. p. 218° (corr.); $[\alpha]_{578}$ (0·05%) —39·7° to —20·3° (higher results were obtained for 0·02% solutions in carbon disulphide, *cyclo*hexane, chloroform, and benzene); rotatory dispersion, 1·85—1·74. *l-iso*Bornyl hydrogen phthalate, m. p. about 167° (uncorr.; decomp.); $[\alpha]_{578}$ (0·05%) —85·3° (in alcohol), —80·5° (in chloroform). *l*-Bornyl benzoate, m. p. 24·5—25·5°, b. p. 196—197° (corr.)/18 mm.; d_4^{16} 1·0543; n_D^{16} 1·526; $[\alpha]_{578}$ (0·05%) —43·3° (in alcohol), —39° (in benzene). l-iso*Bornyl benzoate*, b. p. 185° (corr.)/11 mm.; d_4^{16} 1·057; n_D^{16} 1·529; $[\alpha]_{578}$ (0·05%) —81·8° (in alcohol), —76·9° (in benzene). *d*-Bornyl hydrogen succinate, m. p. 61—62°; $[\alpha]_{578}$ (0·05%) +37·6° (in alcohol), +30·2° (in benzene). *l-iso*Bornyl hydrogen succinate, m. p. 63·5—64·5°; $[\alpha]_{578}$ (0·05%) —57·3° (in alcohol), —49·7° (in benzene). d-*Bornyl* iso*valerate*, b. p. 153—154° (corr.)/26 mm.; d_4^{18} 0·9486; n_D^{18} 1·4605; $[\alpha]_{578}$ (0·05%) +38·6° (in alcohol), +33·4° (in benzene). *l-iso*Bornyl *iso*valerate, b. p. 143·5—145·5° (corr.)/18 mm.; d_4^{18} 0·9523, n_D^{18} 1·462; $[\alpha]_{578}$ (0·05%) —58·7° (in alcohol), —53·8° (in benzene). With valeric acid at 100° or 133°, and with acetic acid at 100°, borneol is esterified about twice as fast as *iso*borneol; with acetic acid containing 1·7% of sulphuric acid at 39° or 15°, about four times as fast. Bornyl esters are hydrolysed 4—25 times as fast as the corresponding *iso*bornyl esters, the latter being submitted to steric hindrance by the *iso*propyl group. When values of [α] are plotted against the wave-length, the curves for *iso*borneol indicate its existence in solution in two molecular forms, the relative proportions of which vary with the concentration and the solvent.

CHEMICAL ABSTRACTS.

Manufacture of synthetic camphor [conversion of bornyl chloride into camphene]. G. H. DUPONT.—See B., 1926, 932.

Manufacture of esters of borneol and *iso*borneol. CHEM. FABR. VORM. SCHERING.—See B., 1926, 932.

Process for making camphor. H. D. GIBBS and A. W. FRANCIS.—See B., 1926, 932.

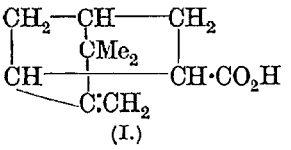
Camphane series. XLI. The unstable modification of *iso*nitrosocamphor. M. O. FORSTER and K. A. N. RAO (J.C.S., 1926, 2670—2675).—The mixture obtained by treatment of camphor with sodium and amyl nitrite is readily separated into equal proportions of the isomeric *iso*nitrosocamphors by fractional precipitation from the dissolved sodium derivatives with dilute acetic acid. Treatment of the unstable modification, m. p. 114°, with magnesium methyl iodide yields only the α-oxime, m. p. 181°, $[\alpha]_D$ + 86·6°, formerly obtained (m. p. 178°, $[\alpha]_D$ +84·2°; *ibid.*, 1905, 87, 232), together with the γ-oxime from the Claisen mixture, whilst the γ-oxime is the sole product from stable *iso*nitrosocamphor. Complete confirmation of the *syn-* and *anti*-configurations ascribed, respectively, to the stable and unstable *iso*nitroso-derivatives is thus obtained. The so-called β-oxime, produced from neither *iso*nitroso-derivative alone, but only from the Claisen mixture, is regarded as an obstinate association of the α- and γ-oximes, and not as a separate individual.

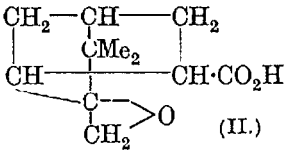
M. CLARK.

New camphorsulphonic acid obtained with new sulphonating agent. M. FRÈREJACQUE (Compt. rend., 1926, **183**, 607—609).—Methyl chlorosulphonate reacts with aromatic hydrocarbons, giving methyl sulphonates. With camphor it yields *methyl camphorsulphonate*, m. p. 77°, which when hydrolysed yields a *camphorsulphonic acid*, $\begin{matrix}CH_2\cdot C\text{——}C\cdot SO_3H\\ |\quad\quad CMe_2\quad\quad ||\\ CH_2\cdot CMe\text{—}C\cdot OH\end{matrix}$, $[M]_D$ +194°. When it is heated with aniline, camphor and sulphanilic acid are formed, and when it is oxidised, it gives camphoric acid. L. F. HEWITT.

Camphor and terpenes. IV. Additions and transformations in the camphor series. *iso*Borneol-, camphor-, camphol-, and camphorquinone-carboxylic acids. J. HOUBEN and E. PFANKUCH (Ber., 1926, **59**, [*B*], 2285—2298; cf. this vol., 731).—Camphene-1-carboxylic acid is converted by bromine in light petroleum into the corresponding *dibromide*, decomp. 182°, which, with alkali, appears to yield *bromocamphene-1-carboxylic acid*. Camphene-1-carboxylamide affords *bromocamphene-1-carboxylamide*, m. p. 232°. Treatment of camphene-1-carboxylamide with phosphorus pentachloride and phosphoryl chloride affords camphene-1-nitrile, m. p. 77—79°, which is transformed by trichloroacetic acid into 6-*trichloroacetoxycamphane-2-nitrile*, m. p. 108°, hydrolysed to 6-*hydroxycamphane-2-nitrile*, m. p. 217—218° (also $+CH_3\cdot CO_2H$). 2-*Chlorocamphane-2-nitrile*, m. p. 170—171°, is prepared from camphene-1-nitrile and hydrogen chloride in ether or from chlorohydropinenecarboxylamide and phosphoryl chloride at 60°. Treatment of camphenecarboxylic acid with acetic or formic and sulphuric acids yields 6-*acetoxycamphane-2-carboxylic acid*, m. p. 107—110°, and 6-*formoxycamphane-2-carboxylic acid*, m. p. 99—100°, which are hydrolysed to 6-*hydroxycamphane-2-carboxylic acid* (*isoborneolcarboxylic acid*), m. p. 216—220° (decomp.). 6-*Trichloroacetoxycamphane-2-carboxylamide*, m. p. 154°, is prepared analogously from the unsaturated amide and hydrolysed to 6-*hydroxycamphane-2-carboxylamide*, m. p. 206—208°. Methyl camphene-1-carboxylate and hydrazine hydrate give *camphene-1-carboxylhydrazide*, m. p. 103°. When heated, 6-hydroxycamphane-2-carboxylic acid passes into *camphene-2-carboxylic acid* (I), m. p. 159—160°

(additive *compound* with mercuric acetate), from which *dihydrocamphene-2-carboxylic acid*, m. p. 170°,


(I.)

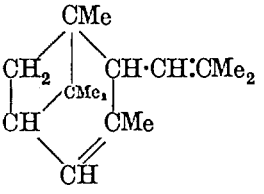

(II.)

and *camphene-2-carboxylic acid dibromide*, decomp. 184—185°, are derived. Addition of hydrogen chloride in presence or absence of water to camphene-2-carboxylic acid affords *6-chlorocamphane-2-carboxylic acid*, m. p. 140—142°, readily reconverted into camphene-2-carboxylic acid. The successive action of thionyl chloride and ammonia on camphene-2-carboxylic acid gives a chlorinated product converted by addition of hydrogen chloride into *6-chlorocamphane-2-carboxylamide*, m. p. 129—130°, which is reduced by hydrogen in the presence of palladium to camphane-2-carboxylamide, m. p. 134—135°. Oxidation of sodium camphene-2-carboxylate by potassium permanganate gives *oxidocamphene-2-carboxylic acid* (II), m. p. 184—185°, and a dicarboxylic *acid*, $C_{11}H_{16}O_4$, decomp. about 300°. The oxido-acid is converted by hydroxylamine hydrochloride into a *lactone*, $C_{11}H_{16}O_2$, m. p. 168°, and by hydrogen chloride into *chlorohydroxyisocamphanecarboxylic acid*, m. p. about 150° (decomp.). *6-Bromocamphane-2-carboxylic acid*, m. p. 169—170° (decomp.), is prepared by the action of hydrogen bromide on the lactone or on camphene-2-carboxylic acid.

Oxidation of 6-hydroxycamphane-2-carboxylic acid by potassium permanganate in alkaline solution gives *camphor-6-carboxylic acid*, m. p. 215°; the corresponding *ethyl* ester, b. p. 148—149°/17 mm., *oxime*, m. p. 229° (decomp.), and *oxime acetate*, m. p. about 210° (decomp.), are described. Fusion with potassium hydroxide at 230—250° transforms camphor-6-carboxylic acid into "*campholcarboxylic acid*" [2 : 3 : 3 : 4-*tetramethylcyclopentane*-1 : 2-*dicarboxylic acid*], m. p. 197—198° [*anhydride*, m. p. 175° (decomp.)]. *3-Oximinocamphor-6-carboxylic acid*, m. p. 195° (decomp.), obtained by the action of amyl nitrite and sodamide on camphor-6-carboxylic ester, is converted by sodium hydrogen sulphite and glacial acetic acid into *camphorquinone-6-carboxylic acid*, m. p. 234—235° (decomp.). H. WREN.

Oxidation of sabinol with hydrogen peroxide. G. G. HENDERSON and A. ROBERTSON (J.C.S., 1926, 2761—2762).—By oxidation with hydrogen peroxide, the same two isomeric glycol anhydrides, $C_{10}H_{16}O(OH)_2$, m. p. 172° and 174°, respectively, are obtained from sabinol, b. p. 208—209°/760 mm., d_4^{20} 0·9420, n_D 1·4874, as from sabinene (*ibid.*, 1923, **123**, 1849). This result supports the view that the glycol anhydrides are derived from 1 : 2 : 3 : 4-tetrahydroxymenthane, which is possibly formed as an intermediate product of the oxidation process. The glycol anhydride, m. p. 172°, forms a compound, m. p. 159—160° (decomp.), with hydrogen bromide, which is probably 1 : 2 : 3 : 4-tetrabromomenthane. J. S. H. DAVIES.

Mono- and sesqui-terpenes. [**Caryophyllene.**] E. DEUSSEN (J. pr. Chem., 1926, [ii], **114**, 63—122). —The author modifies Semmler's formula for α- and β-caryophyllene (as shown), whilst retaining at present Semmler's constitution of γ-caryophyllene (A., 1912, i, 120). Dehydrogenation of caryophyllene by sulphur affords three hydrocarbons, $C_{10}H_{14}$, b. p. 92—95°/15 mm., $C_{14}H_{16}$, and $C_{14}H_{18}$, b. p. 152—153°/12·5 mm., from which no characteristic derivatives could be obtained (cf. A., 1923, i, 813). Confirmation is obtained that dihydrocaryophyllene is the sole product of catalytic reduction in presence of palladium or nickel, and of the correctness of the earlier work on the caryophyllene glycols, $C_{15}H_{24}O_4$ and $C_{10}H_{18}O_3$ (A., 1909, i, 171), which are not reduced catalytically.



αβ-Caryophyllene forms a *dibromide* (decomp. on distillation), and only reacts with 2 mols. of bromine with evolution of hydrogen bromide. γ-Caryophyllene (A., 1907, i, 945) reacts with 1 mol. of bromine.

The mercuric acetate additive product from caryophyllene reacts with alkali halides (cf. A., 1923, i, 813), and gives with alcoholic sulphuric acid a *compound*, $C_{15}H_{24}OHg$, decomp. 122°; a *carbonate*, $(OH{\cdot}C_{15}H_{24}{\cdot}HgOCO_2)_2Hg$, decomp. 188°; with phosphoric acid, a *phosphate*, $OH{\cdot}C_{15}H_{24}HgPO_4H_2$, decomp. 84°; with oxalic and cinnamic acids, *compounds*, $C_{15}H_{24}HgO{\cdot}Hg(CO_2)_2$, decomp. 179°, and $C_{15}H_{24}HgO{\cdot}Hg(PhC_2H_2CO_2)_2$, decomp. 154°.

γ-Caryophyllene yields a mercuric acetate *compound*, $OH{\cdot}C_{15}H_{24}HgAc$, in which the acetyl group may be replaced by halogen (Cl, m. p. 94°; Br, m. p. 99°; I, m. p. 96°) or by the cyano-group (decomp. 134°; γ-caryophyllene is regenerated by hydrogen sulphide), in which case a second *substance*, $C_{15}H_{24}OHg{\cdot}Hg(CN)_2$, decomp. 156°, is also formed.

The investigation of the action of potassium hydroxide in solution in various alcohols on blue β-caryophyllene nitrosite (A., 1915, i, 274) has been repeated and extended to α-propylene glycol (*α-isomeride*, decomp. 132°, *β-isomeride*, decomp. 146°) and allyl alcohol (the *substance*, decomp. 136°, forms a *tetrabromide*). A by-product in the case of ethyl alcohol is the colourless, unimolecular nitrosite, from which the blue compound is re-formed by acetic acid—reactions which are represented by the scheme ·CH(NO)·⇌·C(:NOH).

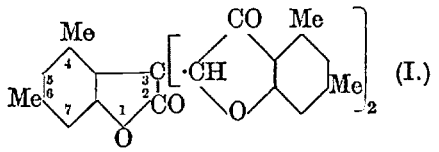
The iodo-β-nitrosite forms a *hydrochloride*, decomp. 143°, but the hydrochloro-β-nitrosite does not react with iodine. α-, β-, and γ-Caryophyllenes are not reduced by sodium and amyl alcohol, which precludes the presence of a conjugated system of double linkings.

The behaviour of santene has been observed for comparison. The mercuric acetate *compound*, decomp. 126—127°, yields an iodo-*derivative*, $C_9H_{14}(OH)HgI$, decomp. 130—131°, and treatment with hydrogen sulphide produces santene glycol and a *substance*, $C_9H_{14}O$, b. p. 89—90°/24 mm. Blue santene nitrosite (*hydrochloride*, decomp. 98°) passes into a colourless, unimolecular *modification*, decomp. 105°, on treatment with 20% potassium hydroxide, but shows no tendency to form alkyloxy-derivatives. Reduction attacks the N_2O_3 grouping, a colourless dihydro-*compound*, m. p. 87—88°, being formed;

exposure to sunlight produces a *nitrosate*, $C_9H_{14}N_2O_4$, decomp. 216°. Green santene nitrosite is possibly a mixture.

β-*iso*Caryophyllene alcohol forms a chromic ester, decomp. 116°, and is therefore a tertiary alcohol (cf. Wienhaus, A., 1914, i, 300), whereas α-caryophyllene alcohol forms no ester. J. M. GULLAND.

Condensation of coumarandiones with coumaranones. R. STOLLÉ and H. STAMM (J. pr. Chem., 1926, [ii], **114**, 242—248).—The synthesis of tetramethyloxindirubin (3 : 2′-diketo-4 : 6 : 4′ : 6′-tetramethyl-2 : 3′-dicoumaran) by Fries and Bartens (A., 1925, i, 568) has led to the re-examination of the substance to which this constitution was previously assigned (*ibid.*, 1921, i, 578). The latter on dissolution in concentrated sulphuric acid breaks up into 1 mol. of the former and 1 mol. of 4 : 6-dimethylcoumaran-3-one. It is therefore *di*-3-(3-*keto*-4 : 6-*dimethyl*-2-*coumaranyl*)-4 : 6-*dimethylcoumaran*-2-*one*. (I), m. p., with darkening, 245°



(233°, *loc. cit.*). 5-Chloro-4 : 6-dimethylcoumaran-2 : 3-dione condenses with 4 : 6-dimethylcoumaranone in presence of glacial acetic acid and a little concentrated hydrochloric acid to form 5-*chlorodi*-3-(3-*keto*-4 : 6-*dimethyl*-2-*coumaranyl*)-4 : 6-*dimethylcoumaran*-2-*one*, m. p. 270°, from which 5-*chloro*-3 : 2′-*diketo*-4 : 6 : 4′ : 6′-*tetramethyl*-2 : 3′-*dicoumaran*, m. p. 218°, with previous sintering, is obtained by means of sulphuric acid. Similarly, from 7-methyl-4-*iso*propylcoumaran-2 : 3-dione, *di*-3-(3-*keto*-4 : 6-*dimethyl*-2-*coumaranyl*)-7-*methyl*-4-iso*propylcoumaran*-2-*one*, m. p. 232° (cf. Ziegler, Diss., Heidelberg, 1923), and 3 : 2′-*diketo*-7 : 4′ : 6′-*trimethyl*-4-iso*propyl*-2 : 3′-*dicoumaran*, m. p. 206°, are obtained. Reduction of tetramethyloxindirubin with zinc dust and acetic acid gives a colourless *substance*, m. p. 184°.

H. E. F. NOTTON.

Catalytic hydrogenations under pressure in the presence of nickel salts. XI. Xanthone. J. VON BRAUN and O. BAYER (Ber., 1926, **59**, [*B*], 2317—2323; cf. this vol., 172).—Xanthone is very rapidly hydrogenated at about 200° mainly to xanthen, m. p. 99°. Further addition of hydrogen (8 atoms) leads to a mixture of xanthone, xanthen, hexahydroxanthen, and products richer in hydrogen from which a homogeneous material can be isolated with great difficulty. It is therefore preferable to continue the action until all the xanthen has been reduced; *hexahydroxanthen*, $C_6H_4<^{CH_2}_{O}>C_6H_8$, m. p. 78°, and (?) *tetrahydroxanthen*, m. p. 42—43°, are then readily isolated. Further hydrogenation at 220—230° affords *dodecahydroxanthen*, b. p. 135—137°/13 mm., d_4^{20} 0·9733, n_D^{20} 1·4930, and o-*hexahydrobenzyl*cyclo*hexanol*, b. p. 151°/13 mm., m. p. 55°, which may be a mixture of *cis*- and *trans*-isomerides, since the m. p. (104—106°) of the corresponding *phenylurethane* is not quite definite. Still further hydrogenation increases the yield of o-hexahydrobenzyl*cyclo*hexanol, but causes also production of dodecahydrodiphenylmethane. o-*Hexahydrobenzyl*cyclo*hexanone*, b. p. 143—145°/13 mm., $d_4^{18\cdot5}$ 0·9805, n_D^{21} 1·4946, and its *semicarbazone*, m. p. 154—155°, are described. H. WREN.

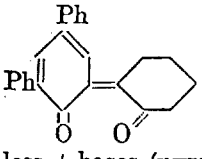
***iso*Flavone group. II. Synthesis of methylgenistein (methylprunetol) dimethyl ether and the constitution of prunetol (genistein).** W. BAKER and R. ROBINSON (J.C.S., 1926, 2713—2720; cf. A., 1925, i, 1299).—Prunetol and genistein have been found to be identical by direct comparison, and Finnemore's formulation (*ibid.*, 1910, ii, 1102) of the former as a trihydroxy*iso*flavone has been proved correct by synthesis of a trimethyl derivative. 2 : 4 : 6-*Trihydroxyphenyl* p-*hydroxybenzyl ketone*, $+H_2O$, m. p. 259° (decomp.), obtained by condensation of phloroglucinol and *p*-hydroxyphenylacetonitrile, gives, on acetylation, a poor yield of 5-*hydroxy*-7 : 4′-*diacetoxy*-2-*methyl*iso*flavone*, m. p. 171°, hydrolysed to 5 : 7 : 4′-*trihydroxy*-2-*methyl*iso*flavone* (I) [2-*methylgenistein*], $+H_2O$, m. p. 258—259° (slight decomp.) (O-*triacetyl* derivative, m. p. 214°). 2 : 4 : 6-*Trihydroxyphenyl* p-*methoxybenzyl ketone* (II), $+H_2O$, m. p. 192—193°, obtained by condensation of phloroglucinol and *p*-methoxyphenylacetonitrile, gives, on acetylation and hydrolysis, a satisfactory yield of 5 : 7-*dihydroxy*-4′-*methoxy*-2-*methyl*iso*flavone*, m. p. 205° (*diacetyl* derivative, m. p. 208—209°). Methylation of this compound gives a mixture of 5-*hydroxy*-7 : 4′-*dimethoxy*-2-*methyl*iso*flavone*, m. p. 197—199°, and 5 : 7 : 4′-*trimethoxy*-2-*methyl*iso*flavone*, m. p. 175—176°. Demethylation gives (I). Treatment of (II) with cinnamic anhydride and sodium cinnamate at 180—200° gives 5-*hydroxy*-7-*cinnamoxy*-4′-*methoxy*-2-*styryl*iso*flavone*, m. p. 230—231°, hydrolysed to 5 : 7-*dihydroxy*-4′-*methoxy*-2-*styryl*iso*flavone*, +EtOH, m. p. 278—279°[*diacetyl* derivative (III), $+\frac{1}{2}Me{\cdot}CO_2H$, m. p. 225—226°]. Methylation of the latter gives 5-*hydroxy*-7 : 4′-*dimethoxy*-2-*styryl*-6(?)-*methyliso*-*flavone*, m. p. 217—218° [*acetyl* derivative (IV), m. p. 218—219°]. Oxidation of (III) and (IV) in pyridine solution with potassium permanganate gives benzoic acid only. Oxidation of (IV) in acetone solution with permanganate gives benzoic and anisic acids, together with an uncharacterised carboxylic acid which, after hydrolysis and decarboxylation by heating in glycerol, gives methylgenistein dimethyl ether, alternatively obtained by methylation of prunetol (J.C.S., 1900, **77**, 1312). M. CLARK.

Colouring matter of "Fukugi." I. Constitution of fukugetin. J. SHINODA (J. Pharm. Soc. Japan, 1926, No. 535, 736—742).—Fukugetin (Perkin, J.C.S., 1904, **85**, 58; cf. Ito, J. Soc. Chem. Ind. Japan, **9**, 221; Maniwa, Chiba Yakugaku Si, 1924, No. 2) has been prepared from fukugi bark (from the plant produced in Okinawa). Di-, tri-, and tetra-*acetyl* derivatives of fukugetin (m. p. 252—254°, 272—273°, and 160°, respectively) have been obtained; the tetra-acetyl derivative was not coloured by ferric chloride. Fukugetin was not reduced catalytically in glacial acetic acid solution, but when reduced by magnesium and alcoholic hydrochloric acid in presence of mercury, gave a reddish-

violet coloration similar to that of quercetin, evidence that fukugetin is a flavone derivative. Possible formulæ for fukugetin are suggested.

K. KASHIMA.

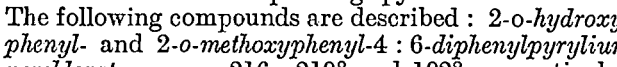
Pyrylium compounds. XVII. Arylated pyridines. VIII. o-Violones. W. DILTHEY, G. FRÖDE, and H. KOENEN (J. pr. Chem., 1926, [ii], **114**, 153—178).—A number of substituted triphenylpyrylium salts have been prepared by condensing derivatives of phenyl styryl ketone with substituted acetophenones, in presence of acetic anhydride and a trace of sulphuric acid. Those salts which contain a 2-*o*-hydroxyphenyl group react with pyridine in alcoholic solution, forming blue anhydro-bases, which



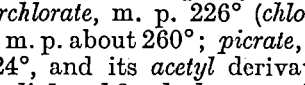
are derivatives of 2-*o*-violone (annexed formula). Unlike the 4-*o*-violones, these are quite stable and resemble the corresponding *p*-violones (A., 1921, i, 429; 1925, i, 55). They combine with water, forming colourless ψ-bases (pyranols). The constitution of these is doubtful, since it is difficult, and in many cases impossible, to regenerate the anhydro-base from them by heating. The corresponding pyridines and phenylpyridinium salts have been prepared from the pyrylium salts by treatment with ammonia and aniline, respectively. The method of comparing the ease of hydrolysis of pyrylium salts previously described (*ibid.*, 1925, i, 1441) has been abandoned as untrustworthy, but the stability of 4 : 6-diphenyl-2-*p*-hydroxyphenylpyrylium perchlorate is confirmed. 2 : 6-Diphenyl-4-*p*-hydroxyphenylpyrylium perchlorate is also very stable, but the corresponding *p*-methoxy-derivative and 4 : 6-diphenyl-2-*o*-hydroxyphenylpyrylium perchlorate are no more stable than triphenylpyrylium perchlorate. The colours (yellowish-orange to violet-red) of the pyrylium salts, and their fluorescence colours in sulphuric acid, are tabulated. The introduction of methyl and methoxyl groups has generally a bathochromic effect. The same effect is noticed in the corresponding pyridine derivatives. The following compounds are described: 2-*o*-*hydroxyphenyl*- and 2-*o*-*methoxyphenyl*-4 : 6-*diphenylpyrylium perchlorates*, m. p. 216—219° and 192°, respectively; *o*-*methoxy*-p-*methylacetophenone*, b. p. 136—137°/14 mm.; 4 : 6-*diphenyl*-2-*o*-*methoxy*-p-*tolylpyrylium perchlorate*, m. p. 195°; 4 : 6-*diphenyl*-2-*o*-*hydroxy*-p-*tolylpyrylium perchlorate*, m. p. 226° (*chloride*, m. p. 256°; *dichloride*, m. p. about 260°; *picrate*, m. p. 282°; ψ-*base*, m. p. 124°, and its *acetyl* derivative, m. p. 114—115°); 4 : 6-*diphenyl*-2-*o*-*hydroxy*-p-*tolylpyridine*, m. p. 148—149°; 4-*phenyl*-6-*o*-*hydroxyphenyl*-2-*o*-*hydroxy*-p-*tolylpyrylium perchlorate*, m. p. 238° (*chloride*, m. p. 241°; *picrate*, m. p. 244—245°), and its *anhydro-base* (4-*phenyl*-6-*o*-*hydroxy*-p-*tolyl*-2-*o*-*violone*), m. p. 277—278°, and ψ-*base*, m. p. 152°; 4-*phenyl*-6-*o*-*hydroxyphenyl*-2-*o*-*hydroxy*-p-*tolylpyridine*, m. p. 167° (*picrate*, m. p. 236°); 4-*phenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*tolylpyrylium perchlorate*, m. p. 266° (*chloride*, m. p. 235—238°; *sesquichloride*, m. p. 235—238°; *picrate*, m. p. 278°), and its ψ-*base*, m. p. 126° (*acetyl* derivative, m. p. 134°, which gives a *perchlorate*, m. p. 218—219°); 4-*phenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*tolylpyridine*, m. p. 145°; 1 : 4-*diphenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*tolylpyridinium picrate*, m. p. 219° (*perchlorate*, m. p. 304—305°); 4-*phenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyrylium perchlorate*, m. p. 259—260°, and its *anhydro-base*, m. p. 215° (decomp.), and ψ-*base*, m. p. 128—129° (*picrate*, m. p. 289—290°); 4-*phenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridine*, m. p. 145°; 1 : 4-*diphenyl*-6-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridinium perchlorate*, m. p. 210° (decomp.), and *picrate*, m. p. 256—257°; 4 : 6-*di*-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyrylium perchlorate*, m. p. 290—291° (decomp.), and its *anhydro-base*, m. p. 240—242°, and ψ-*base*, m. p. 146° with loss of water (*picrate*, m. p. 277—278°); 4 : 6-*di*-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridine*, m. p. 156—157°; 1-*phenyl*-4 : 6-*di*-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridinium picrate*, m. p. 257—258°, and *perchlorate*, m. p. 160—162° (decomp.); 4 : 6-*di*-p-*hydroxyphenyl*-2-op-*dihydroxyphenylpyrylium chloride*, m. p. 295°; 6-*phenyl*-4-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyrylium perchlorate*, m. p. 208°, and *picrate*, m. p. 275—276°; 6-*phenyl*-4-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridine*, m. p. 115°; 1 : 6-*diphenyl*-4-p-*anisyl*-2-*o*-*hydroxy*-p-*anisylpyridinium perchlorate*, m. p. 166—168°, and *picrate*, m. p. 281—282°; 4-p-*anisyl*-2 : 6-*di*-*o*-*hydroxy*-p-*anisylpyrylium perchlorate*, m. p. 245—246°, and its *anhydro-base*, m. p. 268—270°, and ψ-*base*, m. p. 128° (*picrate*, m. p. 270° with decomp.); 1-*phenyl*-4-p-*anisyl*-2 : 6-*di*-*o*-*hydroxy*-p-*anisylpyridinium picrate*, m. p. 238°; 4-p-*hydroxyphenyl*-2 : 6-op-*dihydroxyphenylpyrylium chloride*, m. p. 272—275°; 2 : 6-*diphenyl*-4-p-*anisylpyrylium perchlorate*, m. p. 257—259°; and 2 : 6-*diphenyl*-4-p-*hydroxyphenylpyrylium perchlorate*, m. p. 310—312°.

H. E. F. NOTTON.

Heteropolar carbon compounds. IV. *spiro*-Dibenzopyrans. W. DILTHEY, C. BERRES, E. HÖLTERHOFF, and H. WÜBKEN (J. pr. Chem., 1926, [ii], **114**, 179—198).—When derivatives of *spiro*di-2 : 2′-β-naphthapyran are heated alone, or in indifferent solvents, they develop an intense bluish-violet colour, which disappears on cooling. Since there is no change in mol. wt., Löwenstein and Katz (this vol., 956) ascribed the colour to a quinonoid rearrangement,



The chemical properties of the coloured solutions are not, however, those of a quinonoid substance, and are best explained by assuming the formation of a heteropolar ion,



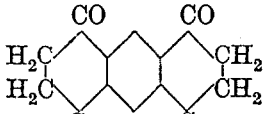
. The reaction is then analogous to the thermo-dissociation of the triarylmethyl halides. In the preparation of the *spiro*dibenzopyrans, derivatives of ethyl acetoacetate have been advantageously replaced by substituted acetones. The reaction between the hydroxyaldehyde and the acetone derivative takes place in two stages. The intermediate product, for which two constitutions are possible, may be isolated and used in preparing unsymmetrically substituted *spiro*dipyrans. Salicylaldehyde condenses with methyl ethyl ketone in alcoholic solution in presence of hydrogen chloride, forming 2-o-*hydroxystyryl*-3-*methylbenzopyrylium chloride* (+0·5HCl), m. p. 172° [*perchlorate*, m. p. 257—258° (decomp.), and its *acetyl* derivative]. 2-o-*Hydr*-

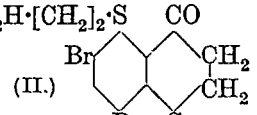
oxy-α-*benzostyryl*-β-*naphthapyrylium chloride* (also +0·5HCl) is prepared in a similar way from β-naphthol-1-aldehyde and acetone. Ammonia converts it into spiro*di*-2 : 2′-β-*naphthapyran*, m. p. 257°. β-Naphthol-1-aldehyde and methyl ethyl ketone afford, in presence of sulphuric acid and perchloric acid, the intermediate product, 2 : 3-*dimethyl*(? 2-*ethyl*)-β-*naphthapyrylium perchlorate*, yellow, m. p. 229°, which yields a *substance*, m. p. 114°, on oxidation with hydrogen peroxide. The perchlorate condenses with further β-naphthol-1-aldehyde, forming 2-o-hydroxy-α-benzostyryl-3-methyl-β-naphthapyrylium perchlorate, m. p. 268° (decomp.) (*acetyl* derivative, m. p. 246—248°). The *hydrochloride* (also +0·5HCl) and amorphous *picrate* are described. The intermediate product also condenses with salicylaldehyde, giving 2-o-*hydroxystyryl*-3-*methyl*-β-*naphthapyrylium perchlorate*, m. p. 290° (decomp.), converted by ammonia into 3(? 3′)-*methyl*spiro-2 : 2′-*benzonaphthadipyran*, m. p. 174°. 2-o-*Hydroxy*-α-*benzostyryl*-3-*phenyl*-β-*naphthapyrylium perchlorate*, m. p. 256° (*acetyl* derivative, m. p. 195°), and *chloride* (also +1HCl); 3-*phenyl*-2-*methyl*(? 2-*benzyl*)-β-*naphthapyrylium perchlorate*, m. p. 225—226°, and its oxidation *product*, m. p. 144°; 3(? 3′)-*phenyl*spiro-2 : 2′-*benzonaphthadipyran*, m. p. 147—148°; 2-o-*hydroxystyryl*-3-*phenyl*-β-*naphthapyrylium perchlorate*, m. p. 238—240°; and 7-*hydroxy*-2-op-*dihydroxystyryl*-3-*methylbenzopyrylium chloride* and *perchlorate* (*acetyl* derivative, m. p. 206—207°), are described. H. E. F. NOTTON.

Manufacture of anthraquinone-thioxanthones and -acridones. SOC. CHEM. IND. IN BASLE.—See B., 1926, 942.

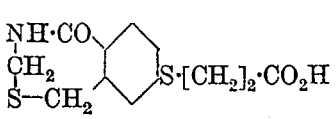
Manufacture of anthracene-2 : 1-"thioindoxyl." SOC. CHEM. IND. IN BASLE.—See B., 1926, 943.

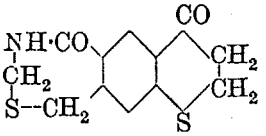
Heterocyclic derivatives of thioresorcinoldipropionic acid. C. FINZI (Gazzetta, 1926, 56, 539—550).—1 : 3-*Phenylenedi*-β-*thiolpropionic acid*, m. p. 123—124°, obtained by the interaction of dithioresorcinol and sodium β-chloropropionate, brominates to the 4 : 6-*dibromo*-acid, m. p. 184°. With dilute nitric acid, it gives the 4-*nitro*-acid, m. p. 157° (decomp.), which reduces to the 4-*amino*-acid, m. p. 122° (*hydrochloride*, m. p. 187°). By the action of concentrated sulphuric acid it condenses to give 2 : 3 : 7 : 8-*tetrahydrobenzodi*-γ-*thiopyrone* (I), sulphur-

(I.) 

(II.) 

yellow, m. p. 163—164°. The dibromo-derivative gives under similar treatment 6 : 8-*dibromo*-2 : 3-

(III.) 

(IV.) 

dihydrobenzo-1 : 4-*thiopyrone*-5-β-*thiolpropionic acid* (II), orange-yellow, m. p. 249—252°. The amino-derivative gives the corresponding 8-*amino*-compound, yellow, m. p. 137°; or, if heated alone at 200°, 2 : 3-*dihydro*-4-*ketobenzo*-1 : 5-*heptathiazine*-8-β-*thiolpropionic acid* (III), m. p. 205°, which when further heated, or treated with sulphuric acid, gives 2 : 3 : 8 : 9-*tetrahydro*-7-*ketobenzo*-1 : 4-*thiopyrone*-10 : 6-*heptathiazine* (IV), pale yellow, m. p. 246°.

E. W. WIGNALL.

Exhaustive oxidation of 2-methylpyrrolidine by chromic acid. T. TAKAHASHI (Helv. Chim. Acta, 1926, 9, 892—893).—This process gives β-aminobutyric acid, with apparently also another amino-acid. E. W. WIGNALL.

Dicyclic morpholines. II. J. VON BRAUN and W. LEISTNER (Ber., 1926, 59, [*B*], 2323—2329; cf. A., 1923, i, 1117).—Ethyl *meso*-αδ-dibromoadipate is converted by *p*-methylbenzylamine into *ethyl* 1-p-*methylbenzylpyrrolidine*-2 : 5-*dicarboxylate*, b. p. 207—209°/13 mm. (non-crystalline salts), which is hydrolysed to 1-p-*methylbenzylpyrrolidine*-2 : 5-*dicarboxylic acid*, m. p. 238°. An oil is obtained as by-product during the preparation, which, when hydrolysed, gives αδ-*di*-p-*methylbenzylaminoadipic acid*, m. p. 164°. Reduction of ethyl 1-*p*-methylbenzylpyrrolidine-2 : 5-dicarboxylate with sodium and alcohol yields 2 : 5-*dihydroxymethyl*-1-p-*methylbenzylpyrrolidine*, b. p. 215—218°/18 mm. (non-crystalline salts), which when heated with 70% sulphuric acid at 175° affords 1-p-*methylbenzylmorphopyrrolidine*, b. p. about 170°/15 mm., m. p. 38° (*hydrochloride*, m. p. 209°; *picrate*, m. p. 161°; *methiodide*, m. p. 240°). The base is converted by cyanogen bromide into *p*-methylbenzoyl bromide and 1-*cyanomorphopyrrolidine*, b. p. 140—145°/17 mm., m. p. 45—46°, transformed by boiling 25% sulphuric acid into *morphopyrrolidine*, $CH_2 \cdot CH \overset{CH_2}{\underset{CH_2}{>}} NH > O$, identified as the *hydrochloride*, m. p. 210°, and p-*nitrobenzoyl* derivative, m. p. 142°.

Ethyl αα′-dibromopimelate and *p*-methylbenzylamine yield (?) *ethyl* αα′-*di*-p-*methylbenzylaminopimelate* and *ethyl* 1-p-*methylbenzylpiperidine*-2 : 6-*dicarboxylate*, b. p. 225°/12 mm. The latter substance is reduced to 1-p-*methylbenzyl*-2 : 6-*dihydroxymethylpiperidine*, b. p. 238—240°/12 mm., which gives 1-p-*methylbenzylmorphopiperidine*, b. p. 183—188°/14 mm. (*picrate*, m. p. 146—148°; *methiodide*, m. p. 204—205°), in very poor yield.

Ethyl bromo-γ-bromopropylmalonate is very smoothly transformed by *p*-tolylmethylamine into *ethyl* 1-p-*methylbenzylpyrrolidine*-2 : 2-*dicarboxylate*, b. p. 200—205°/18 mm. (non-crystalline *hydrochloride*; *methiodide*, m. p. about 80°); the stability of the ring in this compound is so diminished by the presence of the two carbonyl groups that conversion into proline cannot be effected by cyanogen bromide. H. WREN.

Rectification of G. Heller's [theory of] alleged isomerism in the isatin series and of the so-called "structural association." A. HANTZSCH (J. pr. Chem., 1926, [ii], 114, 57—62).—A continuation of the controversy with Heller (cf. A., 1925, i, 1166). α- and β-Isatol are alleged to be true polymerides and not isomerides of isatin. The four isomerides of

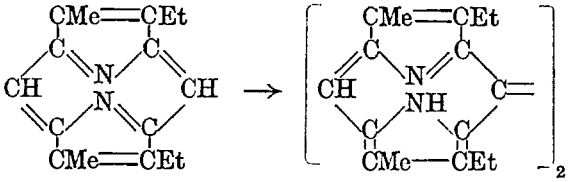
methylisatin are either bimolecular isatoids, or their transformation products, or impure substances (cf. this vol., 740). The author again shows that 3-hydroxyindazole is bimolecular in camphor (A., 1925, i, 702), and again denies the correctness of Heller's conception of structural association, drawing support from the fact that mol. wt. determinations in concentrated solution give high results for acetic acid, tribromophenol, and 4-hydroxy-2-methylquinoline. J. M. GULLAND.

Manufacture of 2 : 3-anthraquinonylindoxyl. SOC. CHEM. IND. IN BASLE.—See B., 1926, 943.

Porphyrin syntheses. III. Degradation of blood-pigments and resynthesis of porphyrins from opsopyrrole and opsopyrrolecarboxylic acid. H. FISCHER and A. TREIBS (Annalen, 1926, **450**, 132—151).—Opsopyrrole (3-methyl-4-ethylpyrrole) is separated from the other basic products of the total reduction of hæmin with hydriodic–acetic acid at 100° by fractional extraction of the ether solution with hydrochloric acid. The corresponding *opsopyrrolecarboxylic acid* (*3-methylpyrrole-4-propionic acid*), m. p. 119° (no picrate; blue *dye* with diazobenzenesulphonic acid), is isolated from the acid portions of the reduction product by ether extraction under special conditions.

When heated in formic acid, opsopyrrole yields an ætioporphyrin identical with a mixture of Fischer and Klarer's ætioporphyrin with an equal weight of Fischer and Halbig's *iso*ætioporphyrin (this vol., 962). Opsopyrrolecarboxylic acid, heated in formic acid, gives coproporphyrin, the methyl ester of which crystallises in two forms, one being identical with natural coproporphyrin methyl ester; separation of coproporphyrin from *iso*coproporphyrin is incomplete. A mixture of opsopyrrole and its carboxylic acid gives with formic acid, in addition to ætioporphyrin (no coproporphyrin found), iso*mesoporphyrin* (*methyl* ester, m. p. 207—208°), the *sodium* salt of which is more soluble than that of mesoporphyrin.

These porphyrin syntheses support the " indigoid " structure, *e.g.*,



The separation of hæmo-, crypto-, and phyllopyrroles by fractional extraction from ether solution with hydrochloric acid of different strengths is described. C. HOLLINS.

Porphyrin syntheses. IV. *iso*Ætioporphyrin, its tetrabromide, and its degradation by oxidation and by reduction. Synthesis of *iso*mesoporphyrin and opsopyrrole. H. FISCHER and P. HALBIG (Annalen, 1926, **450**, 151—164; cf. preceding abstract).—*iso*Ætioporphyrin, obtained by an improved method from bis-(4-methyl-3-ethyl-5-carboxypyrryl)methane by heating in formic acid in a current of air (cf. this vol., 962), gives a *tetrabromide* (*dihydrobromide* described), which loses all its bromine in boiling acetone. *iso*Ætioporphyrin is reduced by hydriodic–acetic acid to a mixture of hæmopyrrole, phyllopyrrole, and opsopyrrole, the last-named remaining in the ether solution after removal of the first two by washing with 12% hydrochloric acid. Oxidation of *iso*ætioporphyrin gives methylethylmaleinimide.

For the synthesis of *iso*mesoporphyrin, a paste of bis-(4-methyl-3-ethyl-5-carboxypyrryl)methane and bis-(4-methyl-3-β-carboxyethyl-5-carboxypyrryl)-methane with formic acid is heated in a current of air; *iso*mesoporphyrin is separated from ætio- and copro-porphyrins by means of its less soluble sodium salt, and purified as methyl ester (two forms, m. p. 270—275° and 235°).

Opsopyrrole, b. p. 70°/11 mm., d_4^{20} 0·9059, n_D^{20} 1·49126 (characteristic blue dye with *p*-diazobenzenesulphonic acid), may be obtained from the mother-liquors in the preparation of *iso*ætioporphyrin from bis-(4-methyl-3-ethyl-5-carboxypyrryl)methane in boiling acetic acid, or by reduction of the bispyrrylmethane with hydriodic–acetic acid. C. HOLLINS.

Halogenated pyrroles. VII. 2 : 3 : 4-Trimethylpyrrole and its conversion into methenes and brominated methenes. Synthesis of 3 : 4-dimethylpyrrole. H. FISCHER and B. WALACH (Annalen, 1926, **450**, 109—132).—Ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate is converted by sodium ethoxide and hydrazine hydrate at 150—170° (40 atm. pressure) into 2 : 3 : 4-trimethylpyrrole, m. p. 148°, in 80% yield. 2 : 3 : 4-Trimethylpyrrole condenses with hydrogen cyanide to give 2 : 3 : 4-*trimethyl-5-pyrrole-5-aldimine*, m. p. 146° [*hydrochloride*, m. p. 226° (indef.); *picrate*, exploding at 245°], readily hydrolysed to 2 : 3 : 4-*trimethylpyrrole-5-aldehyde*, m. p. 147° (*oxime*, m. p. 123°; *semicarbazone*, m. p. 230°); *5-cyano*-2 : 3 : 4-*trimethylpyrrole*, m. p. 137°, is obtained from the oxime. The aldehyde is reduced by sodium methoxide and hydrazine hydrate to 2 : 3 : 4 : 5-tetramethylpyrrole, m. p. 112° (picrate, m. p. 127°). Condensed with 2 : 3 : 4-trimethylpyrrole in alcohol in the presence of hydrogen chloride, the aldehyde yields 2 : 3 : 4-*trimethylpyrryl*-2 : 3 : 4-*trimethylpyrrolenylmethane hydrochloride*, m. p. 287—288° [*base*, m. p. 172°, volatile in steam; *picrate*, decomp. 230—232°; *mercuric chloride* compound, m. p. 243° (decomp.); complex compounds with *zinc*, m. p. 310°, *cobalt* (sublimes above 330°), *nickel*, m. p. 296°, and *copper*, m. p. 208°, of the type $Base_2$ Metal].

2 : 3 : 4-*Trimethylpyrryl*-2 : 4-*dimethylpyrrolenylmethene hydrochloride*, m. p. 244° (decomp.) [*base*, m. p. 98—99°, volatile in steam; *mercuric chloride* compound, m. p. 182—183° (decomp.); complex compounds with *zinc*, m. p. 277°; *cobalt*, m. p. 271°; *nickel*, m. p. 256° (decomp.), and *copper*, m. p. 220°], is prepared from the aldehyde and 2 : 4-dimethylpyrrole, or from 2 : 4-dimethylpyrrole-5-aldehyde and 2 : 3 : 4-trimethylpyrrole. 2 : 3 : 4-*Trimethylpyrryl*-3-*carbethoxy*-2 : 4-*dimethylpyrrolenylmethene hydrochloride*, m. p. 216° (decomp.; *base*, m. p. 127°; *picrate*, m. p. 203°; *mercuric chloride* compound; complex compounds with *zinc*, m. p. 250°, *cobalt*, m. p. 249°, *nickel*, m. p. 288°, and *copper*, m. p. 211°), is prepared similarly by two methods.

2 : 3 : 4-Trimethylpyrrole fails to react with acetonitrile, but *5-acetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p.

137°, is obtained by the Grignard reaction with acetyl chloride, or by the action of sodium acetate and acetic anhydride; reduction with sodium ethoxide and hydrazine hydrate converts the acetyl compound into 2 : 3 : 4-trimethyl-4-ethylpyrrole, m. p. 194°. 2 : 3 : 4-Trimethylpyrrole condenses with chloroacetonitrile to give 5-*chloroacetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p. 177° (decomp.), and with ethyl cyanoformate to give *ethyl imino*-2 : 3 : 4-*trimethyl*-5-*pyrrylacetate*, m. p. 156° (decomp.), readily hydrolysed to *ethyl* 2 : 3 : 4-*trimethyl*-5-*pyrrylglyoxylate*, m. p. 112°. The last-named ester, reduced with sodium ethoxide and hydrazine hydrate, yields 2 : 3 : 4-trimethyl-5-pyrrylacetic acid, which is decarboxylated at 50—60° to 2 : 3 : 4 : 5-tetramethylpyrrole.

Magnesyl 2 : 3 : 4-trimethylpyrrole reacts with ethyl chloroformate to form *ethyl* 2 : 3 : 4-*trimethylpyrrole*-5-*carboxylate*, m. p. 128° [free *acid*, m. p. 126° (decomp.)], which on bromination in acetic acid gives *ethyl* 3 : 4-*dimethyl*-2-*bromomethylpyrrole*-5-*carboxylate*, m. p. 128° (decomp.). The bromo-compound is converted by hydrobromic acid into bis-(5-carbethoxy-3 : 4-dimethylpyrryl)methane, m. p. 198°. On distilling the free *acid* in a vacuum with copper-bronze, 3 : 4-dimethylpyrrole, m. p. 33°, b. p. 65·5—66°/14 mm., easily volatile in ether vapour and steam, is obtained [crystallographic data for 2 : 3 : 4-trimethylpyrrole and 3 : 4-dimethylpyrrole by STEINMETZ].

Bromination of 2 : 3 : 4-trimethylpyrrole in acetic acid yields a separable mixture of 5-*bromo*-3 : 4-*dimethylpyrryl*-2 : 3 : 4-*trimethylpyrrolenylmethene* and -3 : 4-*dimethyl*-2-*bromomethylpyrrolenylmethene hydrobromides*. The monobromo-*base*, m. p. 156°, gives a complex *copper* compound, decomposing explosively at 203—204°. Reduction of the monobromo-hydrobromide with hydriodic–acetic acid affords 3 : 4-dimethyl-, 2 : 3 : 4-trimethyl-, and 2 : 3 : 4 : 5-tetramethyl-pyrroles. Bromination of bis-(5-carboxy-3 : 4-dimethylpyrryl)methane gives 5-*bromo*-3 : 4-*dimethylpyrryl*-5-*bromo*-3 : 4-*dimethylpyrrolenylmethene hydrobromide* [*base*, m. p. 198° (decomp.)]. C. HOLLINS.

Constitution of the dye from 2-methyl-substituted indolenium salts and phenylhydrazine. E. ROSENHAUER and A. FEILNER (Ber., 1926, **59**, [*B*], 2413—2416; cf. A., 1924, i, 768, 1002).—2-Benzeneazomethylene-1 : 3 : 3-trimethylindoline yields a *picrate*, decomp. 203·5°, *hydrochloride*, decomp. 229°, and *hydrobromide*, decomp. 223°. When treated with an excess of methyl iodide, it affords a *compound*, decomp. 253·5°, to which, since it is reduced to methylaniline and 1 : 2 : 3 : 3-tetramethylindolenium iodide, the constitution $C_6H_4<^{CMe_2}_{NMeI}>C{\cdot}CH{:}N{\cdot}NMePh$ is assigned. The hydrazone structure is suggested for salts of the "azo" colour base. H. WREN.

Condensation of indole with triketohydrindene hydrate. M. TOMITA and T. FUKAGAWA (Z. physiol. Chem., 1926, **158**, 62—65).—Indole condenses with triketohydrindene hydrate (ninhydrin) in aqueous solution at water-bath temperature to give a yellow product, 2-α-*indolyl*-2-*hydroxy*-1 : 3-*diketohydrindene*, $\begin{matrix}CH{=}C{-}\!-\!C(OH){\cdot}CO\\ C_6H_4{\cdot}NH\ CO\!-\!-\!C_6H_4\end{matrix}$; whilst in glacial acetic acid and in the presence of a little hydrochloric acid a deep red *substance*, $C_{17}H_9O_3N$, m. p. 220°, is formed (cf. Tomita, J. Oriental Med., 1924, **2**, 189, who shows that traces of indoxyl in urine may be detected by the red coloration produced on addition of ninhydrin solution). C. HOLLINS.

Complex salts of quinoline, mercuric halides, and alkyl halides, and some isomerides. W. M. DEHN and H. COPE (J. Amer. Chem. Soc., 1926, **48**, 2634—2642; cf. this vol., 304).—The reaction between alkyl bromides and chlorides and quinoline (Q), with formation of compounds of the type Q,RX, (I), is less energetic than that between quinoline and the corresponding iodides (cf. Lund and Wise, A., 1919, i, 415), and the chlorides are more inert than the bromides. *Compounds* of this type, obtained either from the undiluted reactants, or from these in presence of suitable solvents, between quinoline and the following alkyl halides, are described: ethyl chloride, m. p. 122°; ethyl bromide, m. p. 80° (cf. Claus and Tosse, *ibid.*, 1883, 1008); ethyl iodide, m. p. 158° (cf. Lund and Wise, *loc. cit.*); *iso*propyl iodide, m. p. 136°; *n*-butyl iodide, m. p. 174°; *iso*butyl iodide, m. p. 161°; and cetyl iodide, m. p. 101°. The *periodide*, $Q,C_{16}H_{33}I,I_2$, m. p. 70°, and *perbromide*, $Q,C_{16}H_{33}I,Br_2$, were also prepared. Compounds of the type Q,RX,HgX_2 (II), are obtained by mixing, in molecular proportions, solutions of compounds of type (I) with solutions of mercuric halides in acetone, acetonitrile, or methyl ethyl ketone, or from mercuric halides and compounds of type $2Q,RX,HgX_2$ in the same solvents. Derivatives of type (II), containing iodine as the halogen in all cases, and the following alkyl groups, are described: *methyl*, m. p. 165°; n-*propyl*, m. p. 155°; iso*propyl*, m. p. 128°; n-*butyl*, m. p. 122°; iso*butyl*, m. p. 151°; iso*amyl*, m. p. 160°; and *cetyl*, m. p. 87°. Compounds of type (III), $2Q,RX,HgX_2$, dissociate readily into quinoline and derivatives of type (II). The following were prepared: *diquinoline–mercuric iodide–methyl iodide*, m. p. 170°; *diquinoline–mercuric iodide*–n-*propyl iodide*, m. p. 108°, and *diquinoline–mercuric iodide*–n-*butyl iodide*, m. p. 86°. Derivatives of type (IV), $HgX_2,2(Q,RX)$, are very insoluble in acetone and methyl ethyl ketone, and very soluble in acetonitrile. Derivatives of this type, containing always iodine as the halogen, and the following alkyl groups, are described: *methyl*, m. p. 210°; n-*propyl*, m. p. 157°; iso*propyl*, m. p. 160°; n-*butyl*, m. p. 158°; iso*butyl*, m. p. 168°; iso*amyl*, m. p. 156°; and *cetyl*, m. p. 84°. By the action of alkyl halides on quinoline mercuric halides, derivatives of type (V), Q,HgX_2,RX, isomeric with type (II), can be obtained. The existence of these isomerides indicates that direct structural relationships are involved in the formation of these complexes, although definite formulæ cannot at present be assigned to them. Of type (V), *quinoline–mercuric iodide*–iso-*propyl iodide*, m. p. 152° after softening at 100°, and –sec.-*butyl iodide*, m. p. 130° after softening at 90°, were obtained. Diquinoline mercuric iodide and alkyl iodides yield derivatives of type (VI), Q_2,HgX_2,RX, of which the *ethyl iodide* derivative, m. p. 140° after softening at 115°, and the n-*propyl iodide* derivative, m. p. 125° after softening at 105°, are described. Type (VII), $Q_2,HgX_2,2RX$, is repre-

sented by *diquinoline-mercuric iodide-di(methyl iodide)*, m. p. 190° (decomp.) after softening at 155°, obtained by combination of diquinoline mercuric iodide with methyl iodide in direct sunlight. Type (VIII), $Q_2HgX_2,3RX$, is represented by *diquinoline-mercuric iodide-tri(propyl iodide)*, m. p. 125° after softening at 115°, obtained similarly, and type (IX), $Q_4,2HgX_2,3RX$, by *tetraquinoline-di(mercuric iodide)-tri*(iso*amyl iodide*), m. p. 124° after softening at 100°. Derivatives of type (X), $Q_3,3HgX_2,2RX$, were prepared containing the following alkyl groups, the halogen being iodine in all cases: *methyl*, m. p. 160—168°; n-*propyl*, m. p. 118—125°; n-*butyl*, m. p. 158°; and iso*amyl*, m. p. 140—160°. In addition to the above iodides, the following series of ethyl derivatives were prepared: type (II), Q,EtX,HgX_2: *ethyl iodide, mercuric iodide*, m. p. 131°; *ethyl iodide, mercuric chloride*, m. p. 133°; *ethyl iodide, mercuric bromide*, m. p. 143—146°; *ethyl bromide, mercuric bromide*, m. p. 169°; *ethyl bromide, mercuric chloride*, m. p. 193°, and *ethyl bromide, mercuric iodide*, m. p. 121°; type (V), Q,HgX_2,EtX: *mercuric iodide, ethyl iodide*, m. p. 131° (conversion into the above isomeride), and *mercuric bromide, ethyl iodide*, m. p. 125°; and type (XI), $Q_2,2EtX,HgX_2$, isomeric with type (VII): *ethyl chloride, mercuric chloride*, m. p. 232—235°; *ethyl chloride, mercuric bromide*, m. p. 221—223°; *ethyl chloride, mercuric iodide*, m. p. 173—175°; *ethyl bromide, mercuric chloride*, m. p. 177—180°; *ethyl bromide, mercuric bromide*, m. p. 189—190°; *ethyl bromide, mercuric iodide*, m. p. 173°; *ethyl iodide, mercuric chloride*, m. p. 155°; *ethyl iodide, mercuric bromide*, m. p. 174°; and *ethyl iodide, mercuric iodide*, m. p. 188°. F. G. Willson.

Influence of the 8-methoxyl group in 8-methoxy-3-arylsulphonyl-2-methylquinoline derivatives on their addition and condensation reactions. Behaviour of the initial and condensation products towards nascent hydrogen. J. Tröger (J. pr. Chem., 1926, [ii], **114**, 199—241).—I. [With C. Pape.] Introduction of an 8-methoxyl group into a 3-arylsulphonyl-2-methylquinoline greatly decreases its reactivity. The product cannot be made to form a methiodide or a phthalophenone. The following derivatives of 8-methoxy-2-methylquinoline were prepared from the appropriate arylsulphonylacetone and 2-amino-3-methoxybenzaldehyde (cf. this vol., 523, 524): 3-*benzenesulphonyl*-, m. p. 180°; 3-p-*toluenesulphonyl*-, m. p. 178°; 3-p-*phenetolesulphonyl*-, m. p. 157°, and 3-β-*naphthalenesulphonyl*-, m. p. 190°. β-Naphthalenesulphonylacetone has m. p. 120° (Tröger and Bolm, A., 1897, i, 536, give 130°). The *hydrochlorides* and *nitrates* of these bases lose part of their acid on heating at 105°, and the latter undergo deep-seated decomposition at 130°. The *hydrogen sulphates*, when dry, are stable at this temperature, but are readily hydrolysed by water. Condensation products of the above bases with benzaldehyde and piperonal are obtained only when they are heated together at 160—170° in a vacuum for 3—4 hrs. In this way, the following derivatives of 8-methoxy-2-styrylquinoline and of 8-methoxy-2-*mp*-methylenedioxystyrylquinoline (m. p. in that order) are prepared: 3-*benzenesulphonyl*-, m. p. 212°, 247°; 3-p-*toluenesulphonyl*-, m. p. 236°, 210°; 3-p-*phenetolesulphonyl*-, m. p. 171°, 198°; 3-β-*naphthalenesulphonyl*-, m. p. 158°, 235°. With acids, they form salts, those of the benzaldehyde derivatives being readily hydrolysed by water. On reduction with tin and hydrochloric acid, the 8-methoxy-3-arylsulphonyl-2-methylquinolines give a practically quantitative yield of the corresponding arylthiophenols, together with 8-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroquinoline (*benzoyl* derivative, m. p. 139—140°). None of the corresponding 5 : 6 : 7 : 8-tetrahydro-derivative is formed. The aldehyde condensation products also give high yields of arylthiophenols with tin and hydrochloric acid, but in these cases the basic product of reduction cannot be isolated. In one instance a small amount of a *hydrochloride*, m. p. 185—186°, was obtained from an 8-methoxy-3-arylsulphonyl-2-styrylquinoline. The same difficulty is encountered when 8-methoxy-2-styrylquinoline is reduced by this method; sodium and alcohol give a gummy product, whilst hydrogen in presence of palladised charcoal affords only 8-methoxy-2-β-phenylethylquinoline.

II. [With J. Kestenbach.] An improved method for preparing 2-amino-3-methoxybenzaldehyde is given. The following derivatives of 8-methoxy-2-methylquinoline are described, the two first being dimorphous: 3-p-*bromobenzenesulphonyl*-, m. p. 230°; 3-p-*chlorobenzenesulphonyl*-, m. p. 217°; 3-o-*anisolesulphonyl*-, m. p. 196°; 3-o-*phenetolesulphonyl*-, m. p. 184°. Their *hydrochlorides*, *nitrates*, and *hydrogen sulphates* when heated behave like those mentioned above. In order to show that the inability of these compounds to form methiodides is not due to the arylsulphonyl group, 3-o-*anisolesulphonyl-2-methylquinoline methiodide*, m. p. 150°, has been prepared. These bases condense with benzaldehyde and piperonal in a vacuum; with paracetaldehyde in presence of zinc chloride at 200—250° at atmospheric pressure, a small yield of the ethylidene derivative is formed. In this way, the following derivatives of 8-methoxy-2-Δ^{α}-propenylquinoline, 8-methoxy-2-styrylquinoline and 8-methoxy-2-*mp*-methylenedioxystyrylquinoline (m. p. being given in this order) are prepared: 3-p-*bromobenzenesulphonyl*-, m. p. 137°, 217°, 219°; 3-p-*chlorobenzenesulphonyl*-, m. p. 144°, 210°, 228°; 3-o-*anisolesylphonul*-, m. p. —, 215°, 224°; 3-o-*phenetolesulphonyl*-, m. p. —, 252°, 217°. The 8-methoxy-3-arylsulphonyl-2-methylquinoline derivatives, and their aldehyde condensation products, behave on reduction exactly analogously to those described in part I. In the case of the latter compounds attempts to isolate the basic product of reduction were again unsuccessful. 8-*Methoxy*-2-mp-*methylenedioxystyrylquinoline*, m. p. 205° (*chloroplatinate*), is reduced by hydrogen and palladised charcoal to 8-*methoxy*-2-β-mp-*methylenedioxyphenylethylquinoline*, m. p. 109° (*chloroplatinate*). H. E. F. Notton.

Anthraquinoneacridine dye. Soc. Chem. Ind. in Basle.—See B., 1926, 943.

Manufacture of compounds from 4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone etc. I. G. Farbenind., Chem. Fabr. vorm. Scherring, and also W. Schulemann and K. Meisenburg.—See B., 1926, 931.

Relative tenacity of cyclic bases. XII. Action of organic amines on quaternary ammonium halides. J. VON BRAUN, M. KÜHN, and O. GOLL (Ber., 1926, 59, [*B*], 2330—2340; cf. A., 1925, i, 1455).—Investigation of the action of ammonia on quaternary ammonium halides is hampered by the incompleteness of the change and necessity of using sealed tubes. These difficulties are largely avoided if primary or secondary amines are employed, particularly if care is taken to choose the components of the reaction so that a homogeneous mixture is obtained; this is frequently accomplished by the addition of water or of the alcohol corresponding with the amine. Trimethylbenzylammonium bromide and benzylamine afford trimethylamine and dibenzylamine, the preferential elimination of the benzyl group being in harmony with the position of the benzyl and methyl groups in the tenacity series as established by other methods; traces of dimethylbenzylamine and methylbenzylamine are present in the benzylamine fraction. With monocyclic compounds, $R>NMe_2Cl$, the methyl groups are so feebly attached that they are removed by amines without rupture even of the unstable piperazine ring. Thus *tetramethylpiperazinium dichloride*, $ClMe_2N<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NMe_2Cl$, m. p. above 300°, when heated with slightly aqueous pyridine at 150°, affords dimethylpiperazine and 1-methylpiperidine. Dimethyltetrahydro*iso*quinolinium iodide is converted by benzylamine or diethylamine into methyltetrahydro*iso*quinoline. Dimethylpiperidinium iodide and β-phenylethylamine yield 1-methylpiperidine. More valuable results are obtained with spiran derivatives, $R>N(Hal)<R'$. Bispiperidinium bromide is smoothly and almost quantitatively transformed by piperidine into αε-*dipiperidinopentane* (*picrate*, m. p. 185°; *dimethiodide*, m. p. 262°) and by benzylamine into 1-*ζ-benzylamino*-n-*amylpiperidine*, $C_5H_{10}N\cdot[CH_2]_5\cdot NH\cdot CH_2Ph$, b. p. 198—200°/12 mm., d_4^{17} 0·969 (non-crystalline *salts* and *nitroso*-compound). Similarly, di-*o*-xylylenium bromide, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>NBr<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4$, and piperidine yield N-o-*xylylene*-N′-*pentamethylene*-o-*xylylenediamine*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>N\cdot CH_2\cdot C_6H_4\cdot CH_2\cdot NC_5H_{10}$, b. p. 218°/15 mm. (*picrate*, m. p. 135°; *dimethiodide*, m. p. 215°), with smaller amounts of dihydro*iso*indole and (?) *o*-xylylenedipiperidine. Piperidiniumtetrahydro*iso*quinolinium bromide and piperidine give o-β-*piperidinoethylpiperidinomethylbenzene*, b. p. 220—224°/15 mm. (non-crystalline *hydrochloride*; *picrate*, m. p. 112—113°; *dimethiodide*, m. p. 230°, and corresponding *chloroplatinate*, decomp. 229—233°, according to rate of heating), the constitution of which is established by degradation of the corresponding diquaternary hydroxide to 1-*o*-vinylbenzylpiperidine. Piperaziniumbistetrahydro*iso*quinolinium bromide and piperidine afford 2-β-*piperidinoethyltetrahydroisoquinoline*, b. p. about 210°/15 mm. (*picrate*, m. p. 173°; *dimethiodide*, m. p. 214°), with small amounts of αβ-di-2-tetrahydro*iso*quinolylethane (cf. this vol., 740) and αβ-dipiperidinoethane. Piperaziniumdipiperidinium dibromide and piperidine give αβ-dipiperidinoethane. Piperidiniumtetrahydro*iso*quinolinium bromide is converted by ethylamine into o-β-*diethylaminoethylpiperidinomethylbenzene*, b. p. below 200°/15 mm., the constitution of which is established by the simultaneous formation of 1-*o*-vinylbenzylpiperidine. H. WREN.

Acetophenonyl (phenacyl) derivatives of barbituric acid. D. T. KEACH and A. J. HILL (J. Amer. Chem. Soc., 1926, 48, 2743—2745).—The following 5-alkyl-5-phenacylbarbituric acids were prepared by treating the appropriate alkylbarbituric acid with bromoacetophenone in boiling 75% alcohol: 5-*ethyl*-, m. p. 248—249°; 5-n-*propyl*-, m. p. 299—300°; 5-*allyl*-, m. p. 270—271°; 5-iso*butyl*-, m. p. 286—287°; and 5-n-*butyl*-5-*phenacylbarbituric acid*, m. p. 294—296°. None except the first-named possesses hypnotic properties, and all are fairly toxic. F. G. WILLSON.

Manufacture of [azo] dyes [from barbituric acid]. SOC. CHEM. IND. IN BASLE.—See B., 1926, 910.

Amino-acid anhydrides and their behaviour towards tannins and dyes. M. BERGMANN, A. MIEKELEY, and E. KANN (Biochem. Z., 1926, 177, 1—9).—Polymeric *allo*methylmethylenediketopiperazine is obtained by heating the monomeric form (cf. A., 1925, i, 235, 1134; this vol., 740, 743) or alanylserine anhydride in a 2½% aqueous solution of arginine at 70—80°. A colloidal *monomethylene* derivative is obtained by heating methylmethylenediketopiperazine with aqueous formaldehyde in a sealed tube. Monomeric and polymeric diketopiperazines, particularly the polymeric *iso* and *allo* forms, adsorb dyes and tannins from aqueous solutions. J. PRYDE.

Racemisation. IV. Action of alkali on diketopiperazines and peptides. P. A. LEVENE and M. H. PFALTZ (J. Biol. Chem., 1926, 70, 219—227; cf. A., 1925, i, 1474).—On keeping in 1 equivalent of 0·1*N*-sodium hydroxide for 48 hrs., diketopiperazines are racemised to the extent of 70—80%, whilst peptides are scarcely affected; with 10 equivalents of *N*-sodium hydroxide, neither diketopiperazines nor peptides are appreciably racemised; this is probably due to the rapid conversion of anhydride into peptide by the stronger alkali. In experiments of longer duration, the degree of racemisation of peptides increases with rise in concentration of alkali, increase of temperature, and increase in the number of amino-acids in the peptide; the optical activity of alanine was entirely unchanged after keeping for 35 days in 0·1—1·0*N*-sodium hydroxide. l-*Bromopropionyl*-l-*alanylglycine*, m. p. 151—154°, $[\alpha]_D^{20}$ +26·2°, gave l-*alanyl*-l-*alanylglycine*, m. p. 241—242° (decomp.), $[\alpha]_D^{21}$ +46·1°; *chloroacetyl*-l-*alanyl*-l-*alanylglycine*, m. p. 180°, $[\alpha]_D^{20}$ +95°, yielded *glycyl*-l-*alanyl*-l-*alanylglycine*, m. p. 263—265° (decomp.), $[\alpha]_D^{20}$ +104·8°. C. R. HARINGTON.

Structure of proteins. E. ABDERHALDEN and E. SCHWAB (Z. physiol. Chem., 1926, 158, 66—76).—The existence of other than polypeptide linkings in proteins is discussed, and several anhydropolypeptides (2 : 5-diketopiperazine derivatives) are in-

vestigated. The ester hydrochloride of leucylglycylleucine, when treated with methyl-alcoholic ammonia, deposits after 12 hrs. leucylglycine anhydride, m. p. 239—240°, and after 24 hrs. a *substance*, m. p. 246°. When no further crystals separate, the solution is evaporated to small volume and then yields *leucylglycyl-leucine anhydride* [1-α-*amino*iso*hexoyl*-2 : 5-*diketo*-3-iso*butylpiperazine*, $CHBu^{\beta}\cdot CO\cdot N(CO\cdot CHBu^{\beta}\cdot NH_2)\cdot CH_2$ (I)], m. p. 231°. From $NH\text{——}CO\cdot CH_2$ the aqueous mother-liquor, alcohol precipitates a *substance*, $C_{14}H_{25}O_3N_3$ [probably $CHBu^{\beta}\cdot CO\cdot NH\cdot CH_2\cdot CO$ (II)], m. p. 252°. By heating $NH\cdot CO\cdot CHBu^{\beta}\text{——}NH$ alanine anhydride with leucylglycine in aniline at 200° there is obtained 1-*leucylglycyl*-2 : 5-*diketo*-3 : 6-*dimethylpiperazine* (III). Compounds (I) and (III) give positive ninhydrin and anhydride reactions, but no biuret reaction; (II) shows the converse behaviour. Their behaviour towards enzymes is under investigation. C. Hollins.

Ionisation of pyrimidines in relation to structure of pyrimidine nucleosides. P. A. Levene, L. W. Bass, and H. S. Simms (J. Biol. Chem., 1926, **70**, 229—241).—Uracil and its 1-, 3-, 4-, and 5-methyl derivatives have only one dissociation constant of approximately the same value (p_k 9·45—9·94); 1 : 3-dimethyluracil has no constant, whilst for 4 : 5-dihydrouracil p_k is 11·5; it is apparent therefore that only one enol group can be formed at the same time in uracil, the second hydroxyl dissociation constant previously reported (A., 1925, i, 1478) being in error. For the 3-hydroxyl group of cytosine, p_k is 12·16, and since cytidine shows only one dissociation constant in the alkaline range, p_k 12·3, the sugar group must be attached in the 3-position; the conversion of cytidine into uridine therefore proves that in the latter also the sugar linking is in the 3-position. For the amino-group of cytosine, p_k is 4·60 and for that of *iso*cytosine 4·01; the hydroxyl group of *iso*cytosine shows the abnormal value p_k 9·42. C. R. Harington.

β-Iminazolyl-(4 or 5)-pyruvic acid. G. Barger and C. P. Stewart (J. Pharm. Exp. Ther., 1926, **29**, 223—226).—When 2-phenyl-4-[1-acetylglyoxaline-4(or 5)-methylidine]oxazolone (cf. Pyman, A., 1916, i, 336) is boiled with 40% sodium hydroxide, β-iminazolyl-4(or 5)-pyruvic acid is obtained, and may be isolated as the hydrochloride $C_6H_6O_3N_2$,HCl, which froths at 108° and becomes liquid at 241° after previous darkening. W. O. Kermack.

Synthesis of 2-2-pyridylpyrrole, and the structure of the isomeric 2-pyridylpyrroles and of the corresponding α-nicotyrins. J. P. Wibaut (Rec. trav. chim., 1926, **45**, 657—670; cf. A., 1923, i, 954, 1232).—The pyrogenic rearrangement of *N*-2-pyridylpyrrole gives rise to two products, m. p. 90° and 132°, respectively. The former is now shown to be 2-2-pyridylpyrrole (I), which has been synthesised, and therefore the isomeride of higher m. p. must be 3-2-pyridylpyrrole (II). Ethyl α-picolinoacetate, $C_5H_4N\cdot CO\cdot CH_2\cdot CO_2Et$, is converted by chloroacetaldehyde and ammonia into *ethyl* 2-2-*pyridylpyrrole*-3-*carboxylate* (III) (m. p. 40—50°, indef.), which forms a crystalline *picrate*, m. p. 204—205°, and is converted by alcoholic sodium hydroxide into 2-2-*pyridylpyrrole*-3-*carboxylic acid*, m. p. 246—248°. By the distillation of the calcium salt of this acid (I) is produced. During the isolation of (III) as the picrate there separated a small quantity of the *picrate* (m. p. 87—89°) of *ethyl* 2-2-*pyridylfuran*-3-*carboxylate* (IV). The ester itself was not obtained pure, but a *gold* salt, m. p. 144—145°, was prepared. W. J. Powell.

Pyrogenic rearrangement of *N*-methyl-2-(2-pyridyl)pyrrole. J. P. Wibaut and (Frl.) E. Dingemanse (Rec. trav. chim., 1926, **45**, 671—673; cf. preceding abstract).—At 700°, *N*-methyl-2-2-pyridylpyrrole is converted into a *C*-methyl derivative, which is probably 2-2-*pyridyl*-5-*methylpyrrole*, as a similar tendency of an *N*-methyl group to wander to the α-position has been observed in many methylpyrrole derivatives. A small amount of 2 : 2′-dipyridyl is also formed. 2-2-Pyridyl-5-methylpyrrole forms a *picrate*, m. p. 196—197° (corr., decomp.). W. J. Powell.

Constitution of pinacyanols. E. Rosenhauer [with A. Schmidt and H. Unger] (Ber., 1926, **59**, [*B*], 2356—2360).—Pinacyanol iodide, decomp. 276—278°, and the corresponding chloride are obtained by treating an alcoholic suspension of 1-methyl-2-methylene-1 : 2-dihydroquinoline with iodoform or chloroform, respectively. If the alkyl halide is replaced by benzenyl chloride, 10-*phenyl*-1 : 1′-*dimethyl*-2 : 2′-*carbocyanine chloride*, decomp. 249°, is obtained; the corresponding *bromide*, decomp. 249°, and *picrate*, decomp. 285°, are described. The formation of these compounds affords synthetic evidence in favour of the constitution proposed by Mills and Hamer (J.C.S., 1920, 117, 1550) for pinacyanol. H. Wren.

Influence of radicals in synthesis of 1 : 2 : 4-triazoles. G. Gastaldi and E. Principalle (Gazzetta, 1926, **56**, 557—566; cf. Rupe and others, A., 1900, i, 258; 1903, i, 535).—The following triazoles are formed very readily. *Acetylformhydroxamic acid α-naphthyldiazone*, m. p. 185—186° (decomp.), obtained from the sodium hydrogen sulphite compound of the acid, gives an *acetyl* derivative, $C_{10}H_{17}\cdot NH\cdot N{:}CMe\cdot C(OH){:}NAc{:}O$ or $C_{10}H_{17}\cdot NH\cdot N{:}CMe\cdot CO\cdot NH\cdot OAc$, m. p. 118°, which on heating gives 5-*hydroxy*-1-α-*naphthyl*-3-*methyl*-1 : 2 : 4-*triazole*, m. p. 225°, yellow. *Benzoylformhydroxamic acid α-naphthylhydrazone*, m. p. 164—165° (decomp.), from the sodium salt of the acid, when treated with acetic anhydride gives the analogous 3-*phenyltriazole*, m. p. 270°, yellow; the corresponding 5-hydroxy-1 : 3-diphenyl-1 : 2 : 4-triazole is obtained from the phenylhydrazone. p-*Bromobenzoylformhydroxamic acid*, m. p. 141° (decomp.), from *p*-bromophenylglyoxal (obtained by hydrolysis of the sodium hydrogen sulphite compound of *p*-bromo*iso*nitrosoacetophenone), gives *p*-bromobenzamide when heated. It forms a *diacetyl* derivative, m. p. 121°, and two yellow *phenylhydrazones*, α, m. p. 185—186° (decomp.), β, m. p. 170° (decomp.). One of these when treated with acetic anhydride gives 5-*hydroxy*-1-*phenyl*-3-p-

bromophenyl-1 : 2 : 4-*triazole*, yellow, m. p. 289°. Similarly, p-*methylbenzoylformhydroxamic acid phenylhydrazone*, yellow, m. p. 164° (decomp.), gives the 3-p-*tolyl* analogue, m. p. 264°; at the same time, the *acetyl* derivative, m. p. 134°, is also formed, in contrast with the other triazoles described, which may be recrystallised unchanged from acetic anhydride. E. W. WIGNALL.

Spontaneous oxidation of 1- and 7-methyluric acid and of 1 : 3-dimethyluric acid in alkaline solution. L. PIAUX (Bull. Soc. chim., 1926, [iv], **39**, 1471—1481; cf. A., 1925, i, 165, 592).—Spontaneous oxidation of 7-methyluric acid in solutions made alkaline with potassium hydroxide yields potassium methyl oxonate, even in the presence of manganous lactate, the catalyst serving only to accelerate the oxidation, which is much slower than in the case of uric acid. 1 : 3-Dimethyluric acid does not oxidise spontaneously in the presence of ammonia. R. BRIGHTMAN.

Production of tetrazoles. K. F. SCHMIDT.—See B., 1926, 932.

Porphyrin syntheses. VI. Synthesis of octamethylporphin, the methyl analogue of ætioporphyrin. H. FISCHER and B. WALACH (Annalen, 1926, **450**, 164—181).—An identical octamethylporphin is synthesised by three different methods, thus making it highly probable that the isomerism of the porphyrins from unsymmetrical pyrroles is not due to differences in structure in the porphin nucleus. The products of reduction by hydriodic acid are the expected 3 : 4-dimethyl-, 2 : 3 : 4-trimethyl-, and 2 : 3 : 4 : 5-tetramethylpyrroles; a 2-ethylated pyrrole was not detected. Oxidation gives dimethylmaleinimide, m. p. 118°. The analysis of octamethylporphin, $C_{28}H_{28}N_4$ or $C_{28}H_{30}N_4$, establishes the C_{34} formula for the blood-pigment. Its sublimation undecomposed and its insolubility except in nitrobenzene are further support for the "indigoid" structure.

Octamethylporphin [crystallographic data by STEINMETZ] (*dihydrobromide*; *tetrabromide dihydrobromide*, $C_{28}H_{28}N_4Br_6$; complex *copper* and *iron* compounds) is prepared (1) by heating bis-(5-carboxy-3 : 4-dimethylpyrryl)methane in acetic, formic, or propionic acid (slowly in formic acid at 37°) in a current of air; (2) by dissolving (5-bromo-3 : 4-dimethylpyrryl)-(3 : 4-dimethyl-2-bromomethylpyrrolenyl)methene hydrobromide in concentrated sulphuric acid, or by heating it alone or with acetic acid at 200°, or from the corresponding monobromomethane hydrobromide alone at 350° or with formic, acetic, or phosphoric acid at 200°; (3) by heating 3 : 4-dimethylpyrrole with formic acid and glyoxal tetramethylacetal (*s*-tetramethoxyethane) at 160°. When the monobromomethene hydrobromide is heated with acetic acid in an iron vessel, the corresponding *bromohæmin* is formed.

Combustion of octamethylporphin is very difficult, but is successful when a new platinum boat is used. C. HOLLINS.

Porphyrin syntheses. VII. Ætioporphyrin from cryptopyrrole and hæmopyrrole. Synthesis of hæmopyrrole. H. FISCHER and J. KLARER (Annalen, 1926, **450**, 181—201).—Cryptopyrrole when brominated in acetic acid gives a mixture of two brominated methene hydrobromides separable by means of chloroform. Methene I hydrobromide, decomp. 245°, differs from methene II hydrobromide, m. p. 161°, in that it yields an ætioporphyrin by treatment with sulphuric acid; both give the porphyrin when heated alone, or in acetic or formic acid, and, when heated with aniline, an *anilide*, m. p. 240°, which is converted into the porphyrin by hydrobromic–acetic acid at 120°. Bromination of the ætioporphyrin gives a *hexabromo*-compound. [Crystallographic data for the porphyrin and its hexabromide by STEINMETZ.] Both the methenes and ætioporphyrin are oxidised by lead peroxide to methylethylmaleinimide, m. p. 65°. By reduction with hydriodic acid, the two methenes give cryptopyrrole, much phyllopyrrole, and little 3-methyl-4-ethylpyrrole, whilst from ætioporphyrin are obtained hæmopyrrole and phyllopyrrole.

Brominated hæmopyrrole methene hydrobromide, decomp. 225°, is converted by boiling formic acid into an *ætioporphyrin* (*copper* and *iron* compounds, and *hexabromide* described). Reduction of the hæmopyrrole methene gives much hæmopyrrole, little phyllopyrrole, and 3-methyl-4-ethylpyrrole. The porphyrin on reduction yields hæmo- and phyllopyrroles.

For the synthesis of hæmopyrrole, dipropionylmethane is converted into its nitroso-compound and reduced with zinc dust in the presence of ethyl acetoacetate. The *ethyl* 5-*propionyl*-2-*methyl*-4-*ethylpyrrole*-3-*carboxylate*, m. p. 153°, so obtained is hydrolysed by sulphuric acid to 2-*methyl*-4-*ethylpyrrole*, b. p. 86°/20 mm., which by treatment with formic acid and perchloric acid gives a *methene perchlorate*, $C_{15}H_{21}O_3N_2Cl$. The magnesium derivative of 2-methyl-4-ethylpyrrole reacts with ethyl chloroformate to form *ethyl* 2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 86°, which is condensed with hydrogen cyanide to give an *aldimine chloride* and thence by hydrolysis *ethyl* 3-*aldehydo*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 118°. Reduction of the formyl group with hydrazine hydrate and sodium ethoxide yields hæmopyrrole, b. p. 113°/16 mm. (picrate, m. p. 123°). C. HOLLINS.

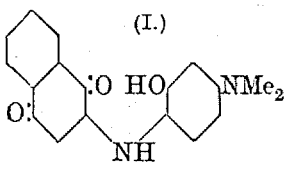
Porphyrin syntheses. VIII. Synthesis of copro- and *iso*copro-porphyrins. H. FISCHER and H. ANDERSAG (Annalen, 1926, **450**, 201—218).—The occurrence, properties, and structure of coproporphyrin are reviewed, and the isomerism possibilities of the "indigoid" formula discussed. Coproporphyrin is synthesised from cryptopyrrolecarboxylic acid by Fischer and Klarer's method (this vol., 962), *iso*coproporphyrin from 5-carbethoxy-2 : 4-dimethyl-3-pyrrylpropionic acid by the method of Fischer and Halbig (*ibid.*, 963).

Cryptopyrrolecarboxylic acid is brominated in acetic acid, and the resulting *brominated methene hydrobromide* (decomp. above 220°) is heated at 210° in acetic acid. The coproporphyrin so obtained is purified as methyl ester, m. p. 243° (complex copper compound, m. p. 269—270°, and *iron* compound), which is hydrolysed by 10% sodium hydroxide to coproporphyrin.

Bis-(5-carboxy-4-methyl-3-ethylpyrryl)methane is converted by boiling formic or acetic acid into a mixture of copro- and *iso*copro-porphyrins (mixed methyl ester, m. p. 220°). Decarboxylation of the methane at 100° in a vacuum yields opsopyrrolecarboxylic acid, m. p. 118°.

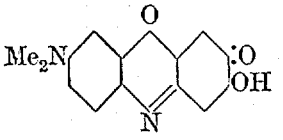
Ethyl 3-aldehydo-2 : 4-dimethylpyrrole-5-carboxylate condenses with malonic acid in the presence of aniline to give 5-carbethoxy-2 : 4-dimethyl-3-pyrrylacrylic acid, m. p. 240° (decomp.), which is reduced with sodium amalgam and water to the pyrrylpropionic acid, m. p. 152° (decomp.). Bromination converts this into *5-carbethoxy-4-methyl-2-bromomethyl-3-pyrrylpropionic acid*, m. p. 176° (decomp.), from which by boiling with water *bis-(5-carbethoxy-4-methyl-3-β-carboxyethyl-2-pyrryl)methane*, m. p. 201°, is obtained, and by subsequent hydrolysis, the corresponding tetracarboxylic *acid*, m. p. 176° (decomp.). The acid, when heated with formic acid in a current of air, yields *iso*coproporphyrin [*methyl* ester, m. p. 256° (sinters at 230°)]. C. HOLLINS.

Synthesis of azoxine colouring matters. F. KEHRMANN, E. GRILLET, and P. BORGEAUD (Helv. Chim. Acta, 1926, 9, 866—880).—By the condensation of 1-amino-5-dimethylaminophenol and 1-amino-5-diethylaminophenol with several *o*-quinones or quinoneimines, various dyes of the azoxine series have been prepared. From the former phenol and the appropriate quinone are obtained: Nile-blue, dimethylaminophenonaphthazoxone (cf. Kehrmann and Herzbaum, A., 1917, i, 591) together with an *amine* (I), the second *isomeride* of Meldola's blue (*nitrate*; *perchlorate*; *chloroplatinate*), the *acetyl* derivative of the isomeride of Nile-blue (*perchlorate*; *chloroplatinate*), and phenyl Nile-blue. Condensation of 1-amino-5-dimethylaminophenol with 2 : 5-dihydroxy-*p*-benzoquinone yields *dimethylaminohydroxyphenazoxone* (II), m. p. 248—250° [which with *o*-phenylenediamine yields *dimethylaminotriphenazoxineazine* (III) (*hydrochloride*)], *tetramethyldiaminotriphendiazoxine*,

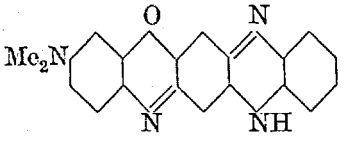


(I.)

$NMe_2 \cdot C_6H_3 \langle \begin{matrix} O \\ N \end{matrix} \rangle C_6H_2 \langle \begin{matrix} N \\ O \end{matrix} \rangle C_6H_3 \cdot NMe_2$, not decomp. below 300°, and a *substance*, not yet identified.



(II.)



(III.)

From the corresponding diethylaminophenol are obtained, on oxidation: 3 : 9-*tetraethyldiaminophenoxazonium nitrate* (*chloroplatinate*, *perchlorate*) (cf. Kehrmann and Poplawski, A., 1909, i, 516); and by condensation with the appropriate quinone, commercial Nile-blue (*acetyl* derivative, *hydrochloride*, and *nitrate* of acetyl derivative), *acetyl* derivative of the isomeride of Nile-blue (*chloroplatinate*, *perchlorate*); *diethyl homologue* of phenyl Nile-blue, m. p. 176° (*hydrochloride*), *iso*Meldola-blue (*perchlorate*, *dichromate*); diethylaminophenonaphthazoxone, and an *anilide* (*chloroplatinate*) of composition similar to (I). J. W. BAKER.

Oximes of α-ketoformhydroxamic acids. I. N. BAIARDO (Gazzetta, 1926, 56, 567—573).—The existence of α and β forms of arylhydroxyglyoximes (cf. Ponzio, this vol., 850) is reasserted. *p*-Methylbenzoylformhydroxamic acid [α-*p*-tolylhydroxyglyoxime] (A., 1924, i, 1209) forms a *triacetyl* derivative, m. p. 107—108°, which saponifies to *3-hydroxy-4-p-tolyl-1 : 2 : 5-oxadiazole* (?), m. p. 192—193° (insoluble *copper* salt), and 5-hydroxy-3-*p*-tolyl-1 : 2 : 4-oxadiazole, m. p. 220° ("*p*-homobenzenylcarbonylimidoxime," A., 1890, 48). This 1 : 2 : 4-oxadiazole is also formed, with *p*-toluonitrile and the β-oxime, by saponification of the *triacetyl* derivative, m. p. 122—123°, of the latter. E. W. WIGNALL.

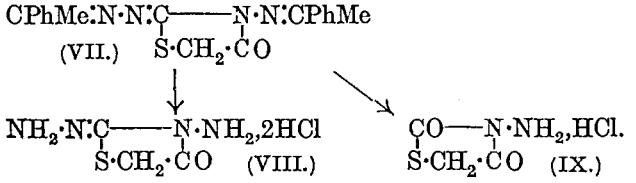
Thiazole derivatives. I. H. W. STEPHEN and F. J. WILSON (J.C.S., 1926, 2531—2538; cf. *ibid.*, 1922, **121**, 870; 1923, **123**, 799).—*Acetone-δ-phenylthiosemicarbazone*, m. p. 130°, reacts in alcoholic solution with esters of α-halogeno-acids to give thiazole derivatives (I). Acid hydrolysis gives small yields of 2 : 4-diketo-3-phenyl-5-*R*-tetrahydrothiazoles (II): $CMe_2{:}N{\cdot}N{:}C(SNa){\cdot}NHPh + CHRX{\cdot}CO_2Et \rightarrow CMe_2{:}N{\cdot}N{:}C\langle \begin{matrix} NPh{\cdot}CO \\ S\text{---}CHR \end{matrix}$ (I) $\rightarrow OC\langle \begin{matrix} NPh{\cdot}CO \\ S\text{---}CHR \end{matrix}$ (II) $+ Me_2CO + N_2H_4,2HCl$. The following are described: 2 : 4-*diketo-3-phenyltetrahydrothiazole-2-isopropylidenehydrazone*, m. p. 200°; 2 : 4-*diketo-3-phenyl-5-ethyltetrahydrothiazole-2-isopropylidenehydrazone*, m. p. 131°, and 2 : 4-*diketo-3-phenyl-5-ethyltetrahydrothiazole*, m. p. 98°; 2 : 4-*diketo-3* : 5-*diphenyltetrahydrothiazole-2-isopropylidenehydrazone*, m. p. 189°. Ethylenethiocarbamide, m. p. 196° (lit. m. p. 194°), reacts similarly with ethyl (or methyl) chloroacetate, giving *ethyl 4 : 5-dihydroiminoazole-2-thioglycollate*, $\begin{matrix} CH_2{\cdot}NH \\ CH_2\text{—}N \end{matrix} \rangle C{\cdot}S{\cdot}CH_2{\cdot}CO_2Et$ (III), decomp. at 160°, m. p. 190° (*methyl* analogue, decomp. at 170°, m. p. 190°). Attempts to effect ring-closure were unsuccessful. Reaction in pyridine solution, however, gives 4 : 5-*dihydroiminoazole-2-thioglycollo-1-lactam*, $\begin{matrix} CH_2{\cdot}N{\cdot}CO{\cdot}CH_2 \\ | \quad\quad\quad \rangle C\text{-}S \\ CH_2{\cdot}N \end{matrix}$ (IV), m. p. 159°. The *sodium* derivative of *o*-phenylenethiocarbamide reacts with ethyl chloroacetate in alcoholic solution, giving

$C_6H_4 \langle \begin{matrix} NH \\ N \end{matrix} \rangle C{\cdot}S{\cdot}CH_2{\cdot}CO_2R \rightarrow C_6H_4 \langle \begin{matrix} N{\cdot}CO{\cdot}CH_2 \\ N \end{matrix} \rangle C\text{-}S$

(V.) (VI.)

ethyl benziminoazole-2-thioglycollate (V), m. p. 73°, changing rapidly to a stable modification, m. p. 97° (*methyl* analogue, metastable form, m. p. 72°, stable form, m. p. 83°). Treatment in benzene solution with sodium powder effects ring-closure, giving *benziminoazole-2-thioglycollo-1-lactam* (VI), m. p. 181°. The *sodium* derivative of diacetophenonethiocarbohydrazone, darkening at 175°, m. p. 199° (cf. Guha and Dey, this vol., 417, m. p. 185°), reacts in alcoholic solution with ethyl chloroacetate, giving 3-*phenylmethylmethyleneamino-2 : 4-diketotetra-*

hydrothiazole-2-phenylmethylmethylenehydrazone (VII), m. p. 175°. Hydrolysis with dilute hydrochloric acid



gives 3-*amino*-2 : 4-*diketotetrahydrothiazole*-2-*hydrazone dihydrochloride* (VIII), very deliquescent solid (*dibenzylidene* derivative, m. p. 138°). Hydrolysis with concentrated hydrochloric acid gives 3-*amino*-2 : 4-*diketotetrahydrothiazole hydrochloride* (IX), a very deliquescent solid (*benzylidene* derivative, m. p. 158°). *Bisdibenzyl ketone thiocarbohydrazone*, $[C(CH_2Ph)_2{:}N{\cdot}NH]_2CS$, has m. p. 143°.

M. CLARK.

Synthesis of "δ-thiopyrindigotin." E. PLAZEK and E. SUCHARDA (Ber., 1926, 59, [*B*], 2282—2284; cf. A., 1925, i, 1331).—3-Aminopyridine-2-carboxylic acid is converted by diazotisation in concentrated hydrochloric acid and addition of thiolacetic acid directly into 2-*carboxypyridinethiolacetic acid*, $CO_2H{\cdot}C_5H_3N{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, m. p. 207—208° (decomp.) [*silver* salt]. This cannot be converted into a dye by fusion with potassium hydroxide and subsequent oxidation, but is transformed by hot, concentrated sulphuric acid into "*δ-thiopyrindigotin*,"

$C_5H_3N<^{S}_{CO}>C{:}C<^{S}_{CO}>C_5H_3N$, decomp. 300—330°.

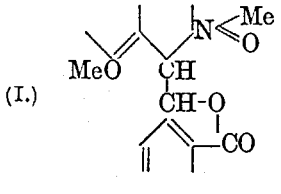
Reducing agents generally decompose the latter substance completely with evolution of hydrogen sulphide, but the corresponding leuco-*derivative* can be obtained by aid of tin and 20% hydrochloric acid.

H. WREN.

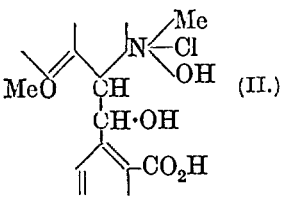
Preparation and properties of ephedrine and its salts. T. Q. CHOU (J. Biol. Chem., 1926, 70, 109—113).—The most convenient method of separating ephedrine from *ψ*-ephedrine is by conversion of the mixed bases into the oxalates; that of ephedrine is very sparingly and that of *ψ*-ephedrine very readily soluble in water. Ephedrine has $[\alpha]_D^{22}$ +13·75° in water and −5·5° in alcohol; the *hydrochloride* has m. p. 216°, $[\alpha]_D^{22}$ −32·5°; *sulphate*, m. p. 257°, $[\alpha]_D^{22}$ −30°; *oxalate*, m. p. 245° (decomp.); *phosphate*, m. p. 178°. *ψ*-Ephedrine has m. p. 118°, $[\alpha]_D^{22}$ +50°; *hydrochloride*, m. p. 179—181°, $[\alpha]_D^{22}$ +58·75°; *sulphate*, $[\alpha]_D^{22}$ +52·5°; *oxalate*, m. p. 218° (decomp.).

C. R. HARINGTON.

Oxidation of narcotine by hydrogen peroxide. A. M. DRUMMOND and A. MCMILLAN (J.C.S., 1926, 2702—2705).—Oxidation of *l*-narcotine in glacial

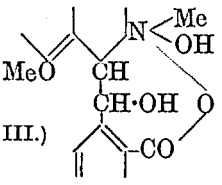


(I.)



(II.)

acetic acid solution with hydrogen peroxide yields *narcotine oxide* (I), m. p. 229°, $[\alpha]_D$ +139° in chloroform. Oxidation of the amine oxide with nitric acid yields hemipinic acid, whilst treatment with hydrochloric acid gives a *hydrochloride* (II), $C_{22}H_{25}O_9N$,HCl, m. p. 191°, containing a carboxyl group. Hydrolysis yields the parent acid, $C_{22}H_{25}O_9N$, m. p. 212° [*lead* salt; *sulphate*, $(C_{22}H_{25}O_9N)_2,H_2SO_4$], regarded as the hydroxy-acid form of the amine oxide (III), produced by rupture of the lactone ring in the narcotine molecule.



(III.)

M. CLARK.

Yohimba alkaloids. I. Yohimbene, a new yohimba alkaloid. G. HAHN and W. BRANDENBERG (Ber., 1926, 59, [*B*], 2189—2197).—Examination of the residues obtained in the technical isolation of yohimbine discloses the presence of yohimboaic acid, frequently in considerable amount (cf. Spiegel, A., 1916, i, 286). In addition, *yohimbenic acid*, $C_{17}H_{22}O_2N_2,2H_2O$, decomp. 230°, $[\alpha]_D^{13}$ −17·1° in pyridine, is present. The acid is conveniently purified through the pyridine or ammonium salt. It dissolves immediately in dilute ammonia and methyl or ethyl alcohol and subsequently separates rapidly from the solution in a form which is subsequently sparingly soluble in these solvents. Yohimbenic acid is converted by methyl-alcoholic hydrogen chloride into *yohimbene hydrochloride*, decomp. 234°, from which *yohimbene*, $C_{16}H_{21}N_2{\cdot}CO_2Me$, decomp. 276°, $[\alpha]_D^{18}$ −43·7° in pyridine, is isolated by means of ammonia. It dissolves freely in alcohol initially, but after crystallisation from this solvent becomes subsequently very sparingly soluble therein. Yohimbene and its hydrochloride are very sensitive to light. Yohimbenic acid is converted by methyl sulphate and alkali hydroxide into "*methylyohimbenic acid methylbetaine*," $C_{19}H_{26}O_2N_2,4H_2O$, decomp. 258°, $[\alpha]_D^{20}$ −29·6° in methyl alcohol.

H. WREN.

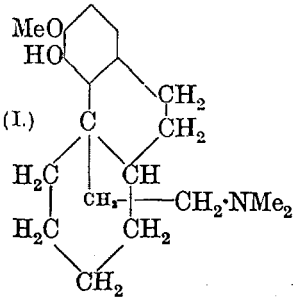
Yohimba alkaloids. K. WARNAT (Ber., 1926, 59, [*B*], 2388—2392).—Examination of the residues from the technical production of yohimbine leads to the isolation of an alkaloid, $C_{21}H_{26}O_3N_2$, m. p. 240—243° (*hydrochloride*, m. p. 280—283°), identical with Spiegel's *meso*yohimbine (A., 1916, i, 286); since the alkaloid is isomeric with yohimbine, the designation iso*yohimbine* is proposed. Contrary to Spiegel's observation (*loc. cit.*), *iso*yohimbine is converted by alkali hydroxide into iso*yohimboaic acid*, $C_{20}H_{24}O_3N_2,0{\cdot}5H_2O$, m. p. 284°, which with ethyl alcohol and hydrogen chloride yields the corresponding *ethyl* ester, m. p. 238—239° (*hydrochloride*, m. p. 295°). *iso*Yohimbine is probably identical with corynanthine (cf. Fourneau and Fiore, A., 1912, i, 49). *Dihydroyohimbine*, $C_{21}H_{28}O_3N_2$ or, possibly, $C_{22}H_{28}O_3N_2$, m. p. 135—140° (*hydrochloride*, m. p. 275—278°), is also present in yohimbine residues. It is hydrolysed to *dihydroyohimboaic acid*, m. p. 248—250°, the *ethyl* ester, m. p. 282—285°, of which is described.

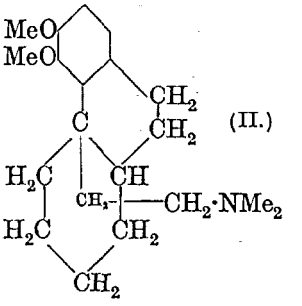
Oxidation of yohimboaic acid by permanganate in cold alkaline solution affords *o*-hydroxyphenylcarbimide; if the temperature during oxidation is raised, the latter substance is replaced by an *acid*, $C_8H_7O_4N$, m. p. 195°, converted by diazomethane into the

substance, $C_{10}H_{11}O_4N$, m. p. 155°. Yohimbine hydrochloride is converted by permanganate in the presence of acetone into an *acid*, $C_9H_7O_2N$, m. p. 197—200°, probably an indolecarboxylic acid. H. WREN.

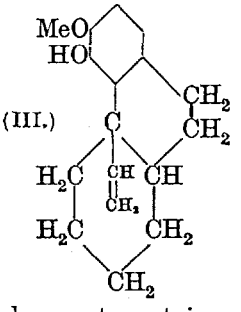
Derivatives of harmalol and harmol. V. HASENFRATZ and R. SUTRA (Compt. rend., 1926, **183**, 605—607).—When treated with dilute sulphuric acid, harmalol and harmol yield sparingly soluble *sulphates*, but with concentrated sulphuric acid the fluorescent *harmalolsulphonic acid* and *harmolsulphonic acid* are obtained. When treated with bromine in acetic acid solution, *bromoharmalol hydrobromide*, *bromoharmol*, and iso*bromoharmol* are produced. After heating with hydrochloric acid in sealed tubes at 140°, both bromoharmine and *iso*bromoharmine yield bromoharmol. *iso*Bromoharmol yields bromoharmol when heated with hydrochloric acid in a sealed tube. L. F. HEWITT.

Degradative experiments in the morphine group. R. S. CAHN (J.C.S., 1926, 2562—2573).—Experiment fails to confirm the conclusion of Speyer and Koulen (A., 1925, i, 59) that chlorotetrahydro-α-methylmorphimethine is converted by treatment with sodium and alcohol into dihydrodeoxytetrahydro-α-methylmorphimethine (I), which yields the compounds (II) and (III), respectively, on methylation and on treatment of the methiodide with boiling alkali. The constitutions (IV), (V), and (VI) are


(I.)


(II.)

assigned to these reaction products, all of which absorb 1 mol. of hydrogen in presence of colloidal platinum. Deoxytetrahydro-α-methylmorphimethine (IV), m. p. 163—164°, gives a *perchlorate*, m. p. 159°. The nitrogen-free compound (VI), m. p. 76—78°,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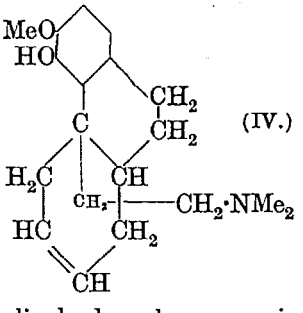
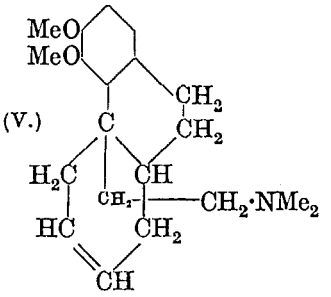

(IV.)

does not contain a phenolic hydroxyl group, since it cannot be methylated or acetylated. The methiodide, m. p. 209—211°, of (V), on heating with amyl-alcoholic potassium hydroxide, loses, not trimethylamine, but one methyl group and regenerates the corresponding base (*hydriodide*, m. p. 170—171°; *perchlorate*, m. p. 206—208°). The catalytic reduction of (IV) gives *dihydrodeoxytetrahydro-α-methylmorphimethine* (I), m. p. 152·5—154° (*hydriodide*, m. p. 219—220°; *perchlorate*, m. p. 150—153°; *methiodide*, m. p.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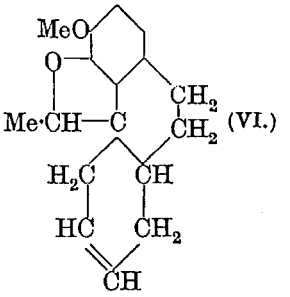
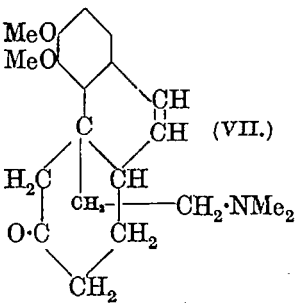

(VI.)

230°). Methylation gives *methyldihydrodeoxytetrahydro-α-methylmorphimethine* (II) [*hydriodide*, m. p. 177·5—178·5°; *methiodide*; *perchlorate*, m. p. 194—195°], whereas treatment of the methiodide with hot alkali causes rapid evolution of methylamine with production of an uncrystallisable nitrogen-free oil, presumably identical with that obtained by the reduction of (VI). The methiodide of (II), like that of (V), regenerates the corresponding base on treatment with amyl-alcoholic potassium hydroxide. Methyldihydrothebainone methiodide, darkening at 255°, m. p. 258—260° (decomp.) [cf. Robinson, J.C.S., 1923, **123**, 1009), when boiled with alkali gives *methyldihydrothebainonemethine* (VII), m. p. 89·5°, b. p. 184—186°/2 mm. (*hydriodide*, m. p. 211—212°; *semicarbazone*, $+H_2O$, m. p. 184°; *monopiperonylidene* derivative; *methiodide*, m. p. 189°). Transformation of the methiodide into the methochloride and reduction with 5% sodium amalgam gave a small quantity of neutral *substance*, m. p. 138—141°.


(VII.)

Catalytic reduction of (VII) gives *dihydromethyldihydrothebainonemethine* (VIII), m. p. 70·5—72° (*hydriodide*, m. p. 224—225°; *perchlorate*, m. p. 216°; *semicarbazone*, $+H_2O$, m. p. 176—178°; *methoperchlorate*, m. p. 185—186°. The last-named compound is alternatively prepared from dihydrodihydrothebainonemethine, m. p. 138—139° (lit. 154—156°). Reduction of (VIII) by Clemmensen's method gives (II). Confirmatory evidence for the isomerism of the α- and β-tetrahydrodeoxycodeines is given. The *hydriodide* of the α-isomeride has m. p. 242—243°. M. CLARK.

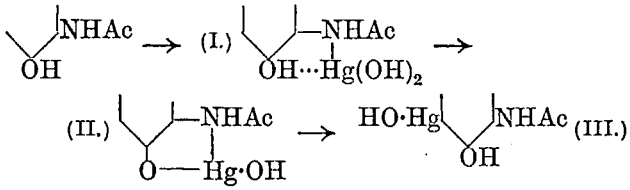
Infra-red absorption spectra of the alkaloids. I. Tropan derivatives. F. K. BELL (J. Pharm. Exp. Ther., 1926, **29**, 533—549).—Tropine, ecgonine, cocaine, tropacocaine, atropine, hyoscyamine, homatropine, noratropine, and scopolamine have been examined spectroscopically between λλ 1 μ and 12 μ. The presence of a hydroxyl group can be ascertained in this way, but primary or secondary amino-groups can be detected only when no hydroxyl group is present. It is not possible to detect the tropan nucleus by means of this technique.

W. O. KERMACK.

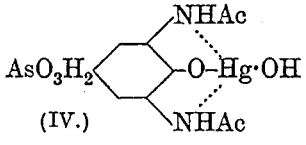
Production of 3-chloro-5-amino-4-hydroxyphenylarsinic acid. I. G. FARBENIND.—See B., 1926, 932.

Arsenic compounds [arsenious oxides] of the aromatic [?] series [benzoxazolones]. L. CASSELLA & Co.—See B., 1926, 932.

Mechanism of mercuration. I and II. E. MASCHMANN (Annalen, 1926, **450**, 85—98, 98—108; cf. this vol., 418).—I. It is shown that mercuration of *o*-acetamidophenols proceeds by way of isolable intermediate additive compounds:



Aqueous sodium 3-acetamido-4-hydroxybenzoate, when treated with mercuric acetate at 0°, gives a white precipitate of a *compound*, $C_9H_{12}O_6NHg$ (as I), which rapidly changes into the more stable *compound*, $C_9H_{10}O_5NHg$ (as II). Neither of these products yields an iodo-acid by the action of iodine in potassium iodide. The second product changes very slowly at 15°, quickly at 100°, into 3-*acetamido*-4-*hydroxy*-5-*hydroxymercuribenzoic acid* (as III), from which 5-*iodo*-3-*acetamido*-4-*hydroxybenzoic acid*, m. p. 234—235°, is readily obtained. Under similar conditions, sodium 3-acetamido-4-hydroxyphenylarsinate gives a *substance*, $C_8H_{10}O_6NAsHg$ (as II), a normal mercuri-compound, and the corresponding iodo-derivative, m. p. 172—173°. An intermediate *product*, $C_{10}H_{13}O_7N_2AsHg$ (IV), is obtained in the mercuration of 3 : 5-diacetamido-4-hydroxyphenylarsinic acid (cf. Maschmann, this vol., 851).



II. In the mercuration of sodium aminobenzoates, two intermediate stages, $Ar{\cdot}NH_2 \ldots Hg(OH)_2$ and $NHAr{\cdot}Hg{\cdot}OH$, are demonstrated, neither of which yields an iodo-acid with iodine. Acetamidobenzoates give a primary intermediate of the type $NHAcAr \ldots Hg(OH)_2 \ldots NHAcAr$. As was to be expected, sodium *p*-dimethylaminobenzoate does not give the secondary intermediate, the primary being converted directly into the final mercuri-compound. Primary and secondary intermediate *compounds* are isolated in the mercuration of sodium *m*- and *p*-aminobenzoates and primary intermediate *compounds* in the case of the *m*- and *p*-acetamidobenzoates. The following products also are new: 3-*amino*-6-*hydroxymercuribenzoic acid*, 4-*acetamido*-3-*hydroxymercuribenzoic acid*, and 3-*acetamido*-6-*hydroxymercuribenzoic acid*.

C. HOLLINS.

Porphyrins from oxyhæmin anhydride. II. A. HAMSIK (Z. physiol. Chem., 1926, **158**, 15—18; cf. this vol., 968).—The orange-red porphyrin prepared by dissolving oxyhæmin anhydride in acetone containing stannous chloride and hydrochloric acid is identical with protoporphyrin prepared by the method of Fischer and Pützer (this vol., 854) from oxyhæmin anhydride, formic acid, and iron. If the crude porphyrin tin salt is warmed with glacial acetic acid, diluted, and treated with hydrochloric acid, it yields a complex tin salt, the so-called violet porphyrin, also described by Fischer and Pützer (*loc. cit.*).

C. HOLLINS.

Substances extracted from muscle. XXVI. Properties of carnosine and its compounds. L. BROUDE (Z. physiol. Chem., 1926, **158**, 22—27).—The solubility of carnosine phosphotungstate corresponds with 0·036 g. of carnosine per litre; the mercurisulphate, 0·00842 g. Carnosine titrates as a mono-acid base in the presence of methyl-orange, cochineal, or methyl-red; it is neutral to phenolphthalein, and very weakly alkaline to α-naphtholphthalein. In Sörensen's "formol" titration, carnosine behaves as a monobasic acid; nitrous-acetic acid shows one free amino-group. Carnosine is completely hydrolysed by 13% sulphuric acid after 5 hrs.' boiling. Carnosine cannot be separated from histidine by means of silver nitrate and barium carbonate, nor by precipitation with potassium bismuth iodide or potassium mercuric iodide.

C. HOLLINS.

Effect of ionisation on optical rotation of nucleic acid derivatives. P. A. LEVENE, H. S. SIMMS, and L. W. BASS (J. Biol. Chem., 1926, **70**, 243—251).—Curves obtained from inosine, inosinic acid, and adenosine by plotting molecular rotation against corrected equivalents of base, *b'*, show the form of straight lines with sharp breaks at integral values of *b'*, as would be expected from the fact that the titration constants of these substances are more than 3 p_H units apart (cf. Simms, this vol., 681); all these compounds have ionisable sugar groups for which p_k is a little above 12.

C. R. HARINGTON.

Relation of chemical structure to rate of hydrolysis of peptides. II. Enzymic hydrolysis of di- and tri-peptides. P. A. LEVENE, H. S. SIMMS, and M. H. PFALTZ (J. Biol. Chem., 1926, **70**, 253—264).—Ereptic hydrolysis of numerous dipeptides has been shown to follow the same course as was previously observed (A., 1925, i, 473); comparison of the rate of ereptic hydrolysis of a dipeptide with that of a similar tripeptide (*e.g.*, glycylglycine with diglycylglycine) shows that the latter is about nine times as fast as the former, which indicates that the stability of the peptide linking is determined by the intrinsic constants of the groups involved rather than by their dissociation constants. Asparagylglycine, which exists as an anion over the p_H range of activity of erepsin, is not hydrolysed by this enzyme. *Methylalanylglycine* has m. p. 237° (decomp.); *sarcosylalanine*, m. p. 171—172° (decomp.); *methylalanylalanine*, m. p. 235° (decomp.); *sarcosylglycylglycine*, m. p. 250—253° (decomp.); *methylalanylglycylglycine*, m. p. 252—253° (decomp.); *bromopropionylsarcosine*, m. p. 84°; *methylalanylsarcosine anhydride*, m. p. 78—80°; *bromoisovalerylsarcosine*, m. p. 76—77°.

C. R. HARINGTON.

Protein structure and proteolysis. A. HUNTER (Trans. Roy. Soc. Canada, 1925, **19**, [v], 1—23).—The Presidential address. The present position of the subject is discussed; some preliminary results

obtained by the author and collaborators are mentioned: there appears quite early in tryptic digestion a product consisting mainly of polypeptides or anhydrides. This was discovered in applying Dakin's butyl alcohol extraction method to the digests. It is also found that arginine, contrary to the usual assumption, appears as soon as, if not sooner than, any other amino-acid, in tryptic digestion, particularly in the case of gelatin and casein, although it appears less rapidly in the case of edestin.

C. RIMINGTON.

Quantitative analysis of mixtures of volatile fatty acids by division between ethyl ether and water. W. U. BEHRENS (Z. anal. Chem., 1926, 69, 97—107).—When an aqueous solution of certain fatty acids or of lactic acid is shaken with ether, the acids are divided in constant proportions between the ether and water layers, so that by performing a number of tests with different ratios of ether to water, it is possible to determine the concentration of each acid in the original solution by titrating the aqueous and ethereal layers with standard alkali. In the case of acetic acid, the distribution factor: (concentration of acid in ethereal layer)/(concentration of acid in aqueous layer) is 0·434. As lactic acid and higher members of the fatty acid group associate in ether, a correction depending on the concentration of acid left in the aqueous layer (C_w) must be applied; the distribution factors for 20° in these cases are therefore as follows: lactic acid, $0{\cdot}0807+0{\cdot}004C_w$; propionic acid, $1{\cdot}685+1C_w$; *n*-butyric acid, $5{\cdot}85+23C_w$; *n*-valeric acid, $21{\cdot}0+250C_w$; *iso*valeric acid, $18{\cdot}8+130C_w$; *n*-hexoic acid, $81{\cdot}5+1800C_w$. The analysis may be conducted somewhat as follows: 50 c.c. of solution are shaken with ether so that the ether : water ratio at the end is 40 : 60; the aqueous layer is withdrawn into another burette and again divided in the ratio 40 : 60, whilst the ether layer is shaken with water in the same ratio. The aqueous layer in each of the two last-named cases is titrated. The process is repeated on a second 50 c.c. of the original solution, using an ether : water ratio of 4 : 96, and on a third 50 c.c., using a ratio of 15 : 85. From the volume of alkali used in the titrations and the above distribution factors, the concentration of all the acids in the original solution may be calculated.

A. R. POWELL.

Titration of quinol with iodine or dichromate according to the ordinary and the potentiometric method. I. M. KOLTHOFF (Rec. trav. chim., 1926, 45, 745—752).—The oxidation of quinol by iodine is quantitative only if the hydrogen-ion concentration is less than $10^{-5}N$ at the end-point. In the ordinary titration, 1 c.c. of 4*N*-acetic acid, about 20 c.c. of 2*N*-sodium acetate, and an excess of standard iodine solution are added to 25 c.c. of 0·1*N*-neutral quinol solution, and the mixture is titrated back with thiosulphate. A 0·0001*N*-solution can thus be titrated to 1%. In the potentiometric method, a platinum gauze electrode is used and the solution titrated with iodine in the presence of sodium hydrogen carbonate and a little hydrochloric acid. The end-point is shown by a sudden increase in *E.M.F.* Quinol is oxidised quantitatively by potassium dichromate, and the end-point can be determined either with diphenylamine as indicator, or potentiometrically, but as the electrode is quickly poisoned, it must be heated to redness after each titration.

S. J. GREGG.

Test for cysteine. M. X. SULLIVAN (U.S. Pub. Health Rep., 1926, 41, 1030—1056; cf. A., 1925, ii, 1211).—In the presence of sodium 1 : 2-naphthaquinone-4-sulphonate, sodium hyposulphite, and aqueous sodium cyanide, cysteine develops a red coloration which is not given by compounds containing the thionyl or amino-group alone, the amino-group and sulphur (as in cystine), mixtures of amino-acids and compounds containing the thionyl group, or compounds containing thionyl and amino-groups far apart in the molecule. A modification of the test to permit of the detection of cystine is described.

CHEMICAL ABSTRACTS.

Determination of selenium in organic compounds. W. E. BRADT and R. E. LYONS (J. Amer. Chem. Soc., 1926, 48, 2642—2646).—If a selenium organic compound (which must not contain halogen) is heated with nitric acid (Carius method) at 240—300°, all the selenium is converted into selenious acid (cf. Wrede, A., 1920, ii, 632), which is determinable by rendering just alkaline, just acidifying with nitric acid, stirring in excess of zinc oxide, and titrating with 0·1*N*-silver nitrate solution, using chromate as external indicator. The selenium content is calculated from the equation $H_2SeO_3+2AgNO_3+ZnO=Ag_2SeO_3+Zn(NO_3)_2+H_2O$. A blank titration of the silver nitrate against a suspension of zinc oxide gives a necessary correction. The method is accurate within the usual limits.

F. G. WILLSON.

Biochemistry.

Influence of carbon dioxide on man during exposure to reduced barometric pressure. E. C. SCHNEIDER, D. TRUESDELL, and R. W. CLARKE (Amer. J. Physiol., 1926, 78, 393—404).—The alveolar carbon dioxide tension in subjects submitted to a gradual reduction of barometric pressure to 250 mm. of mercury (equivalent to an altitude of 30,000 ft.) fell from an average of 39·8 mm. to 22·2 mm. When 4% carbon dioxide was simultaneously administered, the alveolar tension fell to 26·3 mm., and with 8% carbon dioxide to 29·4 mm. The alveolar oxygen tension did not fall so rapidly in the carbon dioxide experiments as in the controls, until extremes of simulated altitudes beyond 20,000 ft. were reached. The carbon dioxide did not mitigate the effects of anoxæmia on the heart, blood pressure, and nervous system.

R. K. CANNAN.

Manoiloff's sex-determination reaction. G. Alsterberg and A. Håkansson (Biochem. Z., 1926, **176**, 251—265).—The reaction is of no value in sex determination and is unsuitable for use in forensic medicine. C. Rimington.

Differences between the blood of men and of women. A. Klisiecki (Biochem. Z., 1926, **176**, 490—500).—The urea-nitrogen of the blood is consistently higher in men than in women, the values lying between 10·8—17·6 mg. and 6·24—10·05 mg. per 100 c.c., respectively. Similar sex differences have been observed in dogs and rabbits.

C. Rimington.

Determination of hæmoglobin in blood. E. M. F. Ithurrat and V. Morera (Rev. Asoc. Med. Argentina, 1926, **39**, 400—426).—The normal content of hæmoglobin in blood for men is 15·65 g. per 100 c.c. and for women 13·5 g. per 100 c.c.

G. W. Robinson.

Action of carbon dioxide on hæmoglobin. W. A. Osborne (Austral. J. Exp. Biol., 1926, **3**, 117—118).—Diluted blood, through which pure carbon dioxide was continuously bubbled, after several hours showed the characteristic absorption in the red of acid hæmatin. W. Robson.

Osmotic pressure of hæmoglobin and of base bound by hæmoglobin. J. H. Austin, F. W. Sunderman, and J. G. Camack (J. Biol. Chem., 1926, **70**, 427—436).—Determinations of the osmotic pressure of alkaline solutions of hæmoglobin, in presence of varying amounts of sodium chloride, indicate that the osmotic activity of the hæmoglobin is less than half of that calculated from the concentration of hæmoglobin (assuming 1 mol. hæmoglobin per mol. oxygen capacity), from which it follows either that the base bound by hæmoglobin is dissociated only to half the extent of that in the corresponding chloride, or that, in presence of hæmoglobin, the activity coefficient of the dissociated base varies with the concentration of salt (cf. Adair, A., 1925, i, 849—851).

C. R. Harington.

Buffering power of the blood of *Maia squinado*. P. M. T. Kerridge (J. Physiol., 1926, **62**, 65—73).—The carbon dioxide tension-p_H curves have been determined for the reduced and for the oxygenated blood. The blood is more heavily buffered than sea water, but much less heavily than mammalian blood. The buffering power and hydrogen carbonate content have been calculated in relation to p_H, and it is argued that oxyhæmocyanin is a stronger acid than is reduced hæmocyanin. R. K. Cannan.

Coagulation of blood. Effect of p_H, dialysis, and electrodialysis on the coagulation of fibrinogen. R. Rabinovitch (Anal. Asoc. Quím. Argentina, 1926, **14**, 139—157).—The coagulation of oxalated plasma by thrombin, *Lachesis* venom, or recalcification is affected by hydrogen-ion concentration, the maximum coagulability being at p_H 6·3—6·8. In the case of fibrinogen, maximum coagulability is at p_H 6·6—6·8. Both plasma and fibrinogen are uncoagulable below p_H 5·0 and above p_H 8·0. The transformation of fibrinogen into fibrin can take place both in acid and in alkaline solution. Fibrinogen after dialysis for a month, and electrodialysis, is coagulable by thrombin or *Lachesis* venom. The isoelectric point of fresh or dialysed and electrodialysed fibrinogen is between p_H 5·86 and 6·2.

G. W. Robinson.

Phosphorus partition in human blood and changes in different individuals. F. Roller (Biochem. Z., 1926, **176**, 483—489).—The inorganic phosphorus of the blood of any individual is subject to large variations similar to those of the serum phosphate; the absolute quantities of the various phosphorus fractions also vary considerably, whilst that of total organic phosphorus shows large differences in different individuals. The organic soluble phosphorus of whole blood is approximately four times that of serum, and a certain constancy in the relationship between inorganic and total phosphorus appears to exist in any single individual.

C. Rimington.

Ammonia and blood-sugar. A. A. Horvath (J. Biol. Chem., 1926, **70**, 289—296).—Increase of the concentration of ammonia in the blood and tissues of rabbits, brought about by injection of ammonium carbonate or of urease, results in a mild hyperglycæmia, which is regarded as the response of the organism to the toxic effects of the ammonia. High concentration of dextrose may lead to fictitiously high values for the urea concentration of the blood when determined in the protein-free filtrate by the method of aëration. C. R. Harington.

I. Specific refraction of the total proteins of blood serum. II. Specific refraction of serum albumin and globulin. G. Schretter (Biochem. Z., 1926, **177**, 335—348, 349—374).—I. The specific refractions of the total proteins of the sera of a number of normal and pathological animals and men are tabulated and compared with the results of other authors.

II. The specific refraction of albumin and globulin fractions of sera, normal and pathological, is determined directly in the isolated material and indirectly in the protein–ammonium sulphate mixture, and compared with the mean values for total protein and with the values of other authors. It is concluded that refractometric methods must not be regarded as proving changes in albumin and globulin content in pathological conditions, since it is not yet possible to decide how much of the differences observed are due to errors of method. P. W. Clutterbuck.

Reaction between serum and alkaloids. R. Beutner (J. Pharm. Exp. Ther., 1926, **29**, 95—103).—The rate at which pilocarpine is bound by sheep- or ox-serum is demonstrated by the addition of potassium mercuric iodide to the mixture, when any of the alkaloid not bound is precipitated. Although no alkaloid may be detected in the serum after 1 hr. unless an excessive quantity has been added, there is no appreciable destruction of the alkaloid in this time, but destruction does take place on prolonged keeping.

W. O. Kermack.

Astringent action of aluminium acetate. W. Straub (J. Pharm. Exp. Ther., 1926, **29**, 83—93).—The action of aluminium acetate solution on blood-

serum and on elastic connective tissue is of the nature of a colloidal precipitation, being maximal with a concentration of aluminium acetate of approximately 0·8%. W. O. KERMACK.

Interferometric application of the Abderhalden reaction and interferometric analysis of fermentative processes. E. KAUFMANN (Biochem. Z., 1926, **177**, 206—238).—An account of interferometric methods applied to the Abderhalden (pregnancy) and similar reactions. J. PRYDE.

Electrodialysis of antitoxic sera. Precipitation of active globulins. R. WERNICKE and F. MODERN (Anal. Asoc. Quím. Argentina, 1926, **14**, 158—169).—The active fractions of antidiphtheritic and antitetanic sera have been separated by electrodialysis. Globulins and antitoxins precipitated by electrodialysis partly redissolve in the albumin solution by simple contact when the current is stopped. G. W. ROBINSON.

Embryos. I. Physico-chemical changes of the proteins of hen's eggs during incubation. G. E. VLADIMIROV. II. Sugar, residual- and total-nitrogen contents of egg-white during incubation. III. Sugar, fat, and residual-nitrogen contents of the blood of embryo chicks. G. E. VLADIMIROV and A. A. SCHMIDT (Biochem. Z., 1926, **177**, 280—297, 298—303, 304—308).—I. The amount of solid substances in egg-white increases during incubation from 13 to 14%, whereas of the yolk it diminishes in the first week from 50 to 40%, then gradually increases, passing the original value on the 12th day, and on the 20th day reaches 55·7%. The electrical conductivity during incubation falls from $7{\cdot}6\times10^{-3}$ to 3×10^{-3}. The relationship between conductivity and concentration of protein is not linear when the latter is large. The osmotic pressure, measured by f.-p. depression of egg-white, and the concentration of hydrogen ions increase during incubation, the p_H, after removal of carbon dioxide, although always decreasing, being greater than 7·0 until the 16th day.

II. The amount of sugar in egg-white (439 mg.%) decreases during incubation and reaches values indeterminable by Michaelis' method. The Hagedorn–Jensen method gives incorrect results when large amounts of solid substances are present. The reducing substances of yolk (200 mg.%) also decrease, and on the 14th day reach a constant value (62 mg.%). The amount of residual nitrogen increases proportionately with the total nitrogen during incubation.

III. The amount of reducing substances of the blood of an embryo chick is almost constant (150 mg.%) and increases on hatching (210 mg.%). The fat content of the blood is surprisingly large, increasing from about 300 to 500 mg.% from the 11th to the 20th day of incubation and then decreasing until in the two-day-old chick it is 138 mg.%. The residual nitrogen of the blood is also fairly high, varying between 48 and 63 mg.%. P. W. CLUTTERBUCK.

Nitrogenous metabolism in the chick embryo. C. H. FISKE and E. A. BOYDEN (J. Biol. Chem., 1926, **70**, 535—556).—Whereas the amniotic cavity of the chick embryo contains traces only of nitrogenous substances, the allantoic cavity contains, besides small and fairly constant amounts of amino-acids and of creatine, uric acid in an amount which increases with the age of the embryo; the rate of increase shows marked acceleration at the 8th and 11th day of incubation; by the 19th day, the uric acid may amount to 100 mg., of which the greater part is in the form of a deposit of urates. It is therefore concluded that the allantoic fluid is a true excretion and that uric acid is the sole end-product of nitrogenous metabolism in the chick embryo; the amount of uric acid indicates that protein forms about 6% of the total organic matter oxidised (cf. Murray, A., 1925, i, 1353). Creatine was detected as early as the 8th day of incubation, in contradiction to the results of Mellanby (A., 1908, ii, 308). C. R. HARINGTON.

Ovarian residue. Protein fraction. B. FULLERTON and F. W. HEYL (J. Amer. Pharm. Assoc., 1926, **15**, 18—30).—Ethyl ether extracted 8·53%, cold absolute ethyl alcohol 6·0% (of which the non-lipin portion was 4%), cold 95% ethyl alcohol 9·8%, boiling alcohol 11·7%. The water- and saline-soluble proteins of the gland, from which corpus luteum has been removed, consist largely of an albumin, *M* 8500, containing C 52·0, H 7·0, N 15·3, S 1·5%, approximating to arginine 3, lysine 7, tyrosine 4, tryptophan 1, cystine 2, monoamino-acids 56 mols. CHEMICAL ABSTRACTS.

Basic proteins. A. KOSSEL and W. STAUDT (Z. physiol. Chem., 1926, **159**, 172—178).—The basic protein fraction of the semen of *Echinus esculentus* is precipitated as sulphate which in aqueous solution gives strong arginine, diazo-, and Millon reactions, but does not give either glyoxylic or dimethylaminobenzaldehyde tests for tryptophan nor the Molisch test. The arginine content is about the mean value for and the lysine and histidine contents rather higher than for known histones. Protamine of the semen of *Coregonus macrophthalmus* is similarly precipitated, and after purification two samples gave an arginine content of 90·85, 90·38%, the rotations referred to the nitrogen content being $[\alpha]_D^N$ −322·59°, −322·73°. This is very close to Kossel's value for salmine, $[\alpha]_D^N$ −320·7°, and it is claimed, therefore, that the protamine of *Coregonus* is identical with salmine. The protamine sulphate on keeping in acid solution at the ordinary temperature is slowly racemised. This accounts for the various specific rotations in the literature. P. W. CLUTTERBUCK.

Phosphorus balance in tissues. JAVILLIER and H. ALLAIRE (Compt. rend., 1926, **183**, 619—620).—The ratio lipin phosphorus ×100 : total phosphorus varies from 1 to 5 in different organs; inorganic phosphorus ×100 : total phosphorus from 1 to 8; nuclein phosphorus ×100 : total phosphorus from 1 to 58; and nuclein phosphorus ×100 : lipin phosphorus from 1 to 309. L. F. HEWITT.

Transformation products of the pigments of flesh and blood. Origin of copratin in the spontaneous putrefaction of blood; spectroscopic reactions of crystallised copratoporphyrin prepared from copratin. O. SCHUMM (Z. physiol. Chem., 1926, **159**, 194—198; cf. this vol., 87, 193).—Copratin of the fæces arises from spontaneous putrefaction of blood pigment. Horse-blood, after putre-

faction for 1 year, contained a pigment consisting chiefly of copratin, which on treatment with hydrazine hydrate gave chiefly copratoporphyrin together with a little hæmateric acid (α-hæmatoporphyroidin), but coproporphyrin could not be detected. Copratoporphyrin obtained by putrefaction of blood crystallises from ether and gives the characteristic spectra of copratoporphyrin naturally occurring in the fæces and also of copratoporphyrin formed from copratin of fæces. P. W. CLUTTERBUCK.

α-Hæmatoporphyroidin (hæmateric acid) and the so-called α-hæmatoporphyrin. O. SCHUMM and A. PAPENDIECK (Z. physiol. Chem., 1926, **159**, 190—191).—α-Hæmatoporphyrin is probably not a single substance, since its solution in hydrochloric acid yields a substance insoluble in chloroform, the properties of which resemble closely those of Nencki's hæmatoporphyrin, and a substance soluble in chloroform resembling hæmateric acid (α-hæmatoporphyroidin). It has not as yet been possible, however, to obtain all the characteristic properties of α-hæmatoporphyrin from a solution containing α-hæmatoporphyroidin and Nencki's or a closely related porphyrin. P. W. CLUTTERBUCK.

Calcium-caseinogen equilibria and their bearing on the secretion of calcium in milk. N. C. WRIGHT (J. Agric. Sci., 1926, **16**, 640—642).—In dialysis experiments with a collodion membrane separating an internal solution consisting of 4% caseinogen in 0·02*N*-sodium hydroxide and external solutions of calcium chloride of varying concentration with and without sodium chloride, added to maintain a constant anionic concentration, a higher concentration of calcium was found within the membrane. The ratio of "internal" to "external" calcium increased as the concentration of the calcium chloride in the outer solution was diminished. It is suggested that the ability of caseinogen to form un-ionised or slightly ionised salts with calcium is mainly responsible for this unequal distribution and also governs the distribution of calcium between blood and secreting cells in the mammary gland. G. W. ROBINSON.

Citric acid content of milk. F. F. SHERWOOD and B. W. HAMMER (Agric. Exp. Sta. Iowa State Coll. Res. Bull., 1926, No. 90, 19—39).—Minimal, maximal, and average values for 335 samples of cow's milk were: citric acid, 0·07, 0·33, 0·18%; acidity, 0·10, 0·25, 0·17%; ash, 0·38, 1·10, 0·70%; fat, 1·60, 9·20, 4·58%; total solids, 8·82, 20·15, 13·52%. The citric acid content was unaffected by the breed, milking time, stage of lactation, or season.

CHEMICAL ABSTRACTS.

Comparative analyses of the milk of carabao and Indian buffalo. J. S. GOMEZ (Philippine Agric., 1926, **15**, 75—84).—The samples, which showed considerable variation, had, respectively: *d* 1·0352, 1·0315; water, 77·66, 80·99; fat, 10·17, 7·31; caseinogen, 4·73, 4·48; albumin, 1·25, 1·26; lactose, 4·93, 4·89; ash, 0·869, 0·806.

CHEMICAL ABSTRACTS.

Milk of Australian women. H. S. H. WARDLAW and E. E. P. DART (Austral. J. Exp. Biol., 1926, 3, 129—147).—The modal values for the composition and physical constants of the milk of Australian women between the first and ninth months of lactation are: Δ 0·0583°; *d* 1·0296; lactose content 6·45%; protein 1·40%; ash 0·19%; fat 5·30%. As lactation continues, the protein and ash contents and Δ fall slightly, whilst the lactose content rises. The older the mother, the less rich is the milk in fat and in ash, the greater the milk volume and lactose content. The milk of women between 22 and 27 compared with that of members of other age groups has greatest Δ and lowest protein content. With increasing number of lactations, up to the fourth, the milk volume increases, whilst the percentage fat content decreases.

W. ROBSON.

Seasonal variations in the urinary excretion of total phenols. H. G. O. HOLCK (Amer. J. Physiol., 1926, **78**, 299—307).—Records covering 2 years show that the excretion of phenols by a human subject was about 120 mg. higher per day in the summer than in the winter. It is suggested that this may be due to the greater exposure to sunlight.

R. K. CANNAN.

Behaviour of dyes in the blood of splenectomised dogs. G. FARKAS and H. TANGL (Biochem. Z., 1926, **177**, 135—139).—Trypan-blue injected into the blood-stream of splenectomised dogs is excreted much more slowly than in normal animals.

J. PRYDE.

Hydrogen-ion concentration of the fæces. Participation of the intestine in the regulating mechanism of the acid-base equilibrium. E. GREPPI (Fol. Clin. Chim. Micro., 1926, **1**, 68—72).—A discussion of recent work. T. H. POPE.

Pernicious anæmia. I. E. W. MONTGOMERY (Canadian Med. Assoc. J., 1926, **16**, 244—250).—Long-continued drinking of slightly alkaline water containing excess of calcium, magnesium, chloride, sulphate, etc. is regarded as a causative agent leading to achlorhydria and anæmia.

CHEMICAL ABSTRACTS.

Pernicious anæmia. II. Chloride metabolism in the anæmias, especially pernicious anæmia. M. G. RIOCH and A. T. CAMERON (Canadian Med. Assoc. J., 1926, **16**, 244—250; cf. preceding abstract).—Plasma chloride is relatively constant and normal in the anæmias. In the active stage of pernicious anæmia there is a slight lowering of cell chlorides. Determination of whole blood chloride is often valueless. CHEMICAL ABSTRACTS.

Relation of iron to nutritional anæmia. H. S. MITCHELL and L. SCHMIDT (J. Biol. Chem., 1926, **70**, 471—486).—Investigation of the effect of administering the same amount of iron, in different forms, to rats suffering from nutritional anæmia as the result of being born of parents which had been kept on a diet deficient in iron, indicates a general correlation between the efficacy of an iron compound and its solubility rather than its specific nature.

C. R. HARINGTON.

Healthy and arteriosclerotic aorta. I. Quantitative proportions of cholesterol and cholesteryl esters. R. SCHÖNHEIMER (Z. physiol. Chem., 1926, **160**, 61—76).—The cholesterol and cholesteryl

ester contents of the aorta of a number of individuals, ages 13—70, are tabulated. The amount of the total ether extract is dependent rather on the degree of arteriosclerosis than on the age of the individual. The ether extract of a normal aorta weighs 20—60 mg., whereas in cases of arteriosclerosis it may be increased to 1—1·8 g. The cholesterol percentage of the total extract remains constant in all the cases at about 25, whereas the cholesteryl ester percentage increases from 13 to 62·8 with the degree of arteriosclerosis. The results support strongly the infiltration theory.

P. W. CLUTTERBUCK.

Adrenaline content of the suprarenals of birds during beri-beri (polyneuritis gallinarium). T. Gō (Ni. Byor. Gak. K. Tokyo, 1922, **12**, 187).—The adrenaline content of the left suprarenal capsule of the hen is 64—147 (average 97)$\times 10^{-5}$ g.; experimental beri-beri causes no significant change.

CHEMICAL ABSTRACTS.

Hydrogen-ion concentration and acid-combining power of the mother's milk in infantile beri-beri. B. MATSUMOTO (Biochem. Z., 1926, **177**, 118—131).—The average p_{H} of boiled cow's milk is 6·59, with extremes of 6·64 and 6·52. The acid-combining power of cow's milk is three to four times that of human milk. On diluting milk with water, the acidity drops and the reaction approaches the neutral point. The hydrogen-ion concentration of unboiled milk increases rapidly at 27—30°, but remains constant for several hours at 0—3°. The average p_{H} of normal milk from Japanese women is 7·17, with extremes of 7·0 and 7·3. It tends to be greater in the earlier than in the later period of lactation. Neither the p_{H} nor the acid-combining power of the mother's milk is appreciably altered from the normal in infantile beri-beri. J. PRYDE.

Blood-sugar and urinary dextrose : nitrogen ratio following pancreatectomy. W. H. CHAMBERS and P. N. CORYLLOS (Amer. J. Physiol., 1926, **78**, 270—280).—An increase in blood-sugar begins within 2 hrs. of the removal of the pancreas. The first notable increase in the elimination of nitrogen is concurrent with the appearance of glycosuria. The D : N ratio is highest about the 15th to the 18th hr., and declines thereafter during 2 or 3 days to the values noted by Minkowski. The results suggest an early effect of lack of insulin on dextrose metabolism, reaching a maximum in about 24 hrs. There is a rapid depletion of the glycogen stores resulting from the glycosuria.

R. K. CANNAN.

Blood-sugar. II. Alimentary hyperglycæmia curves. H. K. BARRENSCHEEN and A. EISLER. **III. Blood-sugar and phosphoric acid curves. 1. Methods. IV. 2. Dextrose. V. 3. Lævulose and galactose. VI. 4. Diabetes.** H. K. BARRENSCHEEN, F. DOLESCHALL, and L. POPPER. **VII. 5. Insulin.** H. K. BARRENSCHEEN and R. BERGER (Biochem. Z., 1926, **177**, 27—38, 39—49, 50—66, 67—75, 76—80, 81—88).—II. In alimentary hyperglycæmia the time taken to reach the maximum value is a constant for the individual and is independent of the amount of sugar given, on which latter, however, the extent and duration of the hyperglycæmia depend. Two types of blood-sugar curve are described. The assimilation type is characterised by a rapid rise and fall, followed by marked hypoglycæmia. The resorption type is flat and protracted, and is not followed by noteworthy hypoglycæmia. The former type of curve is explained as being due to a stimulus from the added sugar leading to an output of the subject's own sugar.

III. The average values for blood phosphorus in twenty normal cases were found to be inorganic 3·91 and total acid-soluble organic 28·3 mg.%, but no constancy was observed from time to time in any one case. Whole-blood phosphorus is generally lower than that of plasma or serum, the last-mentioned being usually highest of all three. Acid-soluble organic phosphorus is practically exclusively confined to the corpuscles, whilst 62·6% of the inorganic phosphorus is found in the plasma. During deproteinisation by the Schenck or trichloroacetic acid method some organic phosphorus is hydrolysed.

IV. Oral administration of dextrose is followed by an increase in the blood phosphorus during the first 15 min. A fall in blood phosphorus follows, the lowest value being reached long after the maximum degree of hyperglycæmia. The total acid-soluble organic phosphorus rises towards the end of the experiment, its highest point usually coinciding with the lowest point in the blood-sugar curve. The phosphorus curves show a behaviour parallel to that of the assimilation and resorption sugar curves. The urinary phosphorus excretion is diminished after administration of dextrose. Arterial and venous blood give similar results during rising hyperglycæmia, but the sugar of venous blood falls sooner and more extensively than that of arterial blood. Venous blood does not show an increase of inorganic phosphorus during hyperglycæmia, but the venous acid-soluble organic phosphorus is greater than that of arterial blood. Intravenous administration of dextrose produces a fall in inorganic blood phosphorus and in total acid-soluble organic phosphorus. The curves are similar to those of the resorption type. Urinary phosphorus excretion also falls. An intravenous injection of dextrose preceding oral administration produces blood-sugar and phosphorus curves of the resorption type.

V. After administration of lævulose the blood-sugar level remains below that reached under an equivalent amount of dextrose. Inorganic phosphorus shows a fall of considerable extent and duration, and the urinary phosphorus excretion also diminishes. It is concluded that lævulose is rapidly assimilated. Galactose produces a hyperglycæmia which is not associated with any marked influence on the inorganic phosphorus nor with any alteration in the urinary phosphorus excretion. Galactose is therefore assimilated but slowly.

VI. After the administration of dextrose to diabetics, the inorganic blood phosphorus shows a slight but prolonged fall, whilst the urinary phosphorus is increased.

VII. Insulin has no marked effect on the inorganic phosphorus of the blood. The inorganic phosphorus in alimentary hyperglycæmia following an insulin injection shows variations from that following

dextrose alone. The acid-soluble organic phosphorus maintains a practically constant level. J. PRYDE.

Blood chemistry in eclampsia. H. J. STANDER and A. H. RADELET (Bull. Johns Hopkins Hosp., 1926, **38**, 423—430).—In the blood of eclampsia patients there is high uric acid, marked increase in lactic acid, decrease in carbon dioxide-combining power, and a definite tendency toward hyperglycæmia. There is usually no increase in non-protein nitrogen, but there is a slight but definite decrease in blood urea-nitrogen. CHEMICAL ABSTRACTS.

Serum-albumin, -globulin, and fibrinogen contents of the blood plasma in acute and chronic nephropathies. G. FAHR and W. W. SWANSON (Arch. Int. Med., 1926, **38**, 510—526).—During glomerulonephritis, decrease of the albumin content of the blood takes place, whilst the globulin content remains constant or increases slightly. W. O. KERMACK.

Urea retention: its determination by the mercury-combining power of blood. P. S. HENCH and M. ALDRICH (Arch. Int. Med., 1926, **38**, 474—488).—Blood deproteinised by trichloroacetic acid is titrated with 5% mercuric chloride solution until a drop of the mixture just gives a dark reddish-brown precipitate when added to sodium carbonate solution. The number of c.c. of 5% mercuric chloride which are equivalent to 100 c.c. of blood is defined as the mercury-combining power of the blood, and from this value the approximate urea concentration may be calculated by means of a formula. W. O. KERMACK.

Fat and glycogen in tissues in experimentally induced obesity in the rat. G. L. FOSTER and C. D. BENNINGHOVEN (J. Biol. Chem., 1926, **70**, 285—287).—Following injury to the brain in the region of the hypophysis, there is observed in rats a great increase in the percentage of fat in the body, and, in most cases, an increase in the glycogen of the liver; the composition of the body fat is not significantly changed from the normal. C. R. HARINGTON.

Formation of organic acids and retention of chlorides in lobar pneumonia. C. HOLTEN (Arch. Int. Med., 1926, **38**, 489—501).—During the febrile period of lobar pneumonia, there is retention of chlorides and an increase in the organic acids excreted in the urine. At the crisis, the chlorides are liberated and there occurs a decrease in the rate of excretion of the acids. W. O. KERMACK.

Combining power of proteins with rose-Bengal. S. M. ROSENTHAL (J. Pharm. Exp. Ther., 1926, **29**, 521—532).—When a solution of rose-Bengal is added to a dilute protein solution, adsorption of the dye on the protein appears to take place, with the result that when the mixture is acidified with mineral acid so that the p_H value is less than 2·2, at which point a solution of rose-Bengal normally becomes colourless, a certain amount of pink colour is retained, depending on the proportion of dye adsorbed. Use is made of this very sensitive reaction for quantitative experiments on the adsorption of the dye by proteins, and it is found that the adsorption decreases on heating, the exact behaviour depending on the particular protein present in solution. Evidence is adduced that the protein particles in solutions of gelatin of concentration greater than 0·001% undergo aggregation rapidly with increasing concentration. W. O. KERMACK.

Combining power of proteins with rose-Bengal. II. Application as a quantitative test to the cerebrospinal fluid. S. M. ROSENTHAL and F. D. ACKMAN (Arch. Int. Med., 1926, **38**, 527—535).—Application to the cerebrospinal fluid of the property of rose-Bengal to combine with proteins (cf. preceding abstract) shows in general an increased protein content in cases of meningitis, neurosyphilis, and certain other conditions. W. O. KERMACK.

Physiology of the liver. I. Effect of legation of the hepatic artery on carbohydrate metabolism. W. S. COLLENS, D. H. SHELLING, and C. S. BYRON (Amer. J. Physiol., 1926, **78**, 349—357).—Death from hypoglycæmic convulsions follows in a period varying from 15 to 50 hrs. according to the initial reserves of glycogen in the body of the animal. At death, glycogen has completely disappeared. Administration of dextrose prevents convulsions and prolongs life. R. K. CANNAN.

Fate of sugar in the animal body. II. Relation between sugar oxidation and glycogen formation, in normal rats and rats treated with insulin, during absorption of dextrose. III. Rate of glycogen formation in liver during absorption of dextrose, lævulose, and galactose. C. F. CORI and G. T. CORI (J. Biol. Chem., 1926, **70**, 557—576, 577—585).—II. During the absorption of approximately the same amounts of dextrose over the same period of time, the proportion of the sugar oxidised is less than that converted into glycogen in normal rats; the converse is true in rats which have been treated with insulin. The difference between the two groups is accounted for by the failure of the insulin-treated animals to deposit glycogen in the liver; this failure is regarded as being due to the increased rate of oxidation of dextrose in the muscles.

III. The deposition of glycogen in the liver of rats, following ingestion of sugar, ceases after 4 hrs.; the liver-glycogen formation is as great after administration of lævulose as of dextrose, but is very much less after galactose; in the case of any sugar, it can be almost completely suppressed by simultaneous administration of large doses of insulin. C. R. HARINGTON.

Pentose metabolism. I. Fate of xylose administered intravenously to the rabbit. R. C. CORLEY (J. Biol. Chem., 1926, **70**, 521—533).—After intravenous injection of xylose into rabbits, the substance disappears from the blood in 4 hrs. in the normal animal and after chloroform poisoning, in 2 hrs. in the phloridzinised animal, and in 8 hrs. in the nephritic animal; the pentose is for the most part eliminated in the urine, but, since the urinary excretion continues for some time after it has disappeared from the blood, it must be partly temporarily stored in the body. Insulin was without effect on the metabolism of xylose. C. R. HARINGTON.

Origin of glycuronic acid in the organism. A. J. QUICK (J. Biol. Chem., 1926, **70**, 397—404; cf.

this vol., 1169).—So long as the supply of carbohydrate in the food is sufficient, excretion of glycuronic acid in the dog, following administration of borneol or of benzoic acid, is not accompanied by a rise in the nitrogenous excretion; such a rise is, however, observed in dogs of which the glycogen stores have been depleted by starvation, even though dextrose be administered together with the benzoic acid. It is therefore concluded that glycuronic acid is most easily formed from glycogen; in the absence of this it is derived from protein more readily than from dextrose. C. R. HARINGTON.

Sugar from methylglyoxal in normal animals. B. SJOLLEMA and L. SEEKLES (Biochem. Z., 1926, **176**, 431—440).—The hyperglycæmia and glycosuria following administration of methylglyoxal to rabbits subcutaneously, intravenously, or *per os* is not due to the direct conversion of the compound into dextrose. The lethal doses for the rabbit are: intravenous 0·3 g., oral 1·5 g. per kg. body-weight.

C. RIMINGTON.

Dihydroxyacetone metabolism. W. R. CAMPBELL, A. A. FLETCHER, J. HEPBURN, and J. MARKOWITZ (J. Pharm. Exp. Ther., 1926, **27**, Proc. 258—259).—Dihydroxyacetone in the presence of dextrose may be determined by reducing molybdenum compounds in phosphoric acid and then reoxidising with permanganate; the sensitivity is 1 in 5×10^5. Dihydroxyacetone is present in normal blood. Intravenous injection is followed by a rise in blood-sugar. Fed to the starved, depancreatised dog, it is quantitatively excreted in the urine as dextrose. In normal human subjects, the administration of equal quantities of dihydroxyacetone and dextrose produces identical results on the phosphate curve.

CHEMICAL ABSTRACTS.

Relation of creatine to protein and carbohydrate metabolism. F. LIEBEN and D. LÁSZLO (Biochem. Z., 1926, **176**, 403—430).—In dogs fed on a creatine-free diet the excretion of creatine substances runs parallel to that of total nitrogen and is uninfluenced by alimentary glycosuria. Following phloridzin injection, the creatinine excretion rises parallel with that of total nitrogen, but bears no relation to the excretion of sugar. Injection of possible creatine precursors such as arginine and methylguanidine during phloridzin glycosuria causes no alteration in the level of creatinine excretion. Administration of the antipyretic, tetrahydro-β-naphthylamine, causes muscular tremor and a large increase in excretion of creatinine substances.

The excretion coefficient of creatine is about 80%, and assuming that the endogenously produced substance is excreted in the same manner, calculation shows that the daily excretion can be more than accounted for in starvation or nitrogenous equilibrium by the arginine metabolised. Feeding gelatin (as a source of arginine) and blood-sausage (as a source of histidine) led to no conclusive evidence that these amino-acids were related to creatinine excretion.

C. RIMINGTON.

Physiology of the liver. XV. Effect of removal of the liver on deamination. J. L. BOLLMAN, F. C. MANN, and T. B. MAGATH (Amer. J. Physiol., 1926, **78**, 259—269).—In a number of dogs surviving complete removal of the liver from 8 to 30 hrs., the recovery of amino-acids from the blood, urine, and tissues was approximately equal to the anticipated formation of urea had the animal been normal. Injected amino-acids were completely recovered from blood, urine, or tissues several hours after injection. No urea is formed in the absence of the liver and no ammonia or dextrose is formed from amino-acids after hepatectomy. The deamination of amino-acids is, therefore, completely dependent on the presence of the liver. R. K. CANNAN.

Relative nutritional value of synthetic fats. J. OZAKI (Biochem. Z., 1926, **177**, 156—167).—There is no regular relationship between the nutritional value of fats and the number of carbon atoms in their fatty acids. In general, fats of uneven fatty acids are of less value than natural fats. Of the former, heptyrin is best, whilst propionin, *iso*-valerin, and undecenoin are toxic. Undecoin, obtained by catalytic hydrogenation of undecenoin, is not only not toxic, but promotes growth. Stearin and margarin are utilised but slowly, but are not directly harmful. There is no ground for substituting margarin for natural fats in a diabetic diet. The nutritional value of fats of hydroxylated fatty acids depends rather on the position of the hydroxyl groups than on their number. Fats of α-hydroxy-acids are of less value than the corresponding saturated fats—this observation is used as an argument against α-oxidation. Tho fats of the higher α-hydroxy-acids are better utilised than those of the lower members. Acetylation increases the nutritional value of ricinolein, but not of dihydroxyundecolin, dihydroxystearin, or trihydroxystearin. Ricinolein is better utilised than the isomeric ricino-elaidin. J. PRYDE.

Destruction of a hydantoin nucleus (β-methylhydantoin) in the animal body. O. H. GAEBLER (J. Pharm. Exp. Ther., 1926, **27**, Proc. 242).—When 1·5—4 g. of β-methylhydantoin is administered to a dog subcutaneously, only 15% is excreted unchanged; an equal amount appeared as methylhydantoic acid. Urea excretion rises sufficiently to account for 20% of the compound given. The oxalic acid output is increased 50 times. β-Methylhydantoin gives a strong positive reaction with Rothera's nitroprusside test for acetone substances; methylhydantoic acid gives a negative test. CHEMICAL ABSTRACTS.

Detoxication of nitriles. M. ADELINE, L. R. CERECEDO, and C. P. SHERWIN (J. Biol. Chem., 1926, **70**, 461—469).—After feeding to dogs and rabbits of a variety of substituted benzonitriles no metabolic end-products could be found in the urine; certain phenylacetonitriles gave rise to the corresponding benzoic acids, which were excreted in the free condition; in these cases also the ethereal sulphates and the thiocyanates of the urine were generally increased, and there was sometimes observed a positive Millon's reaction. C. R. HARINGTON.

Reciprocal effect of sodium, potassium, and calcium ions on the weight of animals on an artificial diet. L. REDINA (Biochem. Z., 1926, **177**, 253—265).—When potassium chloride is added to a diet containing sodium chloride and *vice versa*,

until the ratio Na : K equals 1 : 0·2, the condition of the animal improves and loss in weight is inhibited. Considerable loss in weight occurs, however, when the ratio equals 1 : 0·05, 1 : 0·5, 1 : 1, or 0·05 : 1. This result depends, not on the absolute amounts of potassium and sodium ions, but on their proportion. In similar experiments with mixtures of calcium and potassium chlorides, of calcium and sodium chlorides, and of calcium, sodium, and potassium chlorides, no antagonistic action could be detected, the decrease in weight running parallel with the increase of calcium just as when calcium chloride alone was added to the diet. P. W. CLUTTERBUCK.

Potassium in animal nutrition. IV. Potassium requirements for normal growth and maintenance. V. Influence of potassium on excretion of sodium, chlorine, calcium, and phosphorus. H. G. MILLER (J. Biol. Chem., 1926, **70**, 587—591, 593—598).—IV. Failure of growth and death within 8 weeks is observed in growing rats on a diet containing less than 1 mg. of potassium *per diem*. The minimum daily requirement of potassium for normal growth is 15 mg. for males and 8 mg. for females; 2 mg. *per diem* suffices for maintenance in the adult animal.

V. Administration of potassium salts to rats leads to an increase in the urinary excretion of potassium, sodium, and chlorine, but to no marked change in that of calcium and phosphorus; the fæcal excretion of these elements was in no case affected.

C. R. HARINGTON.

Nutritive value of inorganic substances. I. Normal zinc metabolism with particular reference to the calcium metabolism. L. T. FAIRHALL (J. Biol. Chem., 1926, **70**, 495—512).—On a normal diet, the zinc balance of rats is slightly positive; on administration of sodium hydrogen carbonate the balance first becomes negative and then returns to normal; with feeding of ammonium chloride it becomes persistently negative; the calcium balance is affected only by the acidosis following the ammonium chloride; the total zinc content of adult rats is 7—8 mg. and the rate of storage of zinc, as of calcium, is most rapid in the early period of growth.

C. R. HARINGTON.

Blood pressure, blood-cholesterol, and diuresis after administration of bile-acids. D. ADLERSBERG and M. TAUBENHAUS (Biochem. Z., 1926, **177**, 400—405).—Administration of bile-acid (dehydrocholic acid) to men had no effect in one-third of the cases on blood pressure, but in the remainder caused a decrease of 12—30 mm., with subsequent return to normal in 1 hr. The blood cholesterol, initially normal, in 3 of 7 cases decreased 25—30% and in 4 cases increased 7—12%. In 4 cases with initial high blood-cholesterol, a decrease of 11—30% occurred, and in one case with low initial blood-cholesterol, it remained unchanged. Diuresis was produced in 8 out of 13 cases. P. W. CLUTTERBUCK.

Effect of hydrogen-ion and salt concentration on survival of spermatozoa of *Rana fusca*. H. BARTHÉLEMY (Compt. rend., 1926, **183**, 675—677).—Spermatozoa of *Rana fusca* survive longer in tap-water than in distilled water. Addition of sodium hydroxide does not markedly increase the time of survival, but 0·15% of sodium chloride increases greatly the life of the spermatozoa in ordinary and in distilled water. L. F. HEWITT.

Cardiac reactions to drugs and the c_H of the blood. I. Caffeine. W. SALANT and J. E. NADLER (Amer. J. Physiol., 1926, **78**, 308—321).—When the p_H of the blood is below normal, caffeine depresses the heart. A rise of p_H up to 0·15 above the normal confers a stimulating action on the drug, but with more alkaline blood caffeine again becomes depressant. R. K. CANNAN.

Clinical pharmacology. II. Action of "salicyl" ("aspirin") and caffeine on the acid-base exchange of healthy individuals. W. H. VEIL and W. GRAUBNER (Arch. exp. Path. Pharm., 1926, **117**, 208—231).—The effect of "aspirin," caffeine, and a mixture of the two substances on the acid-base equilibrium in the blood and on the excretion of acid and base in the urine is described.

W. O. KERMACK.

Optical isomerides. VIII. Influence of configuration on the activity of tropeines. A. R. CUSHNY (J. Pharm. Exp. Ther., 1926, **29**, 5—16).—When the hydroxyl group in the acyl group of atropine is replaced by hydrogen, the resultant compound has only one-twohundredth of the action of atropine itself on the myoneural junction, but its action on the nerve ends in striated muscle and on the spinal cord of the frog is not affected to the same extent. W. O. KERMACK.

[Fate of injected] quinine. R. A. HATCHER and S. WEISS (J. Pharm. Exp. Ther., 1926, **29**, 279—296).—Quinine may be determined in blood or tissues by extracting it with chloroform and titrating the extract with bromine water. This method is applied to determine the fate of quinine after injection. Small quantities rapidly disappear from the blood-stream and appear to be adsorbed on the capillary walls. W. O. KERMACK.

Use of lead chloride for the purification of organic liquids in the toxicological investigation of alkaloids. J. MAGNIN (Anal. Asoc. Quím. Argentina, 1926, **14**, 170—176).—In the examination of liquids containing organic matter, in particular acid extracts of viscera, the proteins may be precipitated completely by addition of hot saturated lead chloride solution. After centrifuging, the alkaloids may be extracted from the clear solution with a suitable solvent, *e.g.*, ammoniacal benzene.

G. W. ROBINSON.

Phenyldialkylacetamides as hypnotics. A. LUMIÈRE and F. PERRIN (Compt. rend., 1926, **183**, 617—619).—Phenyldiethylacetamide, *α-phenyl-α-n-propyl-*n*-valeramide*, m. p. 95°, *α-phenyl-α-allyl-*n*-valeramide*, m. p. 55°, and *phenyldiallylacetamide*, m. p. 75°, prepared by hydrolysis of the corresponding nitriles, have pronounced hypnotic properties, but their toxicity and delay in action are prejudicial to therapeutic use. L. F. HEWITT.

Mechanism of chemotherapeutic action. J. A. MANDEL and H. STEUDEL (Z. physiol. Chem., 1926, **160**, 91—95).—"Germanin" (Baeyer 205) readily

combines with protamines (clupein) and histones (thymus), giving sparingly soluble precipitates. Its chemotherapeutic action may depend on a similar fixation by nuclear material. P. W. CLUTTERBUCK.

Chemotherapy of neurosyphilis and trypanosomiasis. A. S. LOEVENHART and W. K. S. THOMAS (J. Pharm. Exp. Ther., 1926, **29**, 69—82).—A discussion of the relation of the chemical constitution of 12 arsenical derivatives to their actions on experimental trypanosomiasis in rats and rabbits and also on neurosyphilis in man. W. O. KERMACK.

Cyanamide poisoning. I. Chemical point of attack of cyanamide. S. GLAUBACH (Arch. exp. Path. Pharm., 1926, **117**, 247—256).—The concentration of reduced glutathione in the muscles of a frog is decreased as the result of cyanamide poisoning. The concentration of sulphydryl groups as determined by iodine titration increases when normal frog muscle is incubated at 37°, but decreases when cyanamide is added or when the muscle is from a frog poisoned by cyanamide. Poisoned muscle is less able than normal muscle to reduce cystine to cysteine. W. O. KERMACK.

Has mercuric sulphide a toxic action? H. NIKLASSON and C. G. SANTESSON (J. Pharm. Exp. Ther., 1926, **29**, 117—134).—Subcutaneous or intramuscular injection of a sufficient quantity of mercuric sulphide gives rise to a marked local reaction, which may be accompanied by symptoms of general mercury poisoning. W. O. KERMACK.

Blood changes in acute mercuric chloride poisoning. J. M. LOONEY (J. Biol. Chem., 1926, **70**, 513—519).—During the course of a fatal case of mercuric chloride poisoning there was observed a progressive increase in the non-protein nitrogen of the blood; in the terminal stages the increase was particularly marked in the case of the residual nitrogen and of the creatine (which exceeded the creatinine); the increase in the amino-acids and uric acid was proportionately less. C. R. HARINGTON.

Fate of cadmium after parenteral administration. G. HESSEL (Biochem. Z., 1926, **177**, 146—155).—The absorption of insoluble basic cadmium salicylate ("cadmiol") is slow, but when introduced into the blood, cadmium disappears rapidly. Both after intramuscular and intravenous administration, cadmium is found in the liver and kidney, the former organ containing the largest absolute amount, the latter the largest relative amount. The excretion of cadmium is slow, 10—12 mg. given intravenously requiring 4 weeks for complete excretion. Elimination takes place through the kidney and the intestine, the metal appearing in the urine on the first day, in the fæces on the fourth or fifth day after administration. J. PRYDE.

Antagonistic action of magnesium and calcium salts and mode of action of some analgæsic drugs. A. D. HIRSCHFELDER and E. R. SERLES (J. Pharm. Exp. Ther., 1926, **29**, 441—448).—Magnesium salts and also the ordinary soporific drugs and analgæsics tend to produce water-in-oil emulsions, whilst calcium salts tend rather to produce oil-in-water emulsion. This is apparently related to the fact that calcium oleate is much less soluble in oil than is magnesium oleate. W. O. KERMACK.

Antagonistic biological action of metallic silver and tin. A. DRZEWINA and G. BOHN (Compt. rend., 1926, **183**, 571—572).—*Convoluta* rapidly undergo cytolysis when in contact with metallic silver, but tin has no effect on the organisms, and metallic silver in contact with tin has no effect. L. F. HEWITT.

Activation by light of effect of silver on *Convoluta*. A. DRZEWINA and G. BOHN (Compt. rend., 1926, **183**, 677—679; cf. preceding abstract).—Exposure to light enhances the effect of silver on *Convoluta* and assists activation of the inactivated metal. L. F. HEWITT.

Non-existence of some enzymes. A. J. KLUYVER (Z. physiol. Chem., 1926, **158**, 111—112; cf. Kluyver and Donker, A., 1925, i, 1215).—A claim for priority over Kostytschev (this vol., 756). C. HOLLINS.

Complement of amylase. V. Sugar-protein condensation. H. PRINGSHEIM and M. WINTER (Biochem. Z., 1926, **177**, 406—417).—Undigested egg-albumin does not stimulate the action of pancreatic amylase, but does so after digestion with pepsin. Digested serum-albumin, myosin, myogen, and yeast protein also activate, but digested gelatin, caseinogen, elastin, fibrin albumose, peptone from albumin, tyrosine, and trypsin-digested peptone from albumin do not. Pepsin-digested egg- and serum-albumin also activate malt amylase, whereas digested peptone from albumin does not. Maltose combines with peptone from albumin and with pepsin-digested caseinogen and myosin, but not with tyrosine (cf. this vol., 864). P. W. CLUTTERBUCK.

Physiology of digestion. XIII. Attempted reactivation of salivary amylase inactivated by acid. C. SCHWARZ and E. GEWISS (Fermentforsch., 1926, **9**, 57—63).—Salivary amylase inactivated by treatment with 0·2—0·025*M*-hydrochloric acid for varying periods regained no activity when the reaction was subsequently adjusted to the optimum p_H of the enzyme. It is concluded that the salivary amylase is destroyed in the stomach and is not reactivated in the intestine. R. K. CANNAN.

Compounds of enzymes with inactivating substances. II. K. MYRBÄCK (Z. physiol. Chem., 1926, **159**, 1—84).—The nature of the inactive or less active inactivator–enzyme complex is investigated, in the case of salivary-, pancreatic-, and malt-amylase. Salt-free amylase at its optimum p_H (6·0) possesses about 40% of the activity of chloride–amylase at its optimum p_H (6·7). Acetate ions do not combine with salivary amylase, but influence the reaction only through alteration in p_H. Phosphate and sulphate similarly do not unite with amylase. Nitrate–amylase has its optimum at p_H 6·9—7·0, the maximal activity being about the same as that of chloride-free amylase. Chlorate–amylase has approximately the same activity as nitrate–amylase. Bromide–, iodide–, fluoride–, and cyanide–amylases are also examined. The different activities of

amylase and its salt compounds do not depend on different affinities for the substrate nor on different reaction velocities. The different maximal activities, together with the different p_H optima, may be explained in terms of a change of the dissociation constant of the enzyme, regarded as an amphoteric substance, on addition of the various substances. This conclusion is strongly supported by a large number of inactivation experiments. Picric and phosphotungstic acids and tannin inactivate amylase, due to their combination with a basic group of the enzyme and metals (copper, mercury, cadmium, nickel, lead, cobalt, manganese), inactivate by combining with the enzyme-acid or enzyme-substrate-acid. The investigation brings further evidence in favour of the supposed identity of pancreatic- and salivary-amylase (cf. A., 1924, i, 593, 594).

P. W. CLUTTERBUCK.

Production of oxydases. O. FERNÁNDEZ and T. GARMENDIA (Anal. Fís. Quím., 1926, **24**, 495—507).—An account of experiments on the growth of *Bacillus coli* in media composed of different carbohydrates together with glutamic acid, cystine, taurine, or sodium taurocholate, under aërobic and anaërobic conditions. The results demonstrate an antagonism between peroxydases and catalases and also an increased production of peroxydases under anaërobic conditions.

G. W. ROBINSON.

Bactericidal power of enzymes. E. GLASER and F. PRINZ (Fermentforsch., 1926, **9**, 64—73).—Some bactericidal action was shown by preparations of plant oxydases from various sources, by preparations of emulsin, amylase, and trypsin and an extract of leucocytes and endocrine organs, all of which gave some of the reactions of oxydase systems.

R. K. CANNAN.

Peroxydase. III. Kinetics. H. UCKO and H. W. BANSI (Z. physiol. Chem., 1926, **159**, 235—257).—The maximum observed rate of oxidation of pyrogallol is at p_H 7·0. The oxidation cannot be studied in more alkaline solutions because of oxygen absorption. The optimum p_H for the oxidation of guaiacol is between 5·0 and 5·2 and of cresol between 3·5 and 5·0. The kind of buffer used is not of importance.

H. I. COOMBS.

Peroxydase. V. Determination of peroxydase. VI. Inhibition of peroxydase by hydrogen peroxide. R. WILLSTÄTTER and H. WEBER (Annalen, 1926, **449**, 156—174, 175—187; cf. A., 1923, i, 1243).—V. Whereas the pyrogallol method of determination (*ibid.*, 1918, i, 555) involves a complicated reaction, the new method involves the action of only one atom of oxygen, and no intermediate products are formed. The method consists of the oxidation of the leuco-base to malachite-green in dilute acetic acid–sodium acetate solution by the action of hydrogen peroxide under the influence of peroxydase (cf. von Czyhlarz and von Fürth, Hofmeister's Beiträge, 1907, **10**, 358). Under optimum conditions, the system is so adjusted that the same amount of leuco-base is oxidised in each successive interval of time, until nearly all the hydrogen peroxide is used up. The amount of malachite-green formed in 5 min. indicates the activity of the peroxydase solution, and is determined colorimetrically. High concentrations of the reagents inhibit the reaction, the optimum concentrations being: acetic acid 0·05*N*, sodium acetate *N*/300, and hydrogen peroxide 0·25 mg./100 c.c. The results obtained show a deviation of less than 1% from the mean except in the case of very dilute solutions, when the deviation is 1·5%.

The activity of a solution of peroxydase fluctuates irregularly, corresponding values being obtained by both the pyrogallol and leuco-base methods. Neither temperature nor light has any influence on the degree of fluctuation, but crude samples of peroxydase show less fluctuation than purified specimens. It is thought that this inconstant activity is a characteristic of peroxydase and is not due to external influences.

VI. Excess of hydrogen peroxide decreases the activity of the enzyme and ultimately prevents all action. Thus, for the same quantity of peroxydase (beet juice), when the concentration of hydrogen peroxide is 0·25 mg./100 c.c., the amount of malachite-green formed in 5 min. is 340 mg., whilst with hydrogen peroxide 100 mg./100 c.c. the amount of dye formed in 5 min. is only 17 mg. Preliminary treatment of the peroxydase with varying quantities of hydrogen peroxide before adding the leuco-base reduced the yield of dye to about 50% of that normally obtained at the concentration of peroxide used, but did not materially affect the time required for the reaction to come to a standstill. The reduction of the hydrogen peroxide content of such an inhibited system by the addition of catalase causes the oxidation to continue in a normal manner.

To explain these phenomena, it is suggested that the peroxydase reacts with the hydrogen peroxide, forming two additive compounds corresponding with the formulæ HO·OH and $H_2O{:}O$ for hydrogen peroxide. One of these compounds (A) is active, whilst the other (B) is relatively inactive and requires a higher concentration of pyrogallol for its decomposition. When either A or B gives up its active oxygen, a hydrate of peroxydase is possibly obtained, which again reacts with hydrogen peroxide, yielding active (D) and inactive (C) compounds. C requires a still higher concentration of pyrogallol than B for its decomposition.

Addition of peroxydase to solutions of hydrogen peroxide has a stabilising effect, which is not due to enzyme action, as peroxydase solutions rendered inactive by heat have a similar effect.

R. W. WEST.

Stability of pepsin solutions. Sterile enzyme preparations. P. ROSTOCK (Fermentforsch., 1926, **9**, 84—88).—Pepsin solutions may be preserved for long periods without loss of activity and in a sterile condition by treatment with "iodonascin" (an iodine preparation).

R. K. CANNAN.

Proteases of urine. I. Effect of diet on the pepsinogen of normal urine and the anti-pepsin of the serum. O. PECZENIK and M. KAWAHARA (Fermentforsch., 1926, **9**, 97—116).—The pepsinogen of the urine varies with the species. The output is stimulated during digestion. The anti-pepsin of serum is thermolabile, non-dialysable, and may be

extracted with ether. Its amount in the serum is related to the diet and state of digestion.

R. K. CANNAN.

Preparation of trypsin. J. A. SMORODINZEV and A. N. ADOVA (Fermentforsch., 1926, **9**, 1—8).—Comparison is made of Fränkel's modifications (Abderhalden's "Biol. Arbeitsmeth.," IV, **1**, 10, 1922) of the methods of von Wittich and Danilewsky for the separation of trypsin from the pancreas. By filtration through paper of the glycerol extract of the gland, followed by precipitation with 4 vols. of alcohol, a product completely soluble in dilute sodium carbonate is obtained which is 20 times as active as that yielded by the method of Danilewsky. Trypsin is not adsorbed by magnesium oxide, but a precipitate of calcium phosphate induced in the trypsin solution removes about half of the enzyme.

R. K. CANNAN.

Nephelometric investigation of enzymic proteolysis. VI. Kinetics of tryptic hydrolysis. H. KLEINMANN (Biochem. Z., 1926, **177**, 89—106).—An investigation of the influence of (1) duration of hydrolysis, (2) variations in the concentration of enzyme alone, of substrate alone, and of both together, (3) acid and tryptic hydrolysis products, boiled and unboiled, (4) temperature, on the course of tryptic hydrolysis of caseinogen.

J. PRYDE.

Anti-enzymes. Anti-trypsin. I. F. STANDENATH (Fermentforsch., 1926, **9**, 9—17).—The juice of ox muscle contains enzymes which actively hydrolyse glycyltryptophan and silk peptone. Their action is not inhibited by strongly anti-tryptic sera and no anti-enzyme is produced when the juice is injected into rabbits.

R. K. CANNAN.

Tissue and serum proteases (peptidases). II. F. STANDENATH (Fermentforsch., 1926, **9**, 18—40; cf. preceding abstract).—Comparison is made of the proteolytic activity on gelatin of extracts of various tissues of the guinea-pig. In these extracts there is present an enzyme which clots solutions of caseinogen in the presence of calcium. The optimum of this enzyme is between p_H 5 and 6. These enzymes are strongly inhibited by guinea-pig serum. Tissue extracts and sera from a variety of animals were able to hydrolyse glycyltryptophan, silk peptone, and Witte peptone. There are recorded observations on the thermolability, relation of activity to p_H, and degree of adsorption of these enzymes by charcoal, kaolin, and colloidal ferric hydroxide. The peptidases of tissues and of serum showed some differences in these respects. Moreover, the enzyme responsible for the hydrolysis of silk peptone is, by the same argument, to be distinguished from that which acts on glycyltryptophan.

R. K. CANNAN.

Specificity of tyrosinase. E. ABDERHALDEN and A. B. GUTMANN (Fermentforsch., 1926, **9**, 117).—Tyrosinase led to no production of colour with *o*- or *m*-hydroxyphenyl-α-aminopropionic acid.

R. K. CANNAN.

Synthesis of urea from ammonium hydrogen carbonate solution by animal charcoal, tissue pulp, or blood. E. ABDERHALDEN and S. BUADZE (Fermentforsch., 1926, **9**, 89—96).—The formation of urea from ammonium hydrogen carbonate under the influence of animal charcoal is confirmed (A., 1925, i, 796). It is shown that liver-tissue, and to a less extent muscle, kidney, and milk, have the same power. Blood was almost inactive. Neither cyanide nor iron had any effect on the reaction.

R. K. CANNAN.

Hylergography. Effect of neutral salts on cells. F. BOAS (Biochem. Z., 1926, **176**, 349—402).—Anions stimulate yeast fermentation as follows: $SCN' < Cl' < NO_3' < SO_4''$. Light has no influence on this order, but greatly enhances the activity of the cells, permeability also increasing. When permeability exceeds an optimum value, the cell activity decreases and anions then have an inhibiting effect. Fermenting cells are more sensitive to salt than to hydrogen-ion concentration.

Salt solutions also exhibit a stimulating effect on the tyrosinase of the potato in the following manner: $SCN' < Cl' < NO_3' < SO_4''$, that is, in the order of increasing hydration. Bile salts also stimulate the tyrosinase reaction even in a concentration of 1 : 16,000, the cell permeability being increased, but digitonin and sapotoxin are without effect.

The efficacy of anions in inhibiting growth of the bacteria *Bacillus prodigiosum* and *Azotobacter chroococcum* follows the order $SCN' > Cl' > SO_4'' > Br'$. In the case of fungi, inhibition of growth occurs in the following order: $Br' > SO_4'' > Cl' > NO_3' > SCN'$.

C. RIMINGTON.

Fermentation and growth in dry yeast-cells. I. H. VON EULER and C. BARTHEL (Z. physiol. Chem., 1926, **159**, 85—92).—Dried bottom yeast-*H* after treatment with alcohol ferments sugar solution at the ordinary temperature under strictly sterile conditions, the velocity becoming constant after about 10—30 min. The number of living cells is not more than 1/20,000 of the number originally present.

P. W. CLUTTERBUCK.

Oxido-reductase of yeast. A. LEBEDEV (Fermentforsch., 1926, **9**, 74—83).—The reducing power of yeast maceration extract is attributed chiefly to a reductase acting on aldehydic substances. The filtrate from boiled fresh maceration extract has no reducing power, whereas that from autolysed maceration extract has. The latter is attributed to glutathione or allied substances liberated by autolysis, although the enhanced reducing power of autolysed extract is also due probably to an oxido-reductase acting on purines which have been liberated by autolysis. The filtrate from fresh extract which had been warmed to 60° retained some reducing power, although there was a separation of coagulated protein. This filtrate was unable to ferment sugar or glyceric acid, but fermented pyruvic acid more actively than did the unheated extract. The relation of these results to the several enzymes involved in the author's scheme for alcoholic fermentation is discussed.

R. K. CANNAN.

Growth-stimulating action of yeast extract for *Saccharomyces saké*. R. TAKADA (J. Soc. Chem. Ind. Japan, 1926, **29**, 358—363).—*Saccharomyces saké* can grow with an extremely minute quantity of "bios," although the growth is very slow and the

yeast cells are small in size.[3] The growth-promoting action of yeast extract is almost proportional to the amount of the extract added, if the duration of culture be short, but in the course of time its effect is gradually lessened. On keeping for a longer time, a culture with no yeast extract contains more cells than one to which yeast extract has been added.

K. KASHIMA.

Action of carbon monoxide on the metabolism of yeast. O. WARBURG (Biochem. Z., 1926, **177**, 471—486).—The respiratory enzyme of yeast combines with carbon monoxide, and when shaken with a mixture of oxygen and carbon monoxide, is distributed between the two. Carbon monoxide, therefore, inhibits respiration, the more strongly the lower the oxygen pressure. The compound of enzyme and carbon monoxide dissociates on exposure to light, and is a pigment which absorbs wave-lengths 436 (most strongly), 546, and 578 μμ. P. W. CLUTTERBUCK.

Action of certain fat solvents on alcoholic fermentation. N. G. KERR and W. J. YOUNG (Austral. J. Exp. Biol., 1926, **3**, 177—185).—Benzene, xylene, ethyl ether, and ethyl butyrate, like toluene, markedly reduce the rate of fermentation of dextrose by yeast. Light petroleum has a less marked effect, whilst chloroform, ethyl and amyl acetates, and butyl alcohol completely inhibit fermentation. After treatment with benzene, xylene, ether, or ethyl butyrate, but not with light petroleum, yeast reacted to phosphate, forming hexosephosphate. Ether and light petroleum, like toluene, increased the rate of autofermentation. When treated with ether or toluene, yeast-cells became more permeable to free and combined phosphates which can be removed by water. After washing yeast with ether, the co-enzyme of alcoholic fermentation could be removed from the cells by washing with water, the cells simultaneously losing their fermentative activity towards dextrose; re-addition of the washings to the cells restores that activity. A method of preparing the mono- and di-hexosephosphates is described. It is suggested that yeast-cells after treatment with light petroleum, toluene, and ether represent three degrees of internal disorganisation of the cells, the change being least pronounced with the first, most pronounced with the last. W. ROBSON.

Action of ether on the yeast-cell. I. Carboxylase. N. G. KERR and W. J. YOUNG (Austral. J. Exp. Biol., 1926, **3**, 187—188; cf. preceding extract).—Yeast treated with ether, and the co-enzyme afterwards removed with water, behaved similarly to washed zymin. W. ROBSON.

Porphyratin of yeast. II. O. SCHUMM (Z. physiol. Chem., 1926, **158**, 77—79; cf. this vol., 758).—Larger quantities of the porphyrin of yeast porphyratin were prepared, and its properties confirmed. The methyl ester, m. p. 219°, identical with that of hæmateric acid, gives by treatment with alkali a modified porphyrin with changed solubility and spectrum, as is the case with hæmateric acid. The identity of two porphyrins of animal and vegetable origin, respectively, is thus established.

C. HOLLINS.

Porphyratin of yeast. III. O. SCHUMM (Z. physiol. Chem., 1926, **159**, 192—193).—Crude porphyratin is obtained by macerating pressed yeast with 3—5 times the amount of acetic acid, extracting twice with 1—1½ times the volume of light petroleum, and then treating the residue with chloroform, the chloroform layer being finally washed with water. The substance gives a pure hæmatin spectrum, and, on addition of a drop of hydrazine hydrate, readily passes into the porphyrin. It is confirmed that the porphyrin obtained by removal of iron from yeast porphyratin gives all the characteristic spectroscopic reactions of hæmateric acid (α-hæmatoporphyroidin). (See this vol., 758, 1269.) P. W. CLUTTERBUCK.

Intermediate formation of methylglyoxal in degradation of dextrose by micro-organisms. E. AUBEL (Compt. rend., 1926, **183**, 572—574).—The intermediate formation of methylglyoxal in the transformation of dextrose into lactic acid by *Bacillus coli* and certain yeasts is considered theoretically. L. F. HEWITT.

Uric acid metabolism. Production of uric acid by bacteria. J. F. MCDONALD, V. E. LEVINE, and M. GLEASON (Amer. J. Physiol., 1926, **78**, 437—448).—*Bacillus fæcalis alkaligenes*, *B. enteritidis*, *B. paratyphosus-B*, a strain of *Staphylococcus pyogenes albus*, and a mixed culture from the mouth showed evidence of production of uric acid in purine-free media. *B. coli*, *B. pyocyaneus*, *B. proteus*, *B. bulgaricus*, and some strains of *S. pyogenes* produced no uric acid. Difficulties in the determination of uric acid are discussed. If uric acid is produced by the intestinal flora and is absorbed, then a new exogenous source of uric acid is indicated. R. K. CANNAN.

Calcium carbonate in a group of sulphur bacteria. E. BERSA (Ber. deut. bot. Ges., 1926, **44**, 474—478).—The calcium compounds of *Achromatium* consist of calcium carbonate, and not of calcium thiosulphate, as claimed by Hannavart.

R. K. CANNAN.

Chemistry of bacteria. XII. Albumin-globulin fraction of tubercle bacillus. XIII. Alkali-soluble protein of tubercle bacillus. R. D. COGHILL (J. Biol. Chem., 1926, **70**, 439—447, 449—455).—XII. Human tubercle bacilli were dried and de-fatted at low temperatures, and the resulting material was extracted with water; the aqueous extract, on acidification with acetic acid, yielded a protein characterised by a high content of basic amino-acids; figures for the nitrogen distribution, according to the method of Van Slyke, are given. Extraction of the bacteria with 5% sodium chloride removed 36% of the total nitrogen, the greater part being dialysable; the non-dialysable residue consisted of water-soluble protein, no globulin being detected; the protein preparations gave the Molisch reaction, but did not reduce Benedict's solution even after hydrolysis.

XIII. Extraction of the residue left after removal of the water-soluble protein, with 0·5% sodium hydroxide, yielded a larger amount of an alkali-soluble protein, analytical figures for which are given; this protein again gave the Molisch reaction, but no reactions for reducing sugars before or after

hydrolysis; it was devoid of biological activity, in contrast to the water-soluble protein described above, which showed a strong tuberculin action.

C. R. HARINGTON.

Action of typhoid bacillus on milk. C. GORINI (Compt. rend., 1920, **183**, 681—682).—*Bacillus typhosus*, when cultured on milk, during the first 30—40 days peptonises the caseinogen and renders the milk clear and alkaline, and then during the next 30—40 days a clot is formed and the milk becomes acid in reaction. L. F. HEWITT.

Enzymes of the "Anka" and of *Monascus purpureus*. S. HAGIWARA and N. AOYAMA (Rep. Dep. Ind. Govt. Res. Inst. Formosa, 1924, **5**, 43).—Amylase, emulsin, peroxydase, and rennin (possibly also trypsin and protease) were present in the "Anka" of Formosa and China, grown at 37—38°. Amylase, maltase, emulsin, peroxydase, and rennin were found in a sample grown at 38—39°.

CHEMICAL ABSTRACTS.

Effect of molecular complexity on end-products of fermentation by *Clostridium thermocellum*. W. H. PETERSON, E. B. FRED, and E. A. MARTEN (J. Biol. Chem., 1926, **70**, 309—317).—Fermentation of the monosaccharides, except galactose, leads to the conversion of the greater part of the sugar into volatile acid, *d*-lactic acid, and alcohol; the formation of lactic acid is most marked in the case of lævulose, where it represents 75% of the sugar. The fermentation of galactose, lactose, and still more that of raffinose and of starch, approximates more closely to that previously observed (this vol., 325) for cellulose, small amounts only of lactic acid being formed. Mannitol and salicin are fermented to a small extent, with production of a small amount of lactic acid; malic acid is not fermented at all.

C. R. HARINGTON.

Influence of hormones on the fat content of blood. A. FLEISCH (Biochem. Z., 1926, **177**, 461—470).—The daily and weekly variations of the fat content of blood (the total light petroleum extract, *i.e.*, fat and cholesterol) in rabbits usually lie between ±20%, but may be much greater in individual cases. Intravenous injection of 0·1—1 mg. of adrenaline produces for 24 hrs. a decrease of 17—30%. Larger quantities (3—6 mg.) injected subcutaneously cause the blood-fat to be increased to twice or four times its original value during the first and second days. Small doses of acetylcholine (0·2—6 mg.) produce for several days a decrease of blood-fat of about 20%. Larger doses (15 mg.) produce an increase of 1½—4 times the original amount during 24 hrs.

P. W. CLUTTERBUCK.

Specific nature of animal proteases. VII. Chemical nature of insulin. K. FELIX and E. WALDSCHMIDT-LEITZ (Ber., 1926, **59**, [*B*], 2367—2370).—The activity of insulin is smoothly and completely destroyed by pepsin and activated trypsin, but is not influenced by non-activated, kinase-free trypsin or by trypsin-free erepsin. If these observations are confirmed with homogeneous insulin, it appears that the latter substance is structurally related more closely to the complex than to the simple peptides. H. WREN.

Lability of sulphur in cystine derivatives and its possible bearing on the constitution of insulin. E. BRAND and M. SANDBERG (J. Biol. Chem., 1926, **70**, 381—395).—The lability towards alkali of the sulphur in dialanylcystine, dialanylcystine dianhydride, and of a sulphur-containing substance obtained from the mother-liquor in the preparation of the latter compound, is much greater than that of the sulphur in cystine itself; the lability of the sulphur in insulin (cf. Abel and Geiling, A., 1925, i, 1218) therefore does not necessarily indicate the absence of cystine from the insulin molecule. A modification of the colour reactions for carbonyl groups proposed by Abderhalden (*ibid.*, 1924, i, 1361) is described, by which positive reactions were obtained with diketopiperazines, with insulin, and, in general, with compounds containing a carbonyl group, but not with proteins or amino-acids except cystine. It is thought that the presence of sulphur compounds in insulin is sufficient to account for the colour reactions given by the latter substance. C. R. HARINGTON.

Activation of insulin. E. GLASER and G. HALPERN (Biochem. Z., 1926, **117**, 196—205).—Insulin is activated by the oxydase of eosinophile granular corpuscles, but not by the peroxydase of bone-marrow nor by the aldehydase of liver. The kinase of the small intestine has a marked activating action. Alteration of the p_H does not appear to be a factor in influencing the action of insulin. Of plant products, tyrosinase and horse-radish peroxydase are inactive, but yeast press-juice which has been boiled for 8 hrs. has a marked activating effect. These and similar activators are supposed to convert preformed inactive insulin into the active form and to have some importance in relation to the preparation of the internal secretion. J. PRYDE.

Insulin and the production of acetone substances by the perfused liver. H. S. RAPER and E. C. SMITH (J. Physiol., 1926, **62**, 17—32).—When the liver of the cat was perfused with its own blood, the amount of acetone substances formed varied directly as the fat and inversely as the glycogen content of the liver. When sodium butyrate was added to the blood, 80% of that destroyed was recovered as acetone substances. In neither case was acetone production affected by insulin, nor did the latter cause glycogenolysis or storage of glycogen —even when there was a considerable hyperglycæmia. The antiketogenic effect of carbohydrate in the intact animal is attributed to an increased carbohydrate metabolism, resulting in a reduction of the fat metabolism below the level at which the acetone substances produced fail to be completely oxidised by the animal. Fat mobilisation results from the depletion of the glycogen stores. R. K. CANNAN.

Glycogen content of the liver under insulin. II. E. FRANK, M. NOTHMANN, and E. HARTMANN (Biochem. Z., 1926, **177**, 132—134; cf. Grevenstuk and Laqueur, this vol., 870).—It is contended that the effect of very small doses of insulin in increasing the glycogen content of the liver is not due to the action of the hydrochloric acid in which the insulin is dissolved. J. PRYDE.

"Neo-glucose." K. IWASAKI (Biochem. Z., 1926, **177**, 10—15).—No confirmation is obtained of the claim of Lundsgaard and Holbøll that "neo-glucose" is formed from dextrose by the action of insulin and muscle-tissue. J. PRYDE.

Desiccated gonadal substances. H. SHARLIT, H. M. NOYES, and K. G. FALK (Med. J. Rec., 1926, June 2, reprint).—In a series of commercial ovarian preparations, the esterase activity was found to follow the amount of soluble nitrogen. Such tests of the enzyme activity are suggested as a control of the efficiency of desiccation in preserving the "freshness" of the tissues for biological purposes. R. K. CANNAN.

Changes in the blood following administration of parathyroid hormone. A. CANTAROW, W. R. CAVEN, and B. GORDON (Arch. Int. Med., 1926, **38**, 502—509).—After administration of parathyroid hormone to man, there is no change in the carbon dioxide combining power of the blood or in the chloride content of the plasma, but there appears to be an increase in the concentration of the blood protein and a decrease in its coagulation time, as well as an increase in its calcium content. W. O. KERMACK.

Relation of secretin formation to the entrance of acid chyme into the small intestine. Properties of secretin. J. MELLANBY and A. ST. G. HUGGETT (J. Physiol., 1926, **61**, 122—130).—Secretin, which is apparently a secondary albumose, being soluble in water, and destroyed by pepsin, trypsin, and the intracellular enzymes of the small intestine, exists in the preformed state in the mucous membrane of the upper two-thirds of the small intestine of the goat. Secretin is not derived from the alimentary digestion of protein, nor is there evidence that hydrochloric acid converts a precursor (prosecretin) in the duodenal mucous membrane into secretin. A. A. ELDRIDGE.

Concentration of vitamin-*B*. III. P. A. LEVENE and B. J. C. VAN DER HOEVEN (J. Pharm. Exp. Ther., 1926, **29**, 227—231).—Purification of vitamin-*B* is effected by extracting the Osborne–Wakeman fraction (A., 1925, i, 1516) with absolute alcohol until a non-hygroscopic powder is obtained; this powder is dissolved in water, brought to p_H 4·0, when an inactive precipitate separates. The active solution is deaminised with barium nitrite and sulphuric acid, the active material adsorbed on silica gel, and then extracted from the gel as previously described (*loc. cit.*). The yellow powder obtained reduces Fehling's solution after hydrolysis, and contains sulphur, liberated on heating with alkali, but no amino-nitrogen. The activity, which is equal to or slightly greater than that of the most potent preparation previously made, corresponds with 35—50% of the original material. W. O. KERMACK.

Plant phosphatides. IV. Relation between vitamin action and surface activity of phosphatides. V. GRAFE and H. MAGISTRIS (Biochem. Z., 1926, **177**, 16—26).—It is suggested that the vitamin activity of plant foodstuffs is a function of their water-soluble phosphatide content and is related to the surface activity of the latter. This correlation is shown only in phosphatides obtained by water dialysis at the ordinary temperature, and not in cell phosphatides obtained by chemical means. The water-soluble native phosphatide fraction contains also carbohydrate, purines, and colouring matter, in addition to various electrolytes. The vitamin activity is regarded as a function of the whole complex "native phosphatide," and is not shown by any of the individual degradation products obtained by chemical means. J. PRYDE.

Relation between peroxidation and vitamin-*D*. L. YODER (J. Biol. Chem., 1926, **70**, 297—307).—In substances which are naturally active in preventing rickets or which have been rendered so by moderate irradiation with ultra-violet light, a general correlation was observed between antirachitic potency and the power to liberate iodine from iodides (the latter being regarded as evidence of the presence of peroxides). On prolonged irradiation, heating in the air, or ageing, however, the peroxide reaction continued to increase, whilst the antirachitic activity was destroyed. C. R. HARINGTON.

Experimental rickets. XXVII. Variation in vitamin-*D* content of butter fat. E. V. MCCOLLUM, N. SIMMONDS, and J. E. BECKER (J. Biol. Chem., 1926, **70**, 437—438).—Variations in the vitamin-*D* content of butter fat, which is a constituent of the diet recommended (A., 1925, i, 1366) for the preparation of rats for experiments involving vitamin-*D*, may introduce errors; the proportion of this fat should therefore be kept as low as possible. C. R. HARINGTON.

Photoactivity. N. HENNING and W. SCHAEFER (Biochem. Z., 1926, **177**, 109—117).—Blood subjected to ultra-violet irradiation, both in open dishes and *in vivo* (mice), shows no photochemical action on a sensitive plate. Cod-liver oil, which is spontaneously photoactive, acquires enhanced photoactivity after ultra-violet irradiation and also after heating for 30 min. at 100°. Kept for 20 min. at its b. p., the photoactivity of the oil is destroyed. The ultra-violet and heat effects are additive, but apparently depend on different mechanisms, since after being kept at its b. p. for 20 min. and then cooled, a portion of the oil could not be activated by heating at 100° for 30 min., whereas another portion of the same oil was readily rendered photoactive by irradiation. Castor oil, initially inactive, also became photoactive on being heated or irradiated. Synthetic inactive tributyrin could be activated by irradiation, but not by heating. On the other hand, glycerol and stearic and palmitic acids are not activated by irradiation. Oleic acid, linseed oil, and turpentine oil are, like cod-liver oil, spontaneously photoactive. No photoactivity is developed on irradiating fruit juices containing vitamin-*C*. Substances with spontaneous photochemical activity, such as turpentine, cod-liver and linseed oils, give a peroxydase reaction with benzidine in the absence of hydrogen peroxide, whilst photoinactive substances give a negative result. Hydrogen peroxide itself has a marked effect on the sensitive plate. Substances with acquired photoactivity (*e.g.*, irradiated tributyrin or castor oil) liberate iodine from potassium iodide. The "photo-

activity" is probably therefore in some way associated with the formation of labile oxygen compounds. Unsaturated compounds show no change in their double linkings after irradiation. J. PRYDE.

Physiological equilibrium in plants. Production of solid matter and the absorption of nitrogen in *Helianthus annuus*, L., with different amounts of nitrogen supply. A. RIPPEL and O. LUDWIG (Biochem. Z., 1926, **177**, 318—334).—The course of growth and nitrogen absorption of *Helianthus annuus*, L., was investigated with varying nitrogen supply. The growth constant with the smaller nitrogen supply is lower, but the relative production of solid material and the relative absorption of nitrogen are greater in the first half of the growth curve. The nitrogen absorption, however, calculated relative to the weight of solid material formed with smaller nitrogen supply, is below that with larger nitrogen supply. The relationships are unaltered when the root is included along with the plant. P. W. CLUTTERBUCK.

Nitrate assimilation by fungi. G. KLEIN, A. EIGNER, and H. MÜLLER (Z. physiol. Chem., 1926, **159**, 201—234).—The assimilation of nitrates by *Aspergillus niger* and other fungi, as in green plants, proceeds through the stages of nitrites and ammonia to amino-acids. H. I. COOMBS.

Differences between nitrogen and helium as inert gases in anaërobic experiments on plants. E. E. FREE (Carnegie Inst. Wash. Pub., 1925, **368**, 38—77).—In experiments with nitrogen and helium containing, respectively, 0·5 and 0·02% of oxygen, nitrogen was less favourable than helium for certain vital activities of plants, but not for others. The percentage of oxygen required for root growth and germination of the field pea and for movement of *Diplacus* was higher in nitrogen than in helium. The results are ascribed to differences in the speed of diffusion. CHEMICAL ABSTRACTS.

Effect of various lengths of day on the development and composition of some horticultural plants. E. C. AUCHTER and C. P. HARLEY (Proc. Amer. Soc. Hort. Sci., 1924, **21**, 199—214).—"Normal day" (15 hrs.) and "short day" (12 hrs.) plants (soya bean, pepper, lettuce, radish) had the same composition at flowering. Blossoming is related to a high carbohydrate : nitrogen ratio, and especially to a high starch content. CHEMICAL ABSTRACTS.

Nutrient solution [for plants]. S. R. ZINZADZE (Ber. deut. bot. Ges., 1926, **44**, 461—470).—There are reported the changes in p_H which occurred in a series of nutrient solutions during the growth of *Zea mais*. A solution is described which gave the best growth and in which the buffering at a suitable range of p_H was effected by control of the amount of ferric sulphate added. R. K. CANNAN.

Sodium cobaltinitrite reaction for potassium in plant cells. F. E. LLOYD (Flora, 1925, **118**—**119**, 369—385).—The sodium cobaltinitrite test for potassium in living cells is inadequate and untrustworthy. There is no evidence of a definite localisation of potassium in the cytoplasm; it is found chiefly in the vacuoles. It was not found in the chloroplasts or nucleus. CHEMICAL ABSTRACTS.

Natural porphyrins. XX. Porphyrins in plants. H. FISCHER and F. SCHWERDTEL (Z. physiol. Chem., 1926, **159**, 120—132).—The porphyrin contents of a variety of materials, *e.g.*, cereals, nettles, potatoes, beet, young leaves of the oak, ash, maple, etc., are tabulated. P. W. CLUTTERBUCK.

Plant phosphatides. III. Water-soluble and -insoluble phosphatides from *Pisum arvense unicolor*. V. GRAFE and H. MAGISTRIS (Biochem. Z., 1926, **176**, 266—290).—By precipitation of the dialysate from Norwegian peas with increasing amounts of lead acetate, fractions were obtained of progressively higher P/N ratio. The phosphatides appear to occur in combination with pigment and with carbohydrate groups, and it is noted that they give insoluble precipitates with many basic dyes. Salts of alkali metals assist their diffusion from the cells, whilst those of the alkaline earths and of iron retard this process.

Analysis of the unfractionated precipitate of phosphatides suggested the presence of a diaminomonophosphatide, but phytin is also present in this mixture. By extracting the peas with warm alcohol, a solution of the phosphatides free from their accompanying pigment and carbohydrate groups is obtained. This fraction is termed "lecithins," to distinguish it from the native "phosphatides." Dialysis of the extracted peas against water yields a further quantity of phosphatides with a P/N ratio suggesting a monoaminodiphosphatide. C. RIMINGTON.

Pentosan theory of cold-resistance applied to conifers. J. DOYLE and (MISS) P. CLINCH (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 219—235).—The pentosan content of *Conifer* leaves varies considerably with the seasons, but there is no evidence of any connexion between this and the hardiness of the trees. The pentosans present are classed in three groups: (*a*) water-soluble pentosans, (*b*) those subsequently extracted by 1% hydrochloric acid, and (*c*) those finally extracted by 12% hydrochloric acid. The p_H value of *Conifer* leaves is between 3 and 4. G. M. BENNETT.

Dehydration rates of *Conifer* leaves in relation to pentosan content. J. DOYLE and (MISS) P. CLINCH (Sci. Proc. Roy. Dublin Soc., 1926, **18**, 265—275).—The rate of dehydration of *Conifer* leaves at 60° does not decrease with increasing content of water-soluble pentosans. Rates of dehydration are, moreover, no index of hardiness. G. M. BENNETT.

Composition of the ash of Spanish moss. E. T. WHERRY and R. BUCHANAN (Ecology, 1926, **7**, 303—306).—The ash was high in sodium, iron, sulphur, chlorine, and silica; samples collected from the sea-coast contained more chlorine and less sodium than those collected far inland. CHEMICAL ABSTRACTS.

Japanese seaweeds. I. Chemical constituents of *Laminaria*. K. ATSUKI and Y. TOMODA (J. Soc. Chem. Ind. Japan, 1926, **29**, 509—517).—The main constituents of *Laminaria saccharina* are mannitol 25%, alginic acid 20%, ash 24%, nitro-

genous material 10%, acid-soluble material 15%, and crude fibre 6%. The oxidation of mannitol by chlorine was best carried out by exposing its solution in chlorine water to direct sunlight, 56% of sugar being produced. When treated with hydrochloric acid (*d* 1·06), alginic acid gave 14·21% of furfuraldehyde and 19·89% of carbon dioxide. Its acid value was 262 and $[\alpha]_D^{20}$ —130°. It contained neither a galactan unit nor methoxyl. In several respects, alginic acid closely resembles pectic acid, and it is supposed that the acid is composed of the galacturonic or glycuronic acid units. The greater part of the crude fibre of *Laminaria* consists of hemicelluloses, and normal cellulose has not been found.

K. KASHIMA.

Comparative plant chemistry. XIII. Chemistry of barks. IV. J. ZELLNER (Monatsh., 1926, **47**, 151—177).—The barks of the privet, red beech, alder, and green alder have been examined by the methods previously used (cf. this vol., 983). Privet (*Lingustrum vulgare*, L.) contained: soluble in light petroleum, 2·22%; ether extract, 2·63%; total water-soluble matter, 38·29%; water-soluble mineral matter, 2·33%; reducing sugars, 3·37%; tannins, 6·94%; polysaccharides, 2·82%; total nitrogen, 2·29%; total ash, 4·42%. From the alcoholic extract was isolated ceryl palmitate and a *substance*, $C_{41}H_{72}O_2$, m. p. 86—87°, which is probably a palmitic ester of the *resin alcohol*, $C_{25}H_{42}O$ (or $C_{26}H_{44}O$), m. p. 215° (*acetyl* derivative, m. p. 217°; *bromine additive* compound, m. p. 192°), isolated together with ceryl alcohol, palmitic and (?) behenic and arachidic acids on hydrolysis of the mother-liquors. The light petroleum extract on hydrolysis yielded the same resin alcohol, ceryl alcohol, a phytosterol, m. p. 134—135° (acetyl derivative 117°), and a *substance*, identical with or similar to platonalic acid, obtained from the bark of the plane tree (cf. Zellner, this vol., 646). From the alcoholic and aqueous extracts were isolated phlobaphens, syringin, and invert-sugar. Red beech (*Fagus silvatica*, L.) contained: light petroleum extract, 0·87%; ether extract, 3·26%; alcoholic extract, 10·40%; water-soluble matter, 14·26%; water-soluble mineral matter, 0·61%; reducing sugars, 3·21%; free acids (as KOH), 1·48%; polysaccharides, 0·39%; total nitrogen, 1·36%; total ash, 8·93%. From the alcoholic extract were isolated a *paraffin*, m. p. 65°, ceryl alcohol, and arachidic acid. From the light petroleum extract were obtained a *substance*, $C_{39}H_{68}O_2$, m. p. 205° (*acetyl* derivative, m. p. 116—117°), the phytosterol, m. p. 135°, [α]—37·1°, and, on hydrolysis, ceryl alcohol, arachidic and stearic acids, together with a small quantity of lower fatty acids. From the ether extract were obtained, on hydrolysis, a substance, m. p. 248° (*acetyl* derivative, m. p. 212°), probably identical with the substance, m. p. 254°, isolated from black alder bark, and ceryl alcohol. Phlobaphens and tannins (which on hydrolysis with 5% hydrochloric acid yielded phlobaphens of somewhat different composition) were also obtained. The alder (*Sambucus nigra*, L.) yielded: light petroleum extract, 3·38%; ether extract, 1·72%; alcoholic extract, 6·09%; water-soluble matter, 14·98%; water-soluble mineral matter, 2·95%; free acids (as KOH), 1·12%; reducing sugars, 0·11%; polysaccharides, 1·52%; tannins, 2·55%; total nitrogen, 1·50%; total ash, 5·85%. The light petroleum extract yielded a *substance*, $C_{23}H_{40}O_2$, m. p. 216°, a *substance*, m. p. 179° (*acetyl* derivative, m. p. 216°); the phytosterol, m. p. 134°; an *alcohol*, m. p. 72°, which may have the composition $C_{20}H_{42}O$ or may be ceryl alcohol with a little hydrocarbon impurity (cf. loranthyl alcohol, Braunhauser, this vol., 983), and (?) stearic and myristic acids. The ether extract yielded a *substance*, m. p. 245° (decomp.), and a *substance*, decomp. 298°, similar to platanolic acid (cf. Zellner, *loc. cit.*). The aqueous extract contained tannins and invert-sugar. The green alder (*Alnus viridis*, D.C.) contained: light petroleum extract, 5·58%; ether extract, 3·57%; alcoholic extract, 23·11%; water-soluble matter, 31·29%; water-soluble mineral matter, 0·66%; free acids (as KOH), 0·96%; polysaccharides, 1·47%; tannins, 16·55%; reducing sugars, 4·91%; total nitrogen, 8·19%; total ash, 3·25%. The light petroleum extract yielded alniresinol (the true m. p. of which is 199°, and the composition $C_{33}H_{60}O_2$, [α]—44°; cf. Feinberg, Herrmann, Röglsperger, and Zellner, A., 1924, i, 814), protalnulin (*loc. cit.*), and, on hydrolysis, a *resin acid*, glycerol, phosphoric acid, ceryl alcohol, alniresinol, and a *substance*, $C_{33}H_{60}O_2$ or $C_{33}H_{58}O_2$, m. p. 194°, [α]—47·7° (*acetyl* derivative, m. p. 144°), for which the name *alniviridol* is suggested. The ether extract yielded a substance, $C_{24}H_{42}O_2$, identical with the substance, m. p. 254°, obtained from black alder bark (see above), ceryl alcohol, (?) platanolic acid, and a small quantity of a *substance*, m. p. 68—69°. Dextrose, lævulose, pectin, a small quantity of oxalic acid, and mineral salts were also isolated. The products obtained from the various species of the genus *Alnus* are compared.

J. W. BAKER.

Lapachol. S. J. RECORD (Tropical Woods, 1925, **1**, 7—9).—Lapachol, $C_{15}H_{14}O_3$, golden-yellow, giving a pink colour with 1% sodium hydroxide solution, occurs in the heartwood of *Avicennia* and in several species of *Bignoniaceæ*. CHEMICAL ABSTRACTS.

Wax from roses. H. PROPHÈTE (Compt. rend., 1926, **183**, 609—611; cf. this vol., 981).—The following hydrocarbons have been isolated from rose wax: triacontane, 6%; heptacosane, 15%; hexacosane, 8%; tricosane, 6%; docosane, 6%; heneicosane, 2%; eicosane, 8%; hexadecane, 0·5%; unsaturated *hydrocarbons* (*bromide*, m. p. 27°), 3% (bromide, m. p. 38·5—39°), 2%. The following alcohols were isolated: ψ-ceryl alcohol, 3%; $C_6H_{12}O$, 8%; *iso*ceryl alcohol, 6%; $C_{10}H_{20}O$, m. p. 49·5°, 1·5%; $C_{10}H_{20}O$, m. p. 43°, 1%; an unsaturated *alcohol*, 0·4%.

L. F. HEWITT.

Oxytocic substances of ergot. II. Histamine. A. W. FORST and H. WEESE (Arch. exp. Path. Pharm., 1926, **117**, 232—239).—From 100 g. of ergot, 1—2·6 mg. of histamine are obtained on exhaustive extraction by percolation with aqueous alcohol or acetone. The histamine is not removed from the extract when the alkaloids are precipitated. Certain commercial extracts of ergot contain up to 0·4 mg. of histamine per c.c. W. O. KERMACK.

Physical and chemical changes of Grimes apples during ripening and storage. H. H. PLAGGE, T. J. MANEY, and F. GERHARDT (Agric. Exp. Sta. Iowa Coll. Agric. Res. Bull., 1926, No. 91, 43—72).—Ripening on the tree or in storage is associated with loss of moisture, acidity, dextrin, starch, and acid-hydrolysable material; there is an increase in density, and in sugar and soluble pectin. Chemical changes detected on the breakdown of normal tissue appear insufficient to account for the formation of diseased tissue during storage.

CHEMICAL ABSTRACTS.

Variations in the urease content of different varieties of soya bean. E. M. HINDMARSH (Austral. J. Exp. Biol., 1926, **3**, 167—172).—None of a large number of Australian-grown varieties of soya bean has an activity for hydrolysing carbamide as great as that of the American jack bean.

W. ROBSON.

Colorimetric micro-method for determining carbohydrate in organs and body-fluids. Z. DISCHE and H. POPPER (Biochem. Z., 1926, **175**, 371—411).—A detailed investigation of the brown or violet colour reactions given by carbohydrates and their derivatives when heated with hydrochloric or sulphuric acids in the presence of indole or scatole. The colour obtained with scatole and hydrochloric acid (*d* 1·175) is not proportionate to the carbohydrate concentration and cannot be used as the basis of a quantitative method. Lævulose and its derivatives give a much stronger colour than other carbohydrates. Using scatole and 20% hydrochloric acid, a violet colour is obtained only in the instances of lævulose, sucrose, and hexosediphosphoric acid. It is concluded that hexosediphosphoric acid contains a lævulose component, and that this reaction may be used for the detection of lævulose or its derivatives. Indole and concentrated hydrochloric acid yield a mahogany-brown colour—the lævulose reaction being three times as intense as the others—proportional in intensity to the amount of carbohydrate present, but too variable with slight alterations in the concentration of hydrogen chloride present to be reliable as a quantitative measure. The use of indole and sulphuric acid proved most suitable for the quantitative determination. 9 C.c. of 77·5 vol.-% sulphuric acid, 1 c.c. of the aqueous solution of carbohydrate, and 0·3 c.c. of a 1% solution of indole in alcohol yield a pure brown colour when heated together. Lævulose gives a colour 12% more intense than dextrose and galactose, polysaccharides a colour corresponding in intensity with that of their individual monosaccharide components, whilst methylglucoside and hexosephosphate give the same colour intensity as the free sugar molecule. Other substances containing carbohydrate, *e.g.*, protein and nucleic acid, also give the colour reaction, whilst certain other non-carbohydrate substances present in tissues etc. yield a positive reaction only in concentrations sufficiently high not to interfere with the quantitative aspect of the carbohydrate determination. The indole–sulphuric acid reaction can also be used in alcoholic solution, and since polysaccharides are insoluble in alcohol, this application may be made the basis of a separate determination of mono- and di-saccharides and of polysaccharides. The general method enables the total carbohydrate of tissues (after 2 hrs.' hydrolysis with 2·2% hydrochloric acid), and the total carbohydrate of blood (after deproteinisation with trichloroacetic acid) to be determined with accuracy. In the latter instance, 0·15 c.c. of blood is sufficient, and somewhat higher values for total carbohydrate are obtained than those recorded as "blood-sugar" by the methods of Bang and Benedict. It is claimed that 0·05 mg. of carbohydrate may be determined with accuracy by this method.

J. PRYDE.

Sugar in urine and in blood. O. FOLIN and A. SVEDBERG (J. Biol. Chem., 1926, **70**, 405—426).—The criticisms of Benedict (this vol., 984) of the authors' recent method for the determination of sugar in urine (this vol., 648) are met by shaking the filtrate, obtained after precipitation by Lloyd's reagent, with permutit. The authors' copper reagent (*loc. cit.*) is subject to deterioration through loss of carbon dioxide on keeping, and should therefore be used fresh; subject to these modifications, the reliability of the method is confirned. The yeast-fermentable sugar in blood determined by the new method is lower than that determined by the method of Folin and Wu (A., 1920, ii, 337), the difference being greater the higher the concentration of sugar; the non-fermentable sugar is also less, as determined by the new method, but its amount is practically constant, irrespective of the total concentration of sugar. The difference between the values obtained by the Folin–Wu method and the new method, designated "non-dextrose sugar," is reduced by administration of insulin, variably affected by adrenaline, and not affected by ingestion of dextrose.

C. R. HARINGTON.

Determination of lactic acid in small amounts of blood. Modification of the Clausen method. T. BREHME and B. BRAHDY (Biochem. Z., 1926, **175**, 348—356).—A modified Clausen method is described. The determination can be carried out on 1·5 c.c. of oxalated blood with an accuracy of 92—95% even when as little as 0·045 mg. of lactic acid is present.

J. PRYDE.

Preparation of the phosphomolybdic acid reagent. G. FONTÈS and L. THIVOLLE (Bull. Soc. Chim. biol., 1926, **8**, 982—983).—Some samples of phosphoric acid contain a substance which spontaneously destroys the blue colour on which the use of the reagent depends. The ammonia and organic impurities present in some of the components of the reagent are also a source of trouble. Directions are given for preparing a reagent which will give with the reducing substance to be determined a blue colour permanent for several hours.

R. K. CANNAN.

Colorimetric method for determination of acetone substances in blood and urine. J. A. BEHRE and S. R. BENEDICT (J. Biol. Chem., 1926, **70**, 487—494).—After preliminary precipitation of proteins in the case of blood or after shaking with copper sulphate and calcium hydroxide in that of urine, preformed acetone is removed from the resulting

fluid by distillation; subsequent distillations in presence of sulphuric acid, or of sulphuric acid and potassium dichromate, remove also acetone corresponding with the acetoacetic acid or with the latter and the β-hydroxybutyric acid, respectively, of the original solution. The acetone in the various distillates is determined colorimetrically by a modification of the method of Csonka (A., 1916, ii, 654) depending on the condensation in alkaline solution of acetone with salicylaldehyde. C. R. HARINGTON.

Determination of acetone substances by the Van Slyke method. E. C. SMITH (Biochem. J., 1926, **20**, 1024—1025).—There are a number of substances which produce precipitates together with that due to acetone in Van Slyke's method (A., 1917, ii, 86) for the determination of acetone substances. When lactic acid is present, it is oxidised to pyruvic acid in the course of the determination, and this gives a precipitate with the reagent, thus vitiating the result. The Van Slyke method cannot be relied on to give an accurate indication of the concentration of acetone substances in biological material.

S. S. ZILVA.

Determination of uric acid in blood. L. FLATOV (Biochem. Z., 1926, **176**, 178—183).—Uric acid in whole blood and in serum is determined by adding a known excess of potassium ferricyanide to the deproteinised blood filtrate and back-titrating the excess with sodium indigosulphate. The method is used for amounts of uric acid of about 0·02 mg., the deviations in single determinations being 0·001 mg. P. W. CLUTTERBUCK.

Determinations of uric acid in human blood. G. W. CLARK and A. A. de LORIMIER (Amer. J. Physiol., 1926, **78**, 368—375).—Incubation of human blood at 37°, or inactivation at 56° for 30 min. followed by a period at the ordinary temperature, has no effect on the value obtained in the indirect determination of uric acid (cf. Hunter and Eagles, this vol., 85), but affects the results by Benedict's direct method. Both thiasine (Benedict, this vol., 421) and the "*X* substance" of Hunter and Eagles are probably determined as uric acid by the latter method. R. K. CANNAN.

Colorimetric determination of cholesterol and lecithin in blood. G. M. DE TONI (J. Biol. Chem., 1926, **70**, 207—210).—The precipitate obtained by treatment of blood with tungstic acid is mixed with plaster of Paris and the mixture dried, powdered, and extracted for 2 hrs. with chloroform. Cholesterol and lecithin are determined in aliquot portions of the extract by standard methods. C. R. HARINGTON.

Gravimetric micro-determination of cholesterol. R. GIRARDIN and E. SPAOH (Bull. Soc. Chim. biol., 1926, **8**, 813—815).—The determination of cholesterol by the digitonin method has been modified for use with amounts of cholesterol of the order of 0·002 g. H. J. CHANNON.

Cholesteryl allophanate. R. FABRE (Compt. rend., 1926, **183**, 679—681).—Gaseous cyanic acid is passed into a solution of cholesterol in ether, when *cholesteryl allophanate*, m. p. 277—278°, $[\alpha]_H$ —33·9° (in benzyl alcohol), yielding cholesterol readily on hydrolysis, separates out. The method is suggested for isolating and characterising cholesterol in biological material. Samples of lecithin examined contained 10—18% of cholesterol. L. F. HEWITT.

Accuracy of Bang's method for the determination of blood-lipins. A. FLEISCH (Biochem. Z., 1926, **177**, 453—460).—The mean error of experiment (=dispersion) is calculated for a number of blood-lipin determinations by Bang's method. The dispersion for 89×10^{-6} g. of olein is 3×10^{-6} g. or 3·44%. Using as substrate rabbit's blood which contains $76{\cdot}8\times10^{-6}$ g. of fat and cholesterol, the dispersion is 4×10^{-6} g. or 5·2%. The dispersion (σ) varies with the amount of lipin (L) according to the equation $\sigma=0{\cdot}026L+2\times10^{-6}$. P. W. CLUTTERBUCK.

Determination of neutral fat in blood by Bang's method. A. LÖW (Biochem. Z., 1926, **177**, 144—145).—It is recommended that the light petroleum used as extractive solvent should be purified by distillation from alkali (1 c.c. of *N*-sodium hydroxide in 500 c.c.). J. PRYDE.

Determination of fat in animal tissues and in entire organs. N. D. ZELINSKY and S. R. ZINZADZE (Biochem. Z., 1926, **175**, 335—347).—A method is described for the determination of fats in tissues and organs, these being previously autoclaved for 2 hrs. at 180° in the presence of dilute acid in order to hydrolyse the proteins. A correction is applied for the amount of fat hydrolysed during this process. The method and apparatus used for extracting the fat and fatty acid from the hydrolysate are described and illustrated. J. PRYDE.

Determination of the fatty acid content of organs. A. FISCHER (Biochem. Z., 1926, **175**, 449—454).—10—15 G. of wet or 2—5 g. of dried organ are hydrolysed for 9 hrs. with 50 c.c. of concentrated hydrochloric acid. The mixture is made slightly alkaline with 60% sodium hydroxide and precipitated with 30 c.c. of lime water. After filtration, the residue is acidified with hydrochloric acid and warmed for 15 min. on the water-bath. It is then shaken with ether after cooling. The aqueous layer is extracted once more and the combined ethereal extracts are evaporated, dried for 1 hr. at 50°, and weighed. The factor 1·046 gives the weight of neutral fat in the organ. J. PRYDE.

Nitrates in animal and vegetable tissues. E. KOHN-ABREST and S. KAWAKIBI (Compt. rend., 1926, **183**, 522—524).—An alkaline extract of the tissue is made, treated with basic lead acetate and boiled, and the filtrate, after removal of the lead and concentration, is treated with sulphuric acid and mercury and the volume of nitrous oxide liberated is measured. Vegetable foodstuffs do not contain appreciable quantities of nitrates. Cow's milk contains 0·008% and human milk 0·0017% of nitrates, drinking-water (Paris) 0·001%, and urine 0·0036%.

L. F. HEWITT.

Colorimetric method of determining pentoses. R. A. MCCANCE (Biochem. J., 1926, **20**, 1111—1113).—The solutions are heated with hydrochloric acid in a water-bath for 2 hrs., after which time they are shaken out with benzene. To an aliquot portion of the benzene extract, benzidine is added; a deep crimson-violet colour is produced if a pentose is

present. For quantitative work, the colour is compared with a set of standards containing known quantities of the pentose determined. A 0·05% solution of arabinose in urine was determined with an error of 6%. S. S. ZILVA.

Determination of β-hydroxybutyric acid in liver and muscles. J. SNAPPER and A. GRÜNBAUM (Biochem. Z., 1926, **175**, 357—365).—A method is described for the determination of β-hydroxybutyric acid in liver and muscle. Protein is removed by tungstate and sulphuric acid, carbohydrate by copper sulphate and calcium hydroxide. The β-hydroxybutyric acid is oxidised by dichromate, and the resulting acetone, after purification by distillation with sodium hydroxide, hydrogen peroxide, and Fehling's solution, is collected and weighed as the mercury derivative, as in the Van Slyke method. The iodine titration is thus avoided, and no β-hydroxybutyric acid is lost by adsorption on the protein or carbohydrate precipitants. J. PRYDE.

Determination of iodine in foodstuffs and body-fluids. I. LEITCH and J. M. HENDERSON (Biochem. J., 1926, **20**, 1003—1007).—Fellenberg's method is modified by eliminating the colorimetric part and concentrating on the titrimetric determination. The error of the method is about ±10% when dealing with quantities of iodine between 0·5 and 2 γ. (γ=0·000001 g.) S. S. ZILVA.

Ashing of physiological material. J. WEBER and W. KRANE (Z. physiol. Chem., 1926, **157**, 171—176).—The substance to be ashed, contained in a porcelain boat, is dried over-night at 250°. It is then placed in a combustion tube of hard glass 18—20 mm. wide and 25 cm. long and carefully heated in a slow stream of oxygen until combustion is complete. By this means, sodium and potassium chloride are quantitatively retained in the ash, whereas ammonium chloride is completely volatilised. H. D. KAY.

Sakaguchi's colour reaction. K. POLLER (Ber., 1926, **59**, [*B*], 1927—1929; cf. Sakaguchi, J. Biochem. [Japan], 1925, **5**, 13, 133).—This reaction is carried out by adding to a solution of protein in concentrated sodium hydroxide a few drops of a 0·1% solution of α-naphthol (in 70% alcohol) and then a few drops of a 5% sodium hypochlorite solution. After a short time, the solution develops a wine-red colour. The reaction was described as a new general colour test for proteins. It is now found that it depends on the presence of arginine and that the guanidine nucleus is necessary for positive results. Substitution of one of the hydrogen atoms of the amino-group does not inhibit the reaction, which is not observed with compounds in which both of the amino-hydrogen atoms are replaced or in which a negative substituent is present. Substitution in the imino-group of guanidine does not inhibit the reaction. H. WREN.

Analytical investigations. V. L. PINOUSSEN Nephelometric determination of phosphate. F. JULIUSBERGER (Biochem. Z., 1926, **177**, 140—143).—An aliquot portion of the exactly neutralised solution obtained after ashing is placed in a 50 c.c. flask; 5 c.c. of 1 : 3 nitric acid are added, the mixture is diluted with water to about 45 c.c., 2 c.c. of the molybdenum–strychnine reagent (Kleinmann) are added, the whole is diluted to the mark, shaken, and kept for 30 min. 5 C.c. of a standard solution are similarly treated. To both flasks 2 c.c. of gum-arabic solution are added and the nephelometric comparison is made within 2½ hrs. J. PRYDE.

Determination of allantoin in rabbit urine. A. A. CHRISTMAN (J. Biol. Chem., 1926, **70**, 173—191).—Hydrolysis of allantoin by boiling for 1 hr. with 20% sodium hydroxide yields 1 mol. of oxalic acid per 2·mols. of allantoin. The urine is diluted to 0·5% urea concentration, acidified, and treated with phosphotungstic acid; the filtrate is treated with basic lead acetate and to the filtrate from the lead salts is added a mixture of mercuric and sodium acetates; aliquot portions of the solution obtained after decomposition of the mercury precipitate with hydrogen sulphide are hydrolysed as described above and the oxalic acid formed is determined by a standard method. Known amounts of allantoin added to urine were determined within the limits −10 to +4%. C. R. HARINGTON.

Determination of xanthine bases in urine. P. FLEURY and P. GENEVOIS (Bull. Soc. Chim. biol., 1926, **8**, 783—803).—The precipitation of the xanthine bases by the zinc ferrocyanide method is not complete, and, further, the precipitate contains some of the uric acid. Separation of the bases and uric acid by precipitation of the latter as ammonium urate is quantitative, but the bases cannot be precipitated quantitatively as the silver salts in the filtrate. The method described is to precipitate both uric acid and the xanthine bases as the silver compounds, and to remove the uric acid and silver from the mixture by treatment with hydrochloric acid. After filtration, the silver compounds are regenerated in the filtrate; determinations of nitrogen and silver are then made. H. J. CHANNON.

Gravimetric determination of bacteria and yeast. H. I. COOMBS and M. STEPHENSON (Biochem. J., 1926, **20**, 998—1002).—At suitable intervals, the broth containing the grown organism is withdrawn, filtered through a Pregl filter, washed, dried, and weighed on a micro-balance. From the gross weight is subtracted the weight due to the broth alone. The latter is constant if the broth is previously treated with charcoal at p_H 7·6 and steamed. In the case of *Bacillus coli*, 1 c.c. of 0·1*N*-sodium hydroxide was found effective in coagulating the growth of bacteria before filtration. With *B. coli*, the growth curve flattens at the 10th hr. S. S. ZILVA.

Determination of lævulose, sucrose, and inulin. W. R. CAMPBELL and M. I. HANNA (J. Biol. Chem., 1926, **69**, 703—711).—Campbell's recently described method (this vol., 443) for the determination of dihydroxyacetone is also applicable, with certain modifications, to the determination of lævulose, sucrose, and inulin. C. R. HARINGTON.